SYNGAS SYNTHESIS USING GASIFICATION OF BIOMASS WITH O₂–CO₂ AND O₂–STEAM MIXTURES

A THESIS

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THESIS CERTIFICATE

This is to certify that the thesis titled SYNGAS SYNTHESIS USING GASIFICA-TION OF BIOMASS WITH O_2 -CO₂ AND O_2 -STEAM MIXTURES, submitted by Jaganathan VM, to the Indian Institute of Technology, Madras, for the award of the degree of **Doctor Of Philosophy**, is a bona fide record of the research work done by him under our supervision. The contents of this thesis, in full or in parts, have not been submitted to any other Institute or University for the award of any degree or diploma.

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Shri NV Munuswamy and Smt. Shanthi Munuswamy

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ABSTRACT

This thesis deals with the experimental and theoretical aspects of counter-current flame propagation behavior in a packed bed biomass reactor in downdraft configuration with mixtures of O_2 – CO_2 and O_2 –steam as oxidizers. Exploring the enhancement of CO and H_2 with O_2 - CO_2 and O_2 -steam mixtures is the main focus of the current study. While syngas from biomass gasification with *air* is suitable for power generation using reciprocating engines and process heating/steam-raising, syngas in pure form (that is, without inerts like N_2 and CO_2) is preferred for catalytic up-gradation to fuels and chemicals (for instance, in Fischer-Tropsch process). Replacing the inert nitrogen in air with reactive components like CO_2 and steam allows for easy separation of H_2 and CO in syngas, will enhance the fuel value and H_2/CO ratio, and thereby increasing the range of applications for the syngas produced through this route.

To study the flame propagation behavior of biomass with O_2-CO_2 and O_2 -steam mixtures, downdraft configuration is chosen due to the following advantages it offers over updraft and fluidized bed configurations - (1) fuel flux as a function of superficial velocity (V_s) exhibits universal characteristics with air as the gasification medium, (2) tar fraction in product gases is much less compared to other configurations, (3) flame propagation in practical configurations like grate furnace is analogous to packed bed systems with a coordinate frame fixed to the unburnt fuel and (4) ignition time (t_{ig}) estimated from packed bed systems i.e. $t_{ig} = d_p/\dot{r}$ where, d_p is the particle diameter and \dot{r} is the flame front velocity as a function of heat flux can be used to validate single particle models.

For gasification with O_2 – CO_2 mixtures, experiments were conducted with oxidizer streams containing 15, 19, 23, 32 and 42% O_2 by mass (rest CO_2) and for a range of oxidizer mass flux. Three fuels namely, wood pellets, coconut shells and agro-residue pellets were used in the study. The choices of O_2 mass fraction and oxidizer mass flux were based on following considerations - (1) to explore the entire range of stable operation i.e. *steady flame propagation* and (2) to study the fuel flux and syngas yield variation with oxygen mass flux. Corresponding reference experiments with O_2 – N_2 mixtures were performed for comparing the net CO_2 conversion. The propagation regimes, similar to earlier studies with air, fall under the following two categories - (1) gasification - 'volatiles' oxidation accompanied by char reduction and (2) char oxidation dominated - simultaneous char and 'volatiles' combustion. Invoking equilibration of 'volatiles' oxidation under gasification conditions, a new procedure is established to estimate the net CO_2 conversion (NCC). In general, NCC is significant around the 'volatiles' stoichiometric point (complete oxidation of 'volatiles' hydrocarbons of biomass, $\phi_v = 1$, which corresponds to a overall equivalence ratio, Φ , around 1.25) and falls off on either side as the oxygen mass flux is decreased or increased. NCC is zero in very rich regime i.e. when $\phi_v > 2$ due to low bed temperatures (since CO₂ conversion happens predominantly through the endothermic reaction, C + CO₂ \rightarrow 2CO which is favored at high temperatures) and also when $\phi_v < 1$ due to char oxidation. Maximum NCC of 627 g/kg of biomass is observed with 23% O₂-77% CO₂ (by mass) case at ϕ_v = 0.96 for agro residue pellets. Cold gas efficiency (η_q) is 85% for the maximum NCC case. Enhanced gasification efficiencies of O₂-CO₂ cases as compared to corresponding O₂-N₂ cases is due to the additional conversion of CO₂ to CO (predominantly C + $\text{CO}_2 \rightarrow 2\text{CO}$). The difference in the fraction of char left over with CO_2 and N_2 cases is consistent with this observation. In spite of the aforesaid interesting results from O₂-CO₂ experiments, the H₂ yield is low (10 - 20 g/kg of biomass) and comparable to that from air gasification.

High O₂ fraction (more than 30%) experiments with O₂–CO₂ and O₂–N₂ mixtures show fuel fluxes in the range of 200 – 250 g/m²s i.e. 3–4 times higher than air cases. Hence, to unify the fuel propagation behavior with diffrent oxidizers, Normalized Fuel Flux (*NFF*) is proposed and is given by,

$$NFF = \left(\frac{\dot{m}_{f_a}''}{\dot{m}_{f_{ref}}''}\right) \left(\frac{(HY_{ox}/s)_{ref}}{(HY_{ox}/s)_a}\right)^2 \left(\frac{\epsilon_{b,act}}{\epsilon_{b,ref}}\right)$$

where, \dot{m}''_f , H, Y_{ox} , s and ϵ_b represent fuel flux, heating value, oxidizer fraction, stoichiometric coefficient and bed voidage respectively. Suffixes (*ref*) and (*a*) represent reference and actual cases. Here, agro residue based pellets with air as reactant is taken as reference case. *NFF* is shown to exhibit universality irrespective of oxygen fraction and fuel type. 'Universal flame propagation model' can explain the observed variation of NFF with equivalence ratio. However, experiments with O₂–CO₂ mixtures at higher O_2 fractions (more than 42%), show 'flame jump' - that is, flame front jumps to the next layer in chaotic manner without complete devolatalization of the current layer. Phenomenon of 'flame jump' occurs when the ignition time (t_{ig}) becomes less than devolatalization time (t_v) and hence, the ignition front propagates upstream without complete conversion of 'volatiles' downstream of the flame front. Another condition under which such jumps can occur (though not as severe as in the cases with higher O_2 fraction) is when the particle size is increased beyond a critical limit. Studies conducted as a part of the current work indicate that this critical limit is about 20 mm with air as oxidizer.

To explore these aspects of flame propagation which go beyond the 'universal flame propagation model', a unified ignition-devolatalization model is developed to predict the t_{ig} and t_v of a single biomass particle subjected to reactor conditions. Comparison of predictions with experimental results from single particles, performed as a part of the current study, is good. In addition, packed bed experiments with larger particles (groundnut shell briquettes; 100 mm diameter and length varying from 40 to 110 mm) is used to validate role of t_v in overall propagation rate. From the results obtained using the model, the phenomenon of 'flame jump' is shown to occur when t_v/t_{ig} exceeds 2. Various operational zones of a packed bed biomass system is mapped using the predicted ratio of t_v/t_{ig} as a function of ϕ_v . Five distinct zones (Zone I – Zone V) and their unique propagation characteristics are identified. Zone I - slow propagation zone (fuel flux < 25 g/m²s), Zone II - near 'volatiles' stoichiometry operation and t_v/t_{ig} ratio below 2, Zone III - fuel rich operation zone i.e. $\phi_v > 2$ (generating more tar due to fuel rich operation) and 5 $\geq {t_v}/{t_{ig}} \geq 2$, Zone IV - flame jump zone with t_v/t_{iq} ratio above 2 and Zone V - char oxidation zone where, $\phi_v < 1$. Out of the five zones classified, Zone II is identified as optimal zone for operation with the following desirable characteristics, (1) steady flame propagation, (2) operation range of $2 \ge \phi_v$ \geq 1 which enhances conversion of the reactants (CO₂ to CO, for instance) and (3) moderate peak bed temperatures i.e. $1200 > T_{pb} > 1600$ K which neither generate tar nor melt the reactor/cause ash fusion problems.

By substituting N_2 with CO_2 , CO yield from gasification increases by a factor of 2 - 2.5 compared to air. But, as expected, there was very little change in H_2 yield compared to air (10 - 20 g/kg of biomass). Gasification with O_2 -steam mixtures is a well known method for enhancing H_2 yield. In the light of the advantages of operating in Zone

II brought out earlier, preliminary experiments were conducted to identify parameter ranges for oxygen fraction and mass flux required for the same. It was found that O_2 fraction in the range of 23-40 % (by mass, rest steam) and oxygen mass flux in the range of 16 to 120 g/m²s were suitable for operation in Zone II. Also, to determine the intrinsic H₂ yield, the upstream temperature is restricted between 120 - 150°C; lower limit to avoid condensation and upper limit to avoid bulk devolatalization of the bed.

In O_2 -steam experiments, wood pellets and agro residue pellets are used as fuel; steady flame propagation is shown to be established for a range of oxygen mass flux (16 to 120 g/m²s) with O_2 fractions of 23, 30 and 40% by mass (rest steam). The intrinsic H₂ yield from biomass is determined over an equivalence ratio (Φ) range of 3.5 to 1.2. This is shown to correspond to a 'volatiles' based equivalence ratio (ϕ_v) of 2.2 to 1 similar to O_2 -CO₂ experiments. Interestingly, the H₂ yield over this entire range is within 30-40 g/kg of biomass. Using equilibrium calculations, it is shown that the 'unburnt volatiles' is the major H₂ source when $\phi_v > 2$ and as $\phi_v \to 1$, 'volatiles' ${
m H_2}$ drops close to zero and the major contribution is through the reaction C + ${
m H_2O} \rightarrow$ CO + H₂. Increase in char conversion from about 20% at $\phi_v \sim 2.1$ to almost 100% as $\phi_v \rightarrow 1$, the corresponding increase in peak bed temperature and decrease in 'higher hydrocarbons' are consistent with the observed H₂ yield. The important insight is, operating close to $\phi_v = 1$, under slightly rich condition, leads to tar free exit gas with little or no compromise on H₂ yield. This hitherto unknown result is perhaps the reason why all earlier works focused on highly fuel rich conditions and/or very high steam temperatures ($\sim 800^{\circ}$ C), tolerating higher tar content.

TABLE OF CONTENTS

A	CKN(OWLEI)GEMENTS	i
A	BSTR	ACT		ii
L	IST O	F TAB	LES	ix
L	IST O	F FIGU	JRES	X
A	BBRF	EVIATI	ONS	xiii
N	ОТАТ	ION		xiv
1	INT	RODU	CTION AND LITERATURE REVIEW	1
	1.1	Lignoo	cellulosic biomass	2
		1.1.1	Biomass - availability and conversion routes	2
		1.1.2	Gasification	4
		1.1.3	Scope of the current study	5
	1.2	Literat	ture Review	7
		1.2.1	Gasification with O_2 -CO ₂ mixtures	7
		1.2.2	Modeling of packed beds	10
		1.2.3	Gasification with O_2 -steam mixtures	15
		1.2.4	Summary and motivation for the current work	18
	1.3	Thesis	organization	19
2	MA	TERIA	LS AND METHODS	23
	2.1	Bioma	ss properties	23
	2.2	Experi	imental methodology	24
		2.2.1	Packed bed experiments	25
		2.2.2	Single particle experiments	36
		2.2.3	Measurement tools	38
		2.2.4	Measurement uncertainties	43

	2.3	Summary				
3	GAS	SIFICA	TION WITH O ₂ -CO ₂ MIXTURES	45		
	3.1	3.1 CO_2 conversion				
		Mass balance	47			
		3.1.2	CHO balance	49		
		3.1.3	'Volatiles' equilibrium calculations	49		
		3.1.4	Energy balance	51		
	3.2	Results and discussion				
		3.2.1	Gas residence time	60		
		3.2.2	'Volatiles' stoichiometry (ϕ_v) and $NCC \ldots \ldots \ldots$	60		
		3.2.3	The case of coconut shells	62		
		3.2.4	Cold gas efficiency (η_g)	63		
	3.3	Summ	nary	64		
4	NEV TIO	EW INSIGHTS IN TO COUNTER–CURRENT FLAME PROPAGA- ION IN PACKED BEDS				
	4.1	Unive	rsal flame propagation (UFP) model	66		
		4.1.1	Normalized Fuel Flux (NFF)	67		
		4.1.2	Particle size effects	69		
	4.2	Unifie	d Ignition - Devolatalization (UID) model	72		
		4.2.1	Ignition	72		
		4.2.2	Devolatilization	73		
		4.2.3	Oxygen fraction and flame jump	75		
	4.3	Opera	tional regimes	79		
	4.4	Summ	nary	80		
5	GAS	SIFICA	TION WITH O2-STEAM MIXTURES	82		
	5.1	Choice	e of experimental conditions	82		
	5.2	Result	ts and discussion	83		
		5.2.1	Char conversion and H_2 yield $\ldots \ldots \ldots \ldots \ldots \ldots$	85		
		5.2.2	Intrinsic H ₂ yield and NSC	89		
		5.2.3	Residence time	91		
		5.2.4	Higher hydrocarbons and tar	92		

B	UNI TIO	FIED IC N	GNITION - DEVOLATALIZATION (UID) MODEL DERIVA-	106
A	EXF	PERIME	ENTAL DATASET	101
	6.1	Future	work	100
6	CON	NCLUS	IONS AND FUTURE WORK	97
	5.3	Summa	ary	95
		5.2.6	Operational zones of O_2 -steam experiments	95
		5.2.5	Gasification Efficiency (η_g)	94

LIST OF TABLES

1.1	Existing plants in operation for FT synthesis	2
2.1	Properties of biomass - proximate and ultimate analysis	24
2.2	Experimental nomenclature	34
2.3	Measured quantities and their corresponding instruments used	43
3.1	Indicative data of P23C case at \dot{m}'_{ox} of 31 g/m ² s	47
3.2	Comparison of equilibrium results with experimental values	51
4.1	Characteristics of flame propagation zones of packed bed systems .	80
5.1	Experimental nomenclature	83
A.1	Experimental data - air and O_2 -CO ₂ experiments with wood pellets	101
A.2	Experimental data - O_2 - CO_2 experiments with agro-residue pellets .	102
A.3	Experimental data - air and O_2 - N_2 experiments with agro-residue pellets	103
A.4	Experimental data - air and O_2 -CO ₂ experiments with coconut shells	104
A.5	Experimental data - O_2 -steam experiments with wood pellets and agro- residue pellets	105

LIST OF FIGURES

1.1	Syngas production routes and typical FT products		
1.2	Total Primary energy (TPE) demand in India by fuel; source: IEA 2015report	3	
1.3	Different types of gasifiers	5	
1.4	Different zones of a biomass in devolatalization stage	12	
1.5	Thesis organization	22	
2.1	Biomass used in the current study	23	
2.2	Schematic of the experimental setup	25	
2.3	Photograph of the experimental setup	26	
2.4	Fuel mass loss and temperature variation with time for PA case at $V_s = 4.2 \text{ cm/s} \dots \dots$	28	
2.5	Variation of temperature with \dot{m}''_{ox} for agro-residue pellets with air .	29	
2.6	Flame jump phenomenon; oxidizer fractions (% mass)	33	
2.7	Photograph of the O_2 -steam experimental setup	35	
2.8	Typical steam and mixture temperature variation with time	36	
2.9	Schematic of single particle experimental setup	36	
2.10	Mass loss rate for GSB of size ϕ 53 mm x L53 mm showing ignition, devolatalization and charring mode	37	
2.11	Construction of the R type thermocouple used in the experiments	39	
2.12	Photograph of the gas chromatograph	40	
2.13	GC plot for air case of agro residue pellets with 12 g/m ² s oxygen flux	41	
2.14	Photograph of the NDIR gas analyser	42	
3.1	Algorithm used for calculation	46	
3.2	Gas composition and T_{pb} variation with \dot{m}''_{ox} ; uncertainties in data smaller than marker size are not reported	48	
3.3	Bed temperature variation with \dot{m}''_{ox} - P23C case; uncertainty smaller than marker size.	52	
3.4	Bed temperature variation with \dot{m}''_{ox} - P19C case; uncertainty smaller than marker size.	53	

3.5	<i>NCC</i> variation with \dot{m}''_{ox} for P23C, P33N, C23C and WP23C cases; uncertainty $\leq \pm 10\%$.	54
3.6	<i>NCC</i> variation with \dot{m}''_{ox} for P32C, P43N, P42C and C32C cases; uncertainty $\leq \pm 10\%$.	55
3.7	<i>NCC</i> variation with \dot{m}''_{ox} for PA, P19C, P28N, CA, C19C and WPA cases; uncertainty $\leq \pm 10\%$.	55
3.8	ECM variation with \dot{m}''_{ox} for P23C, P33N, C23C and WP23C cases; uncertainty $\leq \pm 10\%$.	56
3.9	ECM variation with \dot{m}''_{ox} for P32C, P43N, P42C and C32C cases; uncertainty $\leq \pm 10\%$.	57
3.10	ECM variation with \dot{m}''_{ox} for PA, P19C, P28N, CA, C19C and WPA cases; uncertainty $\leq \pm 10\%$.	57
3.11	Char conversion with \dot{m}''_{ox} in gasification regime of air and 19% O ₂ cases; uncertainty smaller than marker size.	58
3.12	Char conversion with \dot{m}''_{ox} in gasification regime of 23% O ₂ cases; uncertainty smaller than marker size.	59
3.13	Char conversion with \dot{m}''_{ox} in gasification regime of 32%, 42% and 43% O ₂ cases; uncertainty smaller than marker size.	59
3.14	ϕ_v variation with \dot{m}''_{ox} ; uncertainty $\leq \pm 10\%$	61
3.15	η_g variation with \dot{m}''_{ox} of agro-residue pellet cases; uncertainty $\leq \pm 10\%$.	63
3.16	η_g variation with \dot{m}_{ox}'' of a few other cases; uncertainty $\leq \pm 10\%.$	64
4.1	Uncorrected data of fuel mass flux variation with \dot{m}''_{ox} ; uncertainty $\leq \pm 10\%$	67
4.2	Modified universal propagation behavior for different O ₂ –CO ₂ cases with \dot{m}''_{ox} ; uncertainty $\leq \pm 10\%$.	69
4.3	Variation of t_{ig} and t_v with d_p ; data points are from experiments and lines are for model predictions	70
4.4	\dot{m}_{f}'' variation with V_{s} in relation with universal propagation limits; reproduced from Jaganathan <i>et al.</i> (2017)	71
4.5	Mass loss prediction with experiments	74
4.6	Temperature profile of a steady flame front across reactor length at different times - P23C case at \dot{m}''_f of 31 g/m ² s	76
4.7	Variation of t_{ig} , t_v and \dot{q}''_w with increasing O ₂ fraction	78
4.8	Zones of operation of a packed bed of biomass	79
5.1	ϕ_v variation with \dot{m}_f'' ; uncertainty smaller than marker size	83
5.2	ϕ_v variation with \dot{m}''_{ox} ; uncertainty smaller than marker size	84

5.3	T_{pb} variation with \dot{m}_f'' ; uncertainty smaller than marker size	85
5.4	Char conversion with ϕ_v ; uncertainty $\leq \pm 10\%$	86
5.5	Role of ϕ_v in H ₂ yield - WP30 case; uncertainty $\leq \pm 10\%$	88
5.6	H ₂ yield with ϕ_v ; uncertainty $\leq \pm 10\%$.	90
5.7	NSC variation with ϕ_v ; uncertainty $\leq \pm 10\%$	90
5.8	HHC variation with ϕ_v ; uncertainty $\leq \pm 10\%$	92
5.9	CO yield with ϕ_v ; uncertainty $\leq \pm 10\%$	93
5.10	<i>NCC</i> variation with ϕ_v ; uncertainty $\leq \pm 10\%$	93
5.11	η_g with ϕ_v ; uncertainty $\leq \pm 10\%$	94
5.12	Zones of operation of O_2 -steam experiments $\ldots \ldots \ldots \ldots$	95
B .1	Basic elements of the model	106

ABBREVIATIONS

- NCC Net CO₂ conversion, g/kg of biomass
- *ECM* Enhanced CO conversion, g/kg of biomass
- *CFF* Corrected fuel flux
- *NFF* Normalized fuel flux
- *NSC* Net steam conversion, g/kg of biomass
- LHV Lower heating value, kJ/kg of biomass
- SBR Steam to biomass ratio
- GSB Groundnut shell briquettes
- HHC Higher hydrocarbons
- TGA Thermo gravimetric analysis
- DTA Differential thermal analysis
- DTR Drop tube reactor
- UID Unified ignition devolatalization
- UFP Universal flame propagation

NOTATION

A_c	cross-sectional are of the reactor, m ²
A/F	stoichiometric air to fuel ratio
C_p	specific heat of the fuel, J/gK
d_p	equivalent particle diameter, m
G_p	fuel mass flux, g/m ² s
H_a	actual heating value, kJ/g
H_c	heat of combustion, kJ/kg
H_d	heat of decomposition, kJ/kg
ΔH_{fv}	enthalpy of formation of 'volatiles' biomass, kJ/mol
H_{ref}	reference heating value, kJ/g
h_i^s	sensible enthalpy, kJ/g
h_i^0	formation enthalpy, kJ/g
k	thermal conductivity W/m ² k
m_b	mass of biomass, kg
$m_{CO,outlet}$	mass of CO in exit gas, g
$m_{CO,v}$	mass of CO released through 'volatiles' oxidation, g
m_{CO_2}	mass of inlet CO ₂ , g
$m_{CO_2,inlet}$	mass of CO_2 fed in oxidizer, g
$m_{CO_2,outlet}$	mass of CO_2 in exit gas, g
$m_{CO_2,v}$	mass of CO_2 released through 'volatiles' oxidation, g
$m_{H_2O,inlet}$	mass of H_2O fed in oxidizer, g
$m_{H_2O,outlet}$	mass of H_2O in exit gas, g
$m_{H_2O,v}$	mass of H_2O released through 'volatiles' oxidation, g
\dot{m}_f''	fuel mass flux, g/m ² s
$\dot{m}_{f_{ref}}''$	reference mass flux, g/m ² s
$\dot{m}_{f_a}^{\prime\prime}$	actual mass flux, g/m ² s
\dot{m}''_{ox}	oxygen mass flux, g/m ² s
Nu_0	Nusselt number
ϕ_v	'volatiles' stoichiometry
Φ	overall stoichiometry
$ ho_a$	actual bed density, kg/m ³
$ ho_p$	particle density, kg/m ³
$ ho_{ref}$	reference bed density, kg/m ³
\dot{q}_w''	incident heat flux, kW/m ²
\dot{r}	flame propagation velocity, m/s
r_p	radius at pyrolysis front, m
r_s	radius at the surface, m
s_a	actual stoichiometric coefficient
s_{ref}	reference stoichiometric coefficient
t_{ig}	ignition time, s
t_g	gas residence time, ms

t_v	devolatalization time, s
T_{∞}	ambient temperature, K
T_p	temperature at the pyrolysis front, K
T_s	temperature at the surface, K
T_{pb}	average peak bed temperature, K
V_s	superficial velocity, m/s
Y_{ox_a}	actual oxidizer fraction
$Y_{o,\infty}$	free stream oxygen fraction
$Y_{ox_{ref}}$	reference oxidizer fraction
η_g	cold gas efficiency
ϵ	emissivity
σ	Stefan Boltzmann constant

CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

Syngas, or synthesis gas is a fuel gas mixture rich in CO and H_2 . Syngas is used to generate electricity, to produce hydrogen, ammonia, methanol, dimethyl ether, and synthetic hydrocarbon fuels. Numerous techniques for syngas production are available, namely, gasification, carbonization (thermal decomposition of carbonaceous feedstock with little/absence of oxygen), steam reforming of methane or natural gas, auto thermal reforming of hydrocarbons in presence of oxygen and steam, partial oxidation of fossil fuel based hydrocarbons (like coal and natural gas) etc. One of the applications of syngas that is gaining importance is in the area of liquid fuel synthesis using Fischer-Tropsch (FT) process as shown in Fig. 1.1, based on Liu *et al.* (2010).



Figure 1.1: Syngas production routes and typical FT products

At present, syngas is produced mostly from fossil fuels like coal and natural gas due to the abundant availability of the resource. Table 1.1 based on data taken from Guettel *et al.* (2008), shows the details of a few FT synthesis plants operating with fossil fuels.

Company	Site	Capacity (bpd)	Raw material	Commissioning year
Sasol	Sasolburg	2500	Coal	1955
Sasol	Secunda	85,000	Coal	1980
Sasol	Secunda	85,000	Coal	1982
MossGas	Mossel Bay	30,000	Natural gas	1992
Shell	Bintulu	12,500	Natural gas	1993
Sasol/Qatar Petroleum	Qatar	34,000	Natural gas	2006
SasolChevron	Escravos	34,000	Natural gas	2007
Shell	Qatar	140,000	Natural gas	2009

Table 1.1: Existing plants in operation for FT synthesis

Rising concerns over increasing CO_2 emissions has increased interest in utilization of alternate sources to meet the future energy needs. Also, by utilizing locally available resources as much as possible, dependence on oil imports can be reduced. Lignocellulosic biomass is one such source, abundantly available in the form of agro-residues and best suited for conversion to syngas, which in turn can be used for chemical/liquid fuel synthesis route (Naik *et al.*, 2010; Serrano-Ruiz and Dumesic, 2011; Guettel *et al.*, 2008). Out of 500 mmt/year of agro-residues produced in India, 100 - 120 mmt/year is available for energy generation systems (Mukunda, 2011). Also, studies on biomass to liquids (BTL) systems by Ail and Dasappa (2016); Snehesh *et al.* (2017) show that around 40 - 45 bpd of liquid fuel can be produced by catalytic up-gradation of syngas obtained from oxy-steam gasification of 24 tonnes of biomass per day. A conservative estimate using this data for BTL plant using 100 mmt/year of biomass could produce liquid fuel of around 460,000 bpd and this amount is substantial and can replace 70% of oil import of India.

1.1 Lignocellulosic biomass

1.1.1 Biomass - availability and conversion routes

Biomass is defined as any organic substance derived from plant and animal matter. Biodegradable biomass like cow dung, night soil, kitchen and food waste are better suited for bio-chemical conversion techniques like anaerobic digestion. Biomass derived from plant matter or in other words lignocellulosic biomass is the other category which is abundantly available (around 500 mmt/year). Biofuels derived from biomass are classified into two types, (1) first generation biofuel and (2) second generation biofuel. Biodiesel (a mixture of long-chain alkyl esters produced by transesterification of vegetable oils with methanol) and ethanol (produced by bacterial fermentation of corn and sugar cane derived sugars) are some examples of first generation biofuels. Increase in demand of food due to usage of food crops for fuel, low fuel yield versus food in a fixed agricultural space and being an expensive emission abatement technology are some important limitations of first generation biofuels (Naik *et al.*, 2010; Serrano-Ruiz and Dumesic, 2011). Second generation biofuels are derived from agroresidues, forest waste, industrial waste etc., as these make up larger fractions of cheap and abundant non edible materials from plants. The examples of second generation biofuels are cellulosic ethanol and Fischer–Tropsch fuels. According to International



TPE : 441 Mtoe, Year : 2000

TPE : 775 Mtoe, Year : 2013

Figure 1.2: Total Primary energy (TPE) demand in India by fuel; source: IEA 2015 report

Energy Agency report (IEA, 2015), demand for bioenergy (consisting overwhelmingly of solid biomass, i.e. fuel-wood, straw, charcoal or dung) has grown in absolute terms, but its share in the primary energy mix has declined by almost ten percentage points since 2000 (see Fig. 1.2). This is because, households moved to other fuels for cooking, notably liquefied petroleum gas (LPG). Hence, it is clear that biomass potential remains still untapped. A recent report by 'Annual Review of Public Health, (Smith *et al.*, 2014)' indicates, in India, around 3 to 4 lakh people per annum die due to indoor air pollutants and particulate matter emitted through traditional burning methods (like chulas and open fire etc.). While it is important to restrict the traditional burning of

biomass and improve the living standard of rural people, the replacement of biomass by LPG may not be a viable alternative since more than 70% of the crude oil demand of our country is met by import (MNRE report, 2015). Improved, efficient, clean burning systems like gasifier based stoves are shown to be a viable alternative for this problem. More details on these efforts can be found in Varunkumar (2014); Mukunda and Attanoor (2018).

Lignocellulosic biomass typically contains less than 30% moisture and also contains more than 10% lignin. Therefore, it is more suitable for thermo-chemical conversion than other routes like bio-chemical and physio-chemical conversion techniques (which can handle high moisture i.e. > 30% and cannot generally handle lignin). Three main types of thermo-chemical conversion techniques available are, (1) combustion stoichiometric or lean oxidation of biomass, mainly used for power and heating applications, (2) gasification - sub stoichiometric oxidation (30 – 60% of total stoichiometric oxidizer is supplied) combined with hot-char caused reduction to produce syngas and (3) pyrolysis - thermal decomposition of biomass in absence of oxidizer to produce fuel and charcoal. Biomass gasification is most suited for syngas generation from lignocellulosic biomass out of the three routes mentioned above and it is the main focus of the current study.

1.1.2 Gasification

Commonly used biomass gasifier configurations fall under the following categories - (1) updraft, (2) downdraft and (3) fluidized bed and a schematic of these configurations are shown in Fig. 1.3.



Figure 1.3: Different types of gasifiers

In updraft configuration, air is fed from the bottom through the grate and fuel is fed from the top. The exit gas from the oxidation zone passes through the bed expelling the 'volatiles' from the biomass in pyrolysis zone and further heats up the biomass in drying zone and leaves from the top. In downdraft configuration, air is fed to the oxidation zone from the top/sides and the hot gases of oxidation is allowed to pass through a bed of hot char and gases are collected from the bottom of the grate. In fluidized bed configuration, biomass feedstock is suspended in the bed with high velocity oxidizer jets where different modes of conversion (de-volatilization, oxidation, char conversion) occur in a distributed fashion without distinct zones like drying, pyrolysis, oxidation and reduction. Updraft and fluidized bed configurations produce tarry gas (typically around 100 g/m³ of exit gas in updraft and 3 g/m³ in fluidized bed as compared to 200 mg/m³ in downdraft configuration Mukunda, 2011). Hence, gas cleaning and suspended particles removal (in case of fluidized bed) becomes inevitable and increases the complexity of the system.

1.1.3 Scope of the current study

Extensive experimental and theoretical studies on biomass gasification have been carried out in the past (more extensive research and development took place after World War II) with above said configurations. Almost every variety of coal, agro-residues, forest residues, urban solid waste etc., pertaining to a particular geographical terrain is gasified and the syngas quality is studied (Ahmad *et al.*, 2016; Kumar *et al.*, 2009; Ruiz *et al.*, 2013; Kirubakaran *et al.*, 2009; Mukunda *et al.*, 1994). Effect of fuel type, oxidizer type, size, equivalence ratio ($\Phi = (Fuel/Air)_{actual}/(Fuel/Air)_{stoic}$), bed temperature, tar reduction, catalyst effects etc., were the main parameters considered in these studies.

Out of different designs of gasifiers developed over a long time since WWII, 'downdraft open-top re-burn fixed bed gasifier', developed at Indian Institute of Science (IISc), gained significant market reach and proven to be technically and economically viable. A wide range of gasifiers (from a few kW_e to 1.2 MW_e) has been installed throughout the country with this technology. Salient features of this design include, (1) fuel flexibility, (2) maintaining a higher temperature char bed, which cracks the higher hydrocarbons and thereby efficiently contributing to minimum tar in the exit gas (about 100 ppm), (3) arranging air flow from top as well as sides with which the superficial velocity is brought down drastically (~ 10 cm/s) which helps in better tar cracking and avoid ash fusion issues. Refer Sharan *et al.* (1997); Verbong *et al.* (2010); Ravindranath *et al.* (2004); Mukunda (2011) for more details.

Based on these considerations, downdraft configuration is chosen in the current study. Additional advantages of this configuration over updraft and fluidized bed are as follows - (1) fuel flux, as a function of superficial velocity (V_s) exhibits universal characteristics for variety of biomass (Varunkumar *et al.*, 2013) with air as the gasification medium (more details in the next section), (2) flame propagation in these practical configurations is analogous to packed bed systems with a coordinate frame fixed to the unburnt fuel and (3) as inferred from *universal flame propagation* model (Varunkumar, 2014), ignition time (t_{ig}) estimated from packed bed systems i.e. $t_{ig} = d_p/\dot{r}$ where, d_p is the particle diameter and \dot{r} is the flame front velocity as a function of heat flux can be used to validate single particle models (Jaganathan *et al.*, 2017).

Biomass air gasification finds its application in small and medium scale power generation and district heating. Under optimal gasification conditions, product gas composition (% v/v) is CO - 20%, H₂ - 15%, CH₄ - 1.5%, CO₂ - 10% and rest N₂, with a heating value of 4.5 MJ/kg (Mukunda, 2011). Therefore, more than half of the volume of product gases is inert (taking up 28% sensible enthalpy) as shown in Varunkumar (2014). This limits the applicability to only power and heating purposes. Syngas generated from biomass air gasification can be converted to fuel via Fischer-Tropsch. This requires gas separation which becomes inefficient (due to large volume of same molar weight compounds like N_2 and CO) and expensive.

Replacing inert N₂ in air with reactive components like CO₂ and steam, can enhance CO and H₂ yield by promoting endothermic reactions between CO₂ and steam with char. Also, exit gases contain only CO, H₂ and CO₂ which can be separated and fed to processes like Fischer-Tropsch to synthesize fuels and chemicals. Hence, exploring the enhancement of CO and H₂ with O₂–CO₂ and O₂–steam mixtures is the main focus of the current study. Also, the technology of air separation is well matured and O₂ extraction from air will be economically viable in near future with emerging technologies like (1) Chemical Looping Air Separation (CLAS), (2) chemical absorption, (3) adsorption, (4) polymeric and ion transport membrane technologies etc. Typical energy consumption for an economical scale of operation (5MW_e or more) with well matured technology like cryogenic air separation is around 6–10 %. However, integration of heat, refrigeration, process and waste streams between the industrial gas process and other units within the overall facility can improve efficiency and decrease cost further (Wu *et al.*, 2018; Smith and Klosek, 2001).

1.2 Literature Review

In this section, earlier studies relevant to biomass gasification with different oxidizers are discussed. Studies on gasification with O_2 – CO_2 mixtures are discussed first. Theoretical aspects of flame propagation and composition prediction are discussed next. Finally, studies on gasification with O_2 –steam mixtures and their relevance to the current study are discussed. The section ends with summary and motivation of the current work.

1.2.1 Gasification with O₂–CO₂ mixtures

A number of studies have been carried out to explore CO_2 reuse in gasification/combustion systems using biomass and coal. Lab scale TGA/DTA studies with different types of biomass/coal in atmospheres of CO₂ and O₂–N₂/H₂O mixtures covering a range of heating rates (1 to 100 °C/min) and maximum temperatures (700–1400 °C) have been reported - see for instance Dai *et al.* (2017); Huo *et al.* (2014); Sircar *et al.* (2014); Butterman and Castaldi (2009); Lin and Strand (2013); Bouraoui *et al.* (2015). Drop tube reactor (DTR) is another technique with which the reactivity of biomass and coal (powdered to a few hundred μ m diameters) in O₂/N₂/H₂O/CO₂ atmospheres have been studied at very high heating rates of the order of 10⁴ K/s (Kyotani *et al.*, 1993; Riaza *et al.*, 2014; Billaud *et al.*, 2016; Ranzi *et al.*, 2013) as compared to TGA/DTA.

A few other works were done in fluidized beds (FB), for instance Nilsson *et al.* (2012) and Kramb *et al.* (2017) performed experiments with dried sewage sludge and birch wood of particle sizes from 1-5 mm and 14 mm equivalent spherical diameter respectively, with nitrogen based de-volatilization and subsequent gasification of char under various $N_2/CO_2/H_2O$ fractions at 800 - 900°C. The main aim of these experiments was to explore kinetics of char-CO₂ reactions and to estimate Arrhenius parameters. Similar results are reported for coal particles by Bu *et al.* (2017).

Sandeep et al. (2011) conducted experiments in a downdraft gasifier (10 kg/hr of casuarina wood chips) by systematically replacing N2 with 15, 12 and 8.5% CO2 maintaining 21% O₂ and a minimum bed temperature of 800°C. Important features of this work are, (1) maximum CO_2 conversion of up to 55% at 15% CO_2 case, (2) carbon balance with an accuracy of $\pm 20\%$ is reported, and (3) CO₂ conversion efficiency is calculated as the ratio of the difference between CO₂ released from O₂-CO₂ case and air case to that of inlet CO_2 supplied in corresponding O_2 - CO_2 case. It is important to note that even in the air gasification case there will be char reduction due to CO_2 generated by 'volatiles' oxidation. This is not accounted for in the calculation of CO₂ conversion in Sandeep *et al.* (2011). As shown later, CO_2 conversion with air can be substantial (220 g/kg of biomass). Annamalai et al. (2013) carried out experiments with updraft gasifier of mesquite fuel using air, air/steam and O₂-CO₂ (79% O₂-21% O₂ by volume) mixtures in a batch type gasifier. In this work, CO concentration up to 32% (v/v) is reported, which was attributed to CO_2 conversion to CO through Boudouard route at an equivalence ratio of 2.7 and hence the fuel value of the exit gas was higher in O₂-CO₂ cases as compared to corresponding air/steam and air cases. However, the bed was updraft and hence the 'volatiles' products interaction/reduction with char was limited in the above case as compared with downdraft mode. Also as discussed earlier (refer section 1.1.1), exit gas from updraft gasifiers show high tar levels. Hence, when conceived as candidates for practical gasification applications, these configurations will require additional tar cracking/removal systems downstream of the gasifier. Prabowo *et al.* (2014) worked on pyrolysis and gasification of rice straw with mixtures of $H_2O/CO_2/O_2/N_2$ in a lab scale downdraft gasifier at varying proportions and temperatures from 750 - 950 °C in a electrically heated furnace with and without O_2 . Maximum thermal efficiency of 60% was observed in 60% CO₂ fraction rest being O_2 (8.3%) and N_2 (31.7%) case at 950°C. Experiments with oxygen are limited to 8.5% (v/v), wherein CO₂ conversion has been reported. It is also important to note that in any practical biomass gasification/combustion systems, external heating with high fractions of CO₂ (more than 80 to 100%) are of limited use.

Lahijani et al. (2014) worked on microwave enhanced fixed bed gasification of oil palm shell char. Activation energy of microwave induced gasification which operates at a heating rate of 1400°C/min (similar range of fixed and fluidized beds) was found to be 74 and 36 kJ/mol for base case and catalytic microwave heating case respectively as against 250 kJ/mol by conventional (TGA/DTA) heating methods. Moreover, TGA operates at lower heating rates, DTR at very high heating rates, whereas practical systems like fixed bed/fluidized bed operate in between 700 - 7000°C/min and hence reaction rate constants have fundamentally different dependencies on temperature which are manifested from Arrhenius parameters Lahijani et al. (2014). Also, most of the studies of TGA/DTR and FB were aimed at obtaining kinetic parameters to study the intrinsic reactivity of fuel (mostly char) with pure or mixture of N₂/O₂/CO₂/H₂O with external heating. On the other hand, fixed bed biomass combustion systems are self-sustained with 'volatiles' oxidation followed by char reduction. Intrinsic kinetics of 'volatiles' oxidation (releases 70% of total heat and drives flame propagation) is of less relevance in these configurations, as it is limited by oxygen diffusion to the flame Varunkumar et al. (2013); Porteiro et al. (2012).

A few modeling works on CO_2 based conversion of carbonaceous feedstock were studied by Renganathan *et al.* (2012); Dai *et al.* (2017); Lin and Strand (2013); Billaud *et al.* (2016) of which works of Renganathan *et al.* (2012); Billaud *et al.* (2016) are based on thermodynamic equilibrium/Gibbs free energy minimization technique. Other models are based on rate of change of surface area of char $S(X)/S_0$ (random pore model and grain model are extensively used for this purpose in literature) to estimate the reactivity of char under various atmospheres. Relevance of equilibrium models and char kinetic models to the current study is discussed in the next section.

1.2.2 Modeling of packed beds

Flame propagation

Another aspect that has received little attention in literature is flame propagation behavior in biomass packed beds with oxidizers other than air. It is important to mention here that, the major constituents of any biomass by mass are cellulose (28 - 45%), hemicellulose (10 - 29%), lignin (0 - 40%), extractives (crude proteins and oil, less than 5%) and ash (less than 10%). The fraction of these constituents is almost invariant for most of the biomass except some special class of fuels like coconut shells, corn cob and bagasse (with extractives more than 10%) and rice husk (with ash more than 20%). In other words, on moisture and ash free basis, all biomass are similar (Mukunda, 2011). Varunkumar et al. (2013) have shown that the fuel flux variation with air superficial velocity exhibits universality; that is, on a dry and ash free basis, the fuel flux is not dependent on biomass type, but only on superficial velocity. Fuel flux (\dot{m}''_f) increases with increase in superficial velocity in the 'gasification' regime and saturates in 'combustion' regime and reduces to zero at extinction. The range of fuel conversion with air as a gasification medium is shown to be between 70 - 80 g/m²s and this limits the maximum power output that can be obtained with air based combustion/gasification systems. Superficial velocity (V_s) was found to be the most influential parameter to affect fuel flux (\dot{m}''_{f}) , bed temperature (T_{pb}) and syngas composition. Other fuel linked properties like size, density, moisture and ash content are shown to be have only secondary/no effects. Extensive discussion on literature on other flame propagation models from Fatehi and Kaviany (1994); Gort (1995); Porteiro et al. (2010); Ronnback et al. (2008); Yang et al. (2004); Ryu et al. (2007); Collazo et al. (2012) is given in Varunkumar (2014). The conclusion from Varunkumar (2014) is that, biomass conversion in packed beds is governed by heat transfer and hence, models with detailed kinetics to predict the burn rate is of less relevance.

Models to predict the propagation rate is important to design practical gasification/ combustion systems; one example is the design of traveling grate boilers, where the

'universal flame propagation model' was used to set out gasification/combustion parameters like fuel layer height, grate velocity, quantity of air to be supplied and distribution strategies (Varunkumar et al., 2015). The important conclusion from Varunkumar et al. (2013) is that the propagation rate is controlled by radiation heat transfer from flame front, which in turn determines the ignition time of fresh biomass upstream of the flame front. This behavior is shown to be due to ignition time (t_{iq}) being the rate limiting step in flame propagation and the particle density scaled ignition time being independent of biomass type. But when the oxygen fraction in the oxidizer is increased well beyond 21%, which might be required for enhancing char conversion with O_2 -CO₂ and O_2 steam mixtures, there is the possibility of devolatilization time (t_v) becoming rate limiting - this causes the so called 'flame jump', a type of unsteady propagation. Another condition under which this can happen is as follows - starting from conditions of steady propagation, if the particle size is increased beyond a critical size (which is a strong function of oxygen fraction in the oxidizer), the ignition time can become smaller than devolatalization time. These aspects, which go beyond the scope of 'universal flame propagation' model, need further investigation for identifying optimal conditions for steady flame propagation.

In light of this, a 'unified ignition-devolatalization (UID) model' to predict t_{ig} and t_v for a single particle is developed in the current study. This UID model is the essential first step in determining the behavior of biomass in packed beds, which can be further extended to predict flame propagation, temperature profile evolution and syngas composition in practical gasifiers/combustors. The UID model developed in the current work is the extension of devolatalization model developed by Mukunda *et al.* (1984) to capture ignition process. A brief overview of the model is given below.

As a dry particle heats up, 'volatiles' are released from the particle after a critical temperature, called the pyrolysis temperature (T_p) here. Following this, a flame envelopes the particle. This flame resembles the steady flame of droplet combustion. The devolatilization model of Mukunda *et al.* (1984) was evolved on lines of the diffusion limited classical droplet theory. Four zones were identified in the flaming region of the particle as shown Fig. 1.4.



Figure 1.4: Different zones of a biomass in devolatalization stage

Region I constitutes virgin wood, region II shows the charred biomass, region III is the gas phase between the particle and flame, region IV shows the ambient; 'P' shows the propagating pyrolysis front. Pyrolysis front is identified by the thin zone which is at the pyrolysis temperature (T_p) ; T_p is the minimum temperature at which 'volatiles' are evolved. In order to describe the evolution of the pyrolysis front when subjected to high temperatures, species and energy conservation equations are solved for all the four regions. Region I is dominated by transient conduction, whereas the other three zones were taken to be quasi-steady. This assumption is valid as the rate of movement of pyrolysis front is very small compared to gas velocities. This single particle model is further extended in the current work to calculate ignition times. Results from the UID model are used to elucidate aspects of flame propagation with O₂–CO₂ and O₂–steam mixtures.

Exit gas composition

The next important aspect of theoretical modeling is to predict the syngas composition at gasification conditions and this is mostly approached through kinetic rate models and thermodynamic equilibrium models, in earlier literature. Kinetic models predict the rate of thermal pyrolysis and gasification using kinetic rate expressions obtained from experiments at controlled conditions like TGA (Wang and Kinoshita, 1993; Blasi, 2000; Fiaschi and Michelini, 2001; Babu and Sheth, 2006; Gobel et al., 2007; Sharma, 2008). Kinetic parameters obtained from such studies show sensitivity to biomass type, catalyst present in the form of inorganic matter and temperature. When the particle size is increased (say to a few mm), heat and mass transfer processes become rate limiting rather than kinetics and the conversion is truly an 'aero-thermal-chemical' process (Mukunda, 2011). From the studies of Varunkumar et al. (2013) it is clear that the 'volatiles' oxidation in packed beds is diffusion limited. Their conclusion is based on the simultaneous measurement of O_2 fraction (measured using λ sensor) and temperature, for a range of superficial velocity values covering gasification as well as char oxidation regimes, as the flame front propagates into a fresh layer of biomass in a packed bed reactor. It has been shown in Varunkumar *et al.* (2013), that when the measured O_2 fraction is plotted against temperature, it shows a sharp drop from 21% to almost 0% as the temperature crosses the ignition temperature as shown in Fig. 8 from (Varunkumar et al., 2013). This clearly demonstrates that the oxidation process in a packed bed flame propagation phenomenon is clearly diffusion controlled. Hence, intrinsic kinetics of volatile oxidation (releases 70% of total heat release Varunkumar (2014) and drives flame propagation) is of less relevance in these configurations.

Gasification process is predominantly a reaction of char with CO₂ and H₂O. Single particle experiments were done by Dasappa (1999) with char of larger sizes (i.e. equivalent spherical diameter $d_p > 4$ mm) with different oxidizers and at different temperatures. Mass loss with time and temperature were recorded and the conversion times with air, O₂, H₂O and CO₂ were determined. The conversion time is proportional to d^2 for air and O₂ which implies that char oxidation is diffusion limited and the exponent is lower for CO₂ and H₂O which shows combined diffusion-reaction control for reduction reactions of char. The exponent increases further with temperature, which is an indication of higher reactivity and shift towards diffusion limited conditions.

Equilibrium modeling to predict the exit gas composition is the other area much attended in gasification literature (Gomez-Barea and Leckner, 2010; Li *et al.*, 2001; Melgar *et al.*, 2007; Jarungthammachote and Dutta, 2007, 2008; Yoshida *et al.*, 2008; Karamarkovic and Karamarkovic, 2010; Huang and Ramaswamy, 2009). Volatile oxidation is diffusion controlled and hence, equilibrium approach to predict volatile oxidation products is appropriate. Char oxidation is also diffusion controlled and hence, equilibrium modeling is still applicable here too. But, in gasification regime, char ki-

netics plays a key role and equilibrium calculations to predict the overall exit gas composition in gasification regime is not the right choice. Also, as shown by Varunkumar (2014), char conversion is complete in gasification regime. This is due to limitation of char availability in biomass to around 20% by mass. Also, even for the predictions of volatile oxidation products, equilibrium calculations are not accurate at highly fuel rich conditions (i.e. $\Phi > 3$). These inconsistencies may perturb further due to the presence of reactive components like CO₂ and steam in the oxidizer and hence, a new methodology is developed to address these issues, in the current study.

In brief, biomass contains 80% 'volatiles' and releases 70% of the total heat due to 'volatiles' oxidation, and drives the flame propagation which is governed by heat transfer. Hence, models based on detailed kinetics to predict the burn rate is of less relevance. Universal flame propagation (UFP) model with surface heat balance at pyrolysis front can be used to predict the burn rate of the fuel in a fixed bed. Also, the 'volatiles' combustion and char mode of single particle and packed bed are similar beyond the role played by density of the bed in packed bed systems. Hence, single particle model can be used to predict the burn rate of the packed bed systems as well. However, UFP model assumes that the t_{ig} is more or equal to t_v . The assumption of $t_{ig} > t_v$ may not be valid always and two such situations are as follows -

- 1. starting from conditions of steady propagation, if the oxygen fraction in the oxidizer is increased, t_{ig} can become much lower than t_v leading to the so called 'flame jump' (typically occurs when O₂ fractions in the oxidizer exceeds 40%).
- 2. for a fixed oxidizer composition and flux corresponding to steady propagation, if the particle size exceeds a critical value, t_{ig} can become lower than t_v . This critical value is a function of O₂ fraction and mass flux of the oxidizer.

Hence, these cases need further exploration and are addressed in the current study. Also, net conversion of CO_2 or steam with char is the focus of the present work. A novel method, invoking equilibration of 'volatiles' oxidation under gasification conditions is developed to quantify the net CO_2 / steam conversion and the same is explained in chapter 3.

1.2.3 Gasification with O₂–steam mixtures

Studies on steam gasification as similar to O_2 -CO₂ studies of biomass can be broadly classified into two categories - (1) under controlled environments like in TGA/DTA and single particle experiments and (2) practical configurations like packed (updraft or downdraft) and fluidized beds.

TGA/DTA studies mainly focused on the kinetics of char steam reaction (Ahmed and Gupta, 2011; Nipattummakul *et al.*, 2011; Billaud *et al.*, 2016; Huo *et al.*, 2014). Single particle studies with larger particles (i.e. equivalent spherical diameter, $d_{eq} >$ 4 mm) are done in a few studies like Dasappa (1999); Mermoud *et al.* (2006*b,a*) with char, biomass and coal particles in pure steam or steam/inert atmospheres. All the above studies show increased conversion rates with increase in steam temperatures. A few recent studies on TGA (Prestipino *et al.*, 2018; Dupont *et al.*, 2016) brought out the role of ash in enhancing the char - steam gasification reaction rate. Also, as highlighted by Dasappa *et al.* (1998), char steam reactions show dependence on the diameter, $t_c \sim d_0^{1.2}$ at 1250 K and $d_0^{1.3}$ at 1388 K, where t_c is the total conversion time and d_0 is the initial particle diameter. The exponent increases further with temperature, which is an indication of higher reactivity and shift towards diffusion limited conditions. These results are used in interpretation of experimental results from current work.

With updraft gasifiers, a number of studies are carried out using various fuels like, woody biomass, agro and forest residues, wood shavings and coal (Gao *et al.*, 2008; Lucas *et al.*, 2004; Umeki *et al.*, 2010; Chang *et al.*, 2011; Zhang *et al.*, 2014; Balu *et al.*, 2015; Nipattummakul *et al.*, 2010). Most of the above studies use pure steam, air/steam mixture or enriched air/steam mixture as oxidizer. In all of the above studies, steam to biomass ratio (SBR) was varied from 0 - 4, temperature of the bed was maintained above (1000 K) aided by external heating and steam at around 1300 K was used; H₂ yield up to a maximum value of 86 g/kg of biomass was reported. The fuel value of the exit gas is generally between 9 - 12 MJ/Nm³. A few interesting studies on an auto thermal updraft oxy-steam gasifier with steam temperature of 160 °C at fuel rich conditions (Φ inferred to be in the range of 4.5 to 5.55) were reported in Cerone *et al.* (2016, 2017); Cerone and Zimbardi (2018). The H₂ yield from their experiments were in the range of 30 - 45 g/kg of biomass. One other study in updraft configuration is that of Baker *et al.* (1984), in which wet biomass (up to 50% moisture) was used and the oxidizer was a mixture

of O_2 and steam. Three different O_2 to steam fractions were used, namely, 0.5, 1 and 2 and the corresponding fuel flux reported are 74, 127 and 163 g/m²s (corresponding to an oxidizer flux values of 77, 114 and 153 g/m²s); the lower heating value (LHV) of syngas was 11.8, 10.8 and 9.6 MJ/Nm³ respectively. A few studies with fluidized beds are also available for steam gasification. For instance, work reported in Lv *et al.* (2004); Franco *et al.* (2003); Rapagna *et al.* (2000); Dascomb *et al.* (2013); Turn *et al.* (1998) presents SBR and Φ to arrive at optimum H₂ yield for various fuels like wood, forest residues, olivine particles etc., As observed with updraft gasifiers, here also the LHV of the syngas was around 12 MJ/Nm³. Thus, enhancement of H₂ is evident from the experiments with updraft and fluidized bed configurations but the tar levels are high (greater than 2.5 g/kg of biomass Sandeep and Dasappa, 2013), which limits the usage of these configurations for steam gasification.

Downdraft configuration is considered better for gasification as compared to updraft, since, the residence time for the reaction of 'volatiles' oxidation products with hot char is higher in downdraft configuration resulting in lower tar; with the replacement of N₂ in air with CO₂/steam, use of downdraft configuration will lead to enhanced CO and H₂ yield. Studies reported in Sandeep and Dasappa (2013); Kumabe *et al.* (2007); Chiodo *et al.* (2017); Sharma and Sheth (2016); Lv *et al.* (2007); Sandeep and Dasappa (2014) are noteworthy. Studies of Kumabe *et al.* (2007), Chiodo *et al.* (2017) and Sharma and Sheth (2016) were with air/steam mixture or enriched air/steam mixture as an oxidizer in a lab scale downdraft configurations. Varying the SBR, Φ and temperature, optimum conditions for maximum yield of H₂ was explored. Saturated or slightly superheated steam (around 200°C) was used. The fuel value and cold gas efficiency of systems that use air/steam as an oxidizer were low (in the order of 4 - 4.2 MJ/Nm³ and 54%), as compared to enriched air/steam mixtures (about 8 -10 MJ/Nm³ and 65%). H₂ yield was not quantified and char conversion data was not reported.

Lv *et al.* (2007) performed experiments to get maximum H₂ yield from a self sustained (i.e. without external heating) downdraft gasifier with pine wood blocks. O₂– steam mixture (31 to 50% O₂ by mass and rest being steam) was used and hydrogen yield was compared with air experiments. Staged O₂ injection was used in oxy-steam experiments to avoid local O₂ accumulation (similar to 'flame jump' phenomenon as discussed in the current work in detail later). The steam temperature used was about 100 to 120 °C; H₂ yield was in the range of 32 - 44 g/kg of biomass for Φ in the range of 4.5 - 3.3 (corresponds to ER = 0.22 - 0.3, where ER = $1/\Phi$); SBR was in the range of 0.4–0.7. The LHV of the gas was about 9 - 11 MJ/Nm³. However, the estimated values for 'volatiles' stoichiometry for these conditions is 4.5 to 3.8 (corresponding to a fuel flux range of 11 to 22 g/m²s and oxidizer flux range of 8 to 20 g/m²s) and hence highly fuel rich; this is consistent with high tar fraction (about 8 g/kg of biomass) reported in Lv *et al.* (2007). However, in this study, char conversion was not reported.

Sandeep and Dasappa (2013) reported experimental results for gasification of dry casurina wood chips in a downdraft reactor with varying SBR (1 - 4) and Φ (5.6 - 2.7). Steam at a temperature around 820°C was supplied along with 11 to 22% of O_2 (in order to maintain bed temperature around 1000 to 1100 K with SBR increase) to favor H_2 yield. At SBR of 2.7 and Φ of 3.3, maximum H_2 yield of 104 g/kg of biomass were reported with a gasification efficiency of 71% and H₂/CO ratio of 3.9. Hydrogen yield from Sandeep and Dasappa (2013) was high mainly due to following reasons, (1) high steam temperatures (around 1100 K), (2) injection of steam close to char bed, (3) water gas shift reaction in gas phase which is also evident from decreased CO content and H₂O fractions in the exit gas (estimated to be contributing around 36 g/kg of biomass for maximum case) and (4) H₂ content from methane present in syngas is also added to the total hydrogen yield (estimated to be around 15 -20 g/kg of biomass). Experiments with wet biomass are also reported in Sandeep and Dasappa (2013), by varying the H₂O/biomass ratio from 0.75 to 1.4. Maximum H₂ yield of 63 g/kg of biomass and a cold gas efficiency of 56% at H₂O/biomass ratio of 1.41 was reported for the same. Results from the experiments of Dasappa and group (Sandeep and Dasappa, 2013, 2014) indicate that, high energy density of syngas and cold gas efficiency are favored at lower SBR (0.75), but the H_2 yield increases with higher SBR at the expense of efficiency (Sandeep and Dasappa, 2014). Carbon boundary point, as defined in Sandeep and Dasappa (2014) as the point where residual carbon approached 0%, occurs at SBR of 1.5, beyond which gas phase reactions predominate to increase the H₂/CO ratio due to water gas shift reaction. Hence, the efficiency decreases with a proportionate increase of H_2 yield and decrease in CO yield (CO volume fraction in the exit gas was as low as 13%). Interestingly, the H_2 yield predicted by Bhattacharya *et al.* (2012) with a equilibrium model using oxygen blown gasification followed by water gas shift reaction is very close to that obtained by Sandeep and Dasappa (2013) i.e. around 102 g/kg of biomass.

In brief, single particle studies by Dasappa (1999), show increased reactivity of

char steam reaction with temperature rise and hence higher H_2 yield. H_2 yield with steam temperatures less than 200°C can be considered intrinsic and is about 40 g/kg of biomass (Cerone et al., 2016, 2017; Cerone and Zimbardi, 2018; Lv et al., 2007). In all these configurations it was inferred that, the operation was limited to highly fuel rich conditions (i.e. $\phi_v > 2$), hence, H₂ from 'volatiles' is the major contributor with limited contribution from 'char-steam reaction'. Even though the intrinsic H₂ yield is invariant for different configurations, updraft and fluidized bed show high tar levels. Hence, when conceived as candidates for practical gasification applications, these configurations will require additional tar cracking/removal systems downstream of the gasifier. On the other hand, studies aimed at maximizing H₂ yield like Sandeep and Dasappa (2013), use high steam temperatures (>800°C) and hence the H_2 yield in this case cannot be considered intrinsic; in these cases also, the role of 'volatiles' is not clear, since most of the H₂ is from char-steam and water gas shift (WGS) reaction due to high steam temperatures. Current work is aimed at, (1) obtaining intrinsic H_2 yield (that is, by using steam temperatures between 120 - 150°C) from downdraft configuration over a wide range of operating conditions - from highly fuel rich regime to 'volatile stoichiometry' with O_2 -steam mixtures with 23, 30 and 40% O_2 and (2) to bring out the role of 'volatiles' and 'char-steam reaction' on the H₂ yield.

1.2.4 Summary and motivation for the current work

In summary, effect of CO_2 /steam in thermo-chemical conversion route for carbonaceous feedstock is widely studied in controlled atmospheres like TGA/DTA/DTR. The main outcomes of these studies is to explore the reaction kinetics of char when the reacting atmosphere is replaced with CO_2 /steam either partially or totally. The heating rates of practical configurations like fixed and fluidized beds are different from controlled systems like TGA/DTA/DTR and hence experiments under controlled atmospheres like in TGA/DTA/DTR have less relevance in these systems. Reported observations on CO_2 conversion are either qualitative or do not account for the reduction of CO_2 from 'volatiles' oxidation. These aspects require a systematic investigation of flame propagation and CO_2 conversion in biomass packed beds with O_2 -CO₂ mixtures.

Use of oxidizers with O_2 fractions covering a wide range from 15 to 43 % (by mass) requires investigation of aspects of flame propagation behavior that go beyond the 'UFP
model'. There is a need for a generalized theoretical framework for analysis of ignition and devolatilization of particles in packed bed systems.

 H_2 yield with O_2 -steam experiments with steam temperatures less than 200°C can be considered intrinsic and earlier studies indicate that the intrinsic H_2 yield is about 40 g/kg of biomass. But it was inferred that, these studies were conducted under highly fuel rich conditions (i.e. $\Phi > 3$), hence, H_2 from 'volatiles' is the major contributor with limited contribution from 'char-steam reaction'. On the other hand, studies aimed at maximizing H_2 yield, use high steam temperatures (>800°C) and hence, the H_2 yield in these cases cannot be considered intrinsic; in these cases also, the role of 'volatiles' is not clear, since most of the H_2 is from char-steam and water gas shift reaction due to high steam temperatures. Current work is aimed at obtaining intrinsic H_2 yield (that is, by using steam temperatures between 120 - 150°C) from downdraft packed bed reactor over a wide range of operating conditions – with O_2 -steam mixtures with 23, 30 and 40% O_2 .

Motivated by above considerations, the main objectives of the current work are as follows,

- 1. To study the flame propagation behavior of biomass in a packed bed countercurrent reactor with air, O₂–CO₂, O₂–N₂ and O₂–steam mixtures in the entire regime of operation covering 'gasification' and 'combustion'.
- 2. Develop a methodology to estimate net CO₂ and steam conversion invoking volatile equilibration and enforcing elemental, mass and energy balances.
- 3. Develop predictive model to calculate ignition and devolatalization time to establish conditions of steady propagation.
- 4. Estimate the 'intrinsic H₂' yield in a range of operation regimes.
- 5. Elucidate the role of 'volatiles' and 'char-steam reaction' on the H_2 yield.

1.3 Thesis organization

The rest of the thesis is organized as follows -

Chapter 2 deals with experimental setups, procedures used, measurement techniques and equipments used in the current study. Details for the types of fuel used and their relevant thermo-chemical properties are elaborated in this section. This chapter ends with a tabular column showing the measurands and relevant details of the measuring instruments.

Chapter 3 deals with discussion of results from O_2-CO_2 experiments and methodology adopted to find the net CO_2 conversion. Results of fuel flux (\dot{m}''_f) , peak bed temperature (T_{pb}) and gas composition (% v/v) are presented for various O_2-CO_2 mixture fractions against oxygen mass flux (\dot{m}''_{ox}) , a function of superficial velocity (V_s) . Fraction of water vapor in the exit gas is computed by enforcing elemental and energy balance. Invoking equilibration of 'volatiles' oxidation under gasification conditions, a new procedure is established to estimate the net CO_2 conversion. A detailed discussions of the results like NCC, ECM, cold gas efficiency (η_g) , 'volatiles' stoichiometry (ϕ_v) , char conversion for all the cases of O_2 -CO₂ and O_2 -N₂ cases are presented here. The chapter ends with a brief summary explaining the effect of CO_2 as a gasification medium in packed bed reactors.

Chapter 4 deals with theoretical understanding of flame propagation in packed beds. The universal flame propagation limit surpass for some special class of fuels like coconut shell and for higher oxygen fraction is bought out in this chapter through normalized fuel flux (NFF). Role of particle size in prediction of flame propagation of packed beds and its connection with ignition and devolatalization time is clearly brought out. Experimental investigations with various particle sizes show that beyond a critical size of 30 mm, the ignition time becomes very small than devolatalization time. Further experiments in a 500 mm diameter (1000 mm length) with larger particles (groundnut shell briquettes, 100 mm dia and 20 - 100 mm in length) supports this observation and relevant details are presented in this chapter. In light of this, 'unified ignitiondevolatalization model' developed in the current work to predict the ignition and devolatalization time of a single biomass particle when subjected to reactor conditions. Also, with this model, unsteady flame propagation phenomenon like 'flame jump' is explained in this chapter and a map showing five distinct flame propagation zones of packed bed biomass is developed. The fundamental characteristics of each zone of the map is elucidated and the map is universally applicable to a wide range of biomass and oxidizer combinations. Zone II is identified as a optimum zone for thermo-chemical conversion and further O₂-steam experiments are planned in this zone.

Chapter 5 deals with the fundamental studies of packed bed gasification/combustion

of biomass with O_2 -steam as oxidizer. The methodology adopted in chapter 3 is used to compute the intrinsic H_2 yield and net steam conversion (*NSC*) and the same is discussed in this chapter. Choice of experimental conditions like upstream temperature of the reactant mixture, regimes of operation, fuels and O_2 fractions used are justified through the insights from chapter 3 and chapter 4 (i.e. Zone II operation). The important insight is operating close to $\phi_v = 1$, i.e. under slightly rich condition, leads to tar free exit gas with little or no compromise on H_2 yield (around 30 - 40 g/kg of biomass). Near 'volatiles' stoichiometry, char steam reaction releases H_2 which is comparable to 'volatiles' H_2 released at fuel rich conditions. Results of peak bed temperature variation, char conversion, CO yield, H_2 yield, *NSC*, *NCC* and gasification efficiency for all the cases pertaining to the O_2 -steam cases are presented in the chapter.

Chapter 6 contains summary, important contributions of this thesis and scope for future work. Thesis organization is summarized in the Fig. 1.5.

SYNGAS SYNTHESIS USING GASIFICATION OF BIOMASS WITH $\mathbf{O}_2\text{-}\mathbf{CO}_2$ AND $\mathbf{O}_2\text{-}\mathbf{STEAM}$ MIXTURES

1. Introduction and earlier works	This chapter
2. Materials and methods	 Fuels used and their relevant properties - Proximate analysis, CHNO content, sizes, particle and bulk densities Experiments - Packed bed and single particle experimental setup and method used Instrumentation - Accuracies of the instruments used and associated uncertainties in the computed
3. Gasification with O ₂ /CO ₂ mixtures	 Experimental limits - Experimental nomenclature, flame jump Calculation procedure - Volatile equilibration, elemental, mass and energy balances Results and discussions - Net CO₂ conversion, Volatile stoichiometry, Char conversion, CO yield, Gasification
4. New insights in to counter- current flame propagation in packed beds	 Universal flame propagation - Applicability and limitations Unified Ignition-Devolatalization model (UID) - Governing equations, model predictions and validity of the model Particle size effects - Particle size variation effect in overall flame propagation rate from experiments and UID model Flame jump and zones of flame propagation - role of (t_v/t_{ig}) ratio on 'flame jump' and mapping distinct zones of flame propagation
5. Gasification with O ₂ /steam mixtures	 Choice of experiments - Design of experiments from UID model and insights from O₂/CO₂ experiments Results and discussions - Intrinsic H₂ yield , Net steam conversion, Volatile stoichiometry, Char conversion, higher Hydro carbons, CO yield, Gasification efficiency
6. Conclusions	Overview and concluding remarks



CHAPTER 2

MATERIALS AND METHODS

2.1 Biomass properties

Four biomass fuels are used in the current work - (1) agro-residue pellets (from First Energy Limited, Chennai), (2) wood pellets (from Kothari Limited, Chennai), (3) groundnut shell briquettes (GSB, obtained from Thermax Limited, Pune) and coconut shells (from Sri Venkateshwara Traders, Chennai). A photograph of the fuels are shown in Fig. 2.1. Biomass properties relevant to the current study are summarized in Table 2.1.







(a) Photographs of biomass used for 108 mm dia (small) packed bed experiments; from left (1) agro residue pellets, (2) wood pellets and (3) coconut shells





Groundnut shell briquettes and pellets used in large reactor experiments

(b) Photographs of biomass used for single particle and 500 mm dia (large) packed bed reactor experiments

Figure 2.1: Biomass used in the current study

Biomass	Pellets1 (Agro-residue)	Pellets2 (Wood)	Coconut shell	GSB					
Density, kg/m ³	Density, kg/m ³ 1150		1200	1200					
Size, mm	8 dia, 15-20 length	9 dia, 10-40 length	4 (avg)	100 dia, 20-90 length					
Bulk density, kg/m ³	630	664 370		545					
Proximate Analysis**									
'Volatiles' content, %	66	75	71	70					
Char, %	13.5	13.5	17.7	14					
Ash content, % 10		4	1.3	11					
Moisture content, % 10.5		7.5	10	5					
С %	45.7	49.6	52.7	_					
Н %	6.61	6.5	6.03	_					
O % 46.12		43.4	41.2	_					
N % 1.43		0.5	0.5 0.08						
	$CH_{1.74}O_{0.76}$	$CH_{1.57}O_{0.66}$	$CH_{1.37}O_{0.6}$	_					
O/F(Stoichiometric)	1.06	1.06	1.05	_					
LHV (MJ/kg)**	15	16	18	_					

Table 2.1: Properties of biomass - proximate and ultimate analysis

* - reported from an external laboratory on dry ash free basis; ** - as received basis

All four types of fuels are used in as received condition for single particle studies and for packed bed experiments with air, O_2 – CO_2 and O_2 – N_2 mixtures. For experiments with O_2 –steam mixtures, the fuel is heated to 105°C for four to six hours to avoid condensation of steam in the bed. Single particle experiments are done with agro residue pellets and groundnut shell briquettes (GSB) are shaped to varying dimensions to study the effect of ignition and devolatalization time of biomass with respect to particle size and reactor conditions (refer Fig. 2.1b). The composition of GSB is similar to other fuels.

2.2 Experimental methodology

Two types of experiments are performed in this study, (1) packed bed and (2) single particle experiments.

2.2.1 Packed bed experiments

Experimental setup

The schematic of the experimental setup used for experiments with O_2 -CO₂, O_2 -N₂ and O_2 -steam mixtures is shown in the Fig. 2.2.



Figure 2.2: Schematic of the experimental setup

Experiments are carried out in a cylindrical stainless steel reactor SS310 grade of 108 mm diameter and 500 mm length. Perforated grate with 5 mm holes is placed at a distance of 50 mm from the bottom. Six R-type thermocouples of 1.5 mm bead diameter are placed with equal spacing of 75 mm along the length of the reactor to measure the temperature in the entire duration of the experiment. The temperature and mass loss over time are recorded using data loggers for all experiments. Exit gas from the reactor is sampled through vacuum pump via condenser/filter arrangement and sent to the portable gas analyzer from which the gas is sampled to gas bags at regular intervals of the experiment. The gases sampled are further analyzed in a Perkin claurus 680 GC gas chromatograph to quantify the gas composition of the exit dry gas. As pointed out earlier, as received GSB of Thermax was cut into three to four pieces (i.e dia 100 mm and length 20 - 40 mm each) and experiments were done with large scale

reactor (500 mm diameter, 1200 mm length) to explore particle size effect on universal behavior of flame propagation of biomass in packed beds.



Figure 2.3: Photograph of the experimental setup

Method

The entire flow lines like reactants, sampling and purging lines are checked for leaks and set right. The gas cleaning system like dust/moisture filters are checked and replaced after three to four experiments. Biomass is loaded in the reactor and ignited from the top using some kerosene soaked cotton placed over the bed. During the ignition phase, air at a superficial velocity of 7.5 cm/s is used as the oxidizer. After the flame stabilization i.e. after two to three layers of char is established, the flow is switched to either O_2 - CO_2 , O_2 - N_2 or O_2 -steam. This procedure is followed for all experiments in order to ensure smooth ignition. After ignition, the high temperature front (flame front, hereafter) propagates from the top of the reactor towards the grate, devolatilizing the biomass in the process. The product gases that leave from the top of the bed can undergo further oxidation, depending on the bed stoichiometry, by entraining air from the ambient (the visible gaseous flame seen at the top of the reactor in Fig. 2.3 is due to this). Hence this phase is known as *flaming mode*. Depending on the oxygen fraction and the mass flux of the oxidizer, up to 15% char might be left at the end of *flaming mode* (that is, after the flame front has reached the grate). This left over char can react with the incoming oxidizer in surface combustion mode (aka smoldering). But in the current study, the flame front was quenched at the end of the *flaming mode*. This was done for two reasons - (1) char oxidation can raise grate temperatures to very high values leading to material degradation and ash fusion and (2) char samples taken from the reactor was tested for its iodine value to estimate the activation levels achieved under gasification conditions. Reactor is quenched with N₂ at the end of flaming mode till the entire bed temperature drops below 70 °C to avoid any further char oxidation. All experiments are carried out at ambient pressure and the \dot{m}''_{ox} (mass flux of oxygen) values are calculated using flow rates at standard conditions (1 atm and 298 K).

Typical mass loss rate of the fuel with scaled time is shown in Fig. 2.4a. Switch over from *flaming mode* to *char mode* can be identified clearly in the Fig. 2.4a by the change of slope of mass loss curve. At same V_s (4.2 cm/s), the fuel consumption rate per unit cross-sectional area or fuel flux $\dot{m}''_f = 1/A_c \times dm/dt$ is nearly same (28.3 g/m²s from Varunkumar (2014) and 28.9 g/m²s in the current work). The x-axis label refers to the *normalized time* and the normalization procedure is as follows - irrespective of the reactor size, the fuel flux ($\dot{m}''_f = 1/A_c \times dm/dt$) is the same for the same superficial velocity (V_s). However, the reactor area (A_c) and the initial biomass loaded (m_0) are different in the current work and Varunkumar (2014). To account for these differences, the instantaneous mass was scaled with the initial mass and this leads to the following scaled equation,

$$\dot{m}_{f}'' = \frac{d(m/m_{0})}{d(A_{c}t/m_{0})}$$

Therefore, if m/m_0 is plotted against the scaled time (tA_c/m_0) , the mass loss data from the two experiments will collapse on to the same curve (as seen in Fig. 2.4a).

Figure 2.4b shows the variation of bed temperature with time. As seen from the Fig. 2.4b, the temperature rise to the peak is almost instantaneous for every thermocouple and the time interval between the temperature rise is also nearly constant. This means the flame front velocity is constant and hence steady (more details on steady propagation is discussed in section 4.2.3). Propagation rate calculated from the tem-



Figure 2.4: Fuel mass loss and temperature variation with time for PA case at V_s = 4.2 cm/s

perature data (Fig. 2.4b) is consistent with mass loss data (Fig. 2.4a) and that of earlier literature Varunkumar (2014). Also, it can be seen that there are differences in peak values of the temperature measured by thermocouples; this is due to the fact that the

temperature measured by a thermocouple as the flame front propagates through is a weighted average of gas phase and char surface temperatures.



Figure 2.5: Variation of temperature with \dot{m}''_{ox} for agro-residue pellets with air

Peak thermocouple temperatures as a function of oxygen mass flux is shown in Fig. 2.5. It can be seen that the differences in the peak temperature recorded decreases with increase in mass flux. This is because, at low oxygen flux (gasification regime), the oxidation zone consists of de-volatilizing biomass particles burning in *classical single particle mode* (that is, with an envelope diffusion flame). Therefore the difference in temperature between gas phase and condensed phase can be as large as 1000 °C. But as the oxygen mass flux is increased, the bed transitions in to combustion mode where there is simultaneous oxidation of 'volatiles' and char. Under such conditions the bed temperature is more or less uniform and close to the equilibrium temperature. Therefore the differences in the peak temperatures are less compared to gasification regime. Averaged temperature between the gas and condensed phase (i.e. an average of maximum values measured by thermocouples T1 to T6) is taken as average peak bed temperature (T_{pb} , herein) and is used in the energy balance calculation for estimating

sensible enthalpy.

Oxidizers

Three different oxidizers are used for the study - (1) O_2 -CO₂, (2) O_2 -N₂ (air falls under this category) and (3) O_2 -steam. For each oxidizer, experiments are conducted to cover a range of superficial velocities - usually covering the overall equivalence ratio ((Fuel/Oxidizer)_{actual}/ (Fuel/Oxidizer)_{stio}, called as Φ herein) range of relevance to gasification (5 to 1.4). The lower equivalence ratio limit for gasification usually coincides with the 'volatiles' stoichiometry point (complete combustion of 'volatiles' hydrocarbons) i.e. $\phi_v = 1$, as decreasing the equivalence ratio beyond this value leads to char oxidation. Fuel flux (\dot{m}''_f) , is a function of oxidizer mass flux (\dot{m}''_{ox}) and the fraction of O_2 in the oxidizer. Other parameters like flame propagation regime, bed temperature, char conversion, gasification efficiency, gas composition and yield are closely interlinked with \dot{m}''_{ox} and fraction of O₂. A unifying parameter to analyze the dynamics of these systems was found to be 'volatiles' stoichiometry (ϕ_v). 'Volatiles' stoichiometry ratio is equal to the mass of oxygen required for complete combustion of unit mass of 'volatiles' present in the biomass. The CHO composition of 'volatiles', required for calculating the 'volatiles' stoichiometric ratio is deduced from the ultimate and proximate analysis of biomass by subtracting the fixed carbon from the overall carbon in biomass. For example, CHO composition of wood pellets from ultimate analysis is $CH_{1.88}O_{0.81}$. From proximate analysis, 75% and 13.5% (by mass) of the biomass sample is volatiles and char/fixed carbon respectively (refer Table 2.1). By subtracting the fixed carbon content from the carbon content of the biomass and re-normalizing, the 'volatiles' CHO composition of wood pellets is calculated as CH_{2.6}O_{1.1} which corresponds to stoichiometric fuel to O₂ ratio (i.e. $(F_v/O)_{stoi}$) of 0.92. 'Volatiles' equivalence ratio (ϕ_v) is defined as,

$$\phi_v = \frac{(F_v/O)_{act}}{(F_v/O)_{stoi}}$$

Actual F_v , the mass of 'volatiles' consumed in an experiment is taken as the product of total CHO consumed and the 'volatiles' fraction (75% for wood pellet, obtained from proximate analysis). Actual oxidizer amount is calculated from the oxidizer flow rate,

mass fraction and duration of the experiment (i.e. till the end of flaming mode as shown in the Fig. 2.4a). Though focus is on gasification, experiments usually cover ϕ_v in the range of 3 to 0.8. Most of the cases are repeated more than two times to check for repeatability and reproducibility of the results.

Gas sampling and analysis

Gas sampling is started after the bed is ignited i.e. after at least one layer of char is established. Sample gas of 0.5 slpm is sent to a NDIR based portable gas analyzer via condenser, moisture and dust filter, suction pump and mass flow controller to ensure that there is no entrainment of air in the sampling line at any point of time (i.e. the O₂ fraction measured by the NDIR analyzer should read less than 0.5%). Position of the sampling tube is also adjusted to the vicinity of char bed as the char bed recedes over time. Gases from the exit of portable analyzer are filled in gas bags (3 liter capacity) at regular intervals. Sampling intervals are chosen such that when each thermocouple i.e. from T6 to T1 reaches/approaches peak bed temperature, one liter of sample gas (approx) is filled in the bag. Totally two bags are filled for each experiment and analyzed in a gas chromatograph (Perkin Claurus 680 GC with autosampler). Three to four samples from each bag are analyzed in GC to check the repeatability. Exit gas compositions from two bags are averaged to get the final reported composition. Hence the data from one single experiment is equivalent to that obtained from two similar experiments. Also to check the reproducibility of gas composition, a few experiments are repeated and the errors are within \pm 5% maximum for each gas eluted. The biomass/char left unreacted at the end of the experiment is recorded.

O₂ fractions - limiting cases

Flame propagation for a range of O_2 fractions (from 19% to 42%, by mass) is explored in the current study. Low oxygen fraction experiments i.e. when the ambient O_2 % goes below 15 (15% O_2 -85% CO_2 , by mass) the fuel flux can be as low as 25 g/m²s. Experiments with O_2 fraction lower than 15% showed intermittent propagation. In agreement with Dasappa *et al.* (1994), 20% O_2 by volume (corresponds to 15% oxygen mass fraction for O_2 -CO₂ case) is the minimum volume fraction for combustion to sustain and this is fixed as the lower limit. The upper limit for oxygen fraction is set to 42% based on the following considerations, (1) excessive slag formation and (2) damage to the reactor due to hot spots as the T_{pb} went beyond 1800 K. In coconut shell experiments, the maximum O₂ fraction is restricted to 32%. Beyond this, there was 'flame jump' i.e. time taken for the axially positioned thermocouples to reach peak temperatures is faster owing to a flame propagation rate of around 450 mm/min (almost 10 - 20 times higher as compared to steady propagation experiments). The leftover mass at the end is more than 25% of the initial mass which indicates incomplete conversion of 'volatiles' and char due to non-steady propagation.

Figure 2.6 shows representative cases with steady propagation and 'flame jump' for coconut shell with O_2 fractions of 23% and 42% (% mass) respectively. Figure 2.6a shows steady propagation i.e. temperature of the thermocouples placed axially along the length of the reactor peaks at regular time intervals; Fig. 2.6b shows 'flame jump', where three thermocouples T2, T3 and T4 peak around same time or in other words there is no distinct time interval between the peak temperature recorded by the thermocouples. Phenomenon of 'flame jump', along with very high temperatures near 'volatiles' stoichiometry (more than 1800 K) leads to ash fusion and melting of reactors. A theoretical analysis of the phenomenon of 'flame jump' is presented later (refer section 4.2.3).

It is clear from the above discussion that, for steady propagation, O_2 fraction should be neither below 15% nor greater than 42%. Hence, the O_2 fraction is restricted between 19% to 42% (by mass) for all the cases of the current study.



(a) Steady propagation with coconut shell– 23%O₂–77%CO₂ case at V_s of 30 cm/s



(b) Flame jump with coconut shell– $42\%\mathrm{O}_2\text{--}58\%\mathrm{CO}_2$ case at V_s of 3 cm/s



O₂–**CO**₂ experiments

Three different oxidizers are used, namely, (1) air, (2) O_2 -CO₂ mixtures and (3) O_2 -N₂ mixtures. The oxidizer (O_2 -CO₂ or O_2 -N₂) gases are supplied from a bank of high pressure cylinders (99.9% purity). Electric heaters are used at CO₂ cylinder exit to avoid freezing of CO₂. Gas flow rate is regulated using MCR series Alicat mass flow controllers. The component gases are allowed to mix in a long pipe (4-5 m) and thorough mixing is ensured at reactor inlet using a portable gas analyzer. Photograph of the experimental setup is shown in the Fig. 2.3. List of oxidizer combinations explored in the current study is shown in the Table 2.2.

Table 2.2: Experimental nomenclature

S.No	Oxidizer (% mass)	Experiments	S.No	Oxidizer (% mass)	Experiments	
1	Air	PA, CA and WPA	7	33% O ₂ -67% N ₂	P33N	
2	19% O ₂ -81% CO ₂	P19C and C19C	8	43% O_2 –57% N_2	P43N	
3	23% O ₂ –77% CO ₂	P23C, C23C and WP23C	9	23% O ₂ -77% Steam	WP23	
4	32% O ₂ –68% CO ₂	P32C and C32C	10	30% O ₂ -70% Steam	WP30	
5	42% O ₂ -58% CO ₂	P42C	11	40% O ₂ -60% Steam	WP40 and P40	
6	$28\% \text{ O}_2 72\% \text{ N}_2$	P28N				

P - Agro-residue pellet; C - Coconut shell; WP - Wood pellet

To avoid 'flame jump', O_2 fraction for all O_2 – CO_2 experiments is restricted between 19 to 42% for pellets and up to 32% for coconut shells. The purpose of the O_2 – N_2 experiments is to bring out the effectiveness of CO_2 addition to inlet stream on conversion to CO. Fourteen sets of experiments are carried out with O_2 – CO_2 mixtures. Firstly to validate the universal propagation behavior, air experiments with agro residue based pellets, wood pellets and coconut shell (PA, WPA and CA) are done. Next set of experiments are carried out by varying the fraction of O_2 (P19C, P23C, P32C, P42C, C19C, C23C, C32C and WP23C cases) with agro residue pellets, coconut shells and a few cases with wood pellets. In addition to this, a set of experiments are done with agro-residue pellets to compare the effect of replacing N_2 with CO_2 (P28N, P33N and P43N cases). In most of the cases, the V_s is varied to cover gasification as well as char oxidation regimes.

O₂-steam experiments

A photograph of O_2 -steam experimental setup is shown in Fig. 2.7. Procedure of experiments with O_2 -steam mixtures is similar to experiments with O_2 -CO₂ mixtures. Super heated steam is generated using a LPG based combustor and the temperature of the steam is controlled by varying the fuel flow rate (combustor power) from the LPG based burner. The steam is mixed with O_2 and the mixture is fed to the reactor. The mixture temperature was maintained between 120 - 150 °C; lower limit to avoid condensation and higher limit to prevent bulk devolatalization of the bed. By varying the mass fraction of O_2 (rest being steam) in the range given in Table 2.2, flame propagation behavior and effect of steam in enhancing the H₂ production in the syngas are studied.



Figure 2.7: Photograph of the O₂-steam experimental setup

Steam flow rate is determined by the amount of water regulated using the mass flow controller. Typical time for the boiler to reach steady state (i.e. constant steam and mixture temperature with time) is around 100 - 140 minutes. A representative plot of steam and mixture temperature variation with time of WP40 case is shown in the Fig. 2.8.



Figure 2.8: Typical steam and mixture temperature variation with time

As mentioned already the biomass used in these experiments are heated in a furnace to about 105°C and then placed in the reactor, to avoid any steam condensation in the bed away from the flaming zone. The temperature of the bed upstream of the reaction zone is about 100 - 105 °C, during the entire duration of the experiment.

2.2.2 Single particle experiments

A schematic of the single particle experimental set up is shown in Fig. 2.9.



Figure 2.9: Schematic of single particle experimental setup

Principal aim of the single particle experiments is to determine the variation of ignition (t_{ig}) and devolatalization time (t_v) with particle sizes and to extend the understanding to packed beds. Single particle burner consists of 100 mm steel reactor with LPG and air inlets and the reactants are premixed in the burner chamber and a fine mesh of 0.1 mm is placed at 50 mm from the top to ensure a flat flame. LPG flame is established at the mesh surface and the amount of air and LPG are regulated with mass flow controllers and it is ensured that the mixture is lean so that the O₂ fraction in the exhaust stream is around 10 - 12 % (by vol). The O_2 fraction in the exhaust stream is crosschecked with NDIR based gas analyzer and found to be consistent with the estimates from equilibrium calculations. The particle is suspended by fine needle and mounted on a weighing balance. The mass loss is recorded through RS 232 data logger. The hot gas temperature is measured with a K type thermocouple. Single particles (as shown in Fig. 2.1b) are hung by a needle/necessary support and ignited with quiescent flame/LPG burner for small/large particles. Ignition source in general, is removed after ignition but, in some cases not removed away from the burning particle. Both conditions are studied to elucidate the effect of ambient stream. Mass loss with time was



Figure 2.10: Mass loss rate for GSB of size ϕ 53 mm x L53 mm showing ignition, devolatalization and charring mode

tracked with a weighing balance (1 mg accuracy). A typical mass loss curve is shown

in Fig. 2.10. This is similar to the mass loss curve as obtained in packed bed experiments (refer Fig. 2.4a). The mass loss with time plot shows three distinct regimes - (1) ignition, (2) de-volatilization and (3) char oxidation. Ignition is characterized by an accelerating mass loss rate and typically occurs up to 15% loss in the initial mass. This is followed by devolatilization phase characterized by constant mass loss rate (linear mass loss with time). During this phase a diffusion flame envelopes the biomass particle. Transition from devolatilization to char oxidation can be identified as a distinct change in slope in the mass loss curve accompanied by the disappearance of the diffusion flame surrounding the particle. Ignition time (t_{ig}) is taken to be the time for 15% loss in initial mass and de-volatilization time (t_{ig}) is taken as the time from start of ignition to the point on the mass loss curve with a distinct change in the slope (indicating transition to char mode). More details on this are presented in chapter 4.

2.2.3 Measurement tools

As explained earlier, the main aim of the current study is to explore the net CO_2 conversion potential and intrinsic hydrogen yield of biomass in a packed bed reactor. This requires the following measurements, (1) mass loss rate, (2) time-temperature data for the entire duration of the experiment, (3) gas composition measurements and (4) char conversion data at the end of flaming mode. This section provides details about the various measurement tools, their accuracies and other details pertaining to the current study.

Temperature measurement

R type (Platinum Rhodium -13% / Platinum) thermocouples are used in packed bed experiments. The bead size is 1.5 mm and the bead is exposed type. The construction of thermocouple used for the experiments are shown in Fig.2.11. R type thermocouples can measure up to 1800 K which the typical temperature that a biomass bed can encounter. Provisions are made in the thermocouple to hold it firmly in the reactor over the entire duration of the experiment.



Figure 2.11: Construction of the R type thermocouple used in the experiments

Gas composition measurement

Controlled rate of products from combustion/gasification of the bed is sampled in a pipe and fed through vacuum pump via condenser/filter/moisture absorbent unit and to the gas sampling devices. Two types of gas composition measuring instruments are used, (1) gas chromatograph (Perkin Claurus 680 GC model with auto sampler) and (2) NDIR portable syngas analyzer (Bhoomi - AGASTHYA 2013 Series Model BI 7230). This section explains the gas measuring units description and methods.

Gas chromatograph

The photograph of the gas chromatogram used in the current study is shown in Fig. 2.12. This GC analyzes multicomponent hydrocarbon gases and light gases. Gases from packed bed are sampled to the GC through gas bags. The bags are filled at regular intervals. The three channel Model Arnel 1157 provides a guaranteed analysis of he-lium, hydrogen, oxygen/argon, nitrogen, CO_2 , CO, H_2S , C1 through C5 hydrocarbons including olefins and C5=, C6+ composite in less than 15 minutes (with helium carrier)



Figure 2.12: Photograph of the gas chromatograph

and less than 8 minutes (with hydrogen carrier) using an Arnel dual Thermal Conductivity Detector (TCD/TCD) and a Flame Ionization Detector (FID). Channel 1A uses nitrogen carrier gas and performs a full range helium and hydrogen analysis on gas samples using the Arnel dual TCD. Channel 1B uses helium or hydrogen carrier gas and analyzes oxygen/argon, nitrogen, CH₄, CO₂, CO, H₂S, ethane, ethylene and acetylene using the Arnel dual TCD. Channel B uses helium or hydrogen carrier gas and analyzes all C1 through C5 hydrocarbons and $C_5 = ,C_6+$ composite hydrocarbons using an FID. Channel 1A and channel 1B are linked electronically and detector signal switching is not required on the Arnel dual TCD. Therefore, only two signal outputs are required for data handling. All three channels may be run simultaneously or independently. All the gases are analyzed in volumetric percentage from 0.001% to 100% except $C_5 = ,C_6+$ for which the measuring range is up to 40%.



Figure 2.13: GC plot for air case of agro residue pellets with 12 g/m²s oxygen flux

A sample chromatogram for agro-residue pellets with air as a reactant at a superficial velocity of 5 cm/s (corresponds to oxygen mass flux of 12 g/m²s) is shown in Fig.2.13. Tedlar gas bags are used for sampling. The gas is fed to the chromatogram and total sampling time is ten minutes. The calibration of the chromatogram is done with standards provided and also with the pure gas samples.

NDIR Analyzer

The Agasthya series Portable Syn-Gas Analyzer System has been used to monitor the composition of the gases outlet of the reactor. The analyzer uses high-stability NDIR infrared sensors for the simultaneous measurement of CO, CO₂, higher hydrocarbons (HHC) and CH₄. For O₂ and H₂ electrochemical sensor is used. Working range for gases CO, CO₂, O₂ and H₂ is from 0 to 100% (v/v) whereas, for HHC and CH₄ the range is from 0 to 10%. For all the gases the resolution is 0.1% with accuracy of $\pm 1.5\%$. Figure 2.14 shows the photograph of Bhoomi gas analyzer used. The CO₂ sensor has slow response of about 2-3 minutes. All other gas sensors show response time within a minute. The NDIR analyser data is used as indicative data and also to ensure no entrainment of air/oxygen in the sampling line to GC.



Figure 2.14: Photograph of the NDIR gas analyser

2.2.4 Measurement uncertainties

The weighing balance used has an accuracy of 1 g and with this, the scatter in measured fuel flux is less than 0.3%. Calibrated thermocouples with an uncertainty of $\pm 2^{\circ}$ C (from the manufacturer) is used. Fuel characterization instruments like proximate analyzer (0.1% accuracy) and bomb calorimeter (0.1 - 0.2% accuracy) have negligible uncertainty. The uncertainties associated with the flow parameters (like V_s and \dot{m}''_{ox}) are within \pm 5%. The gas composition measured with GC has an error within \pm 5%. This leads to a elemental and energy balance to within \pm 10%. Hence, the error in the estimated values presented in this study (like net carbon conversion, net steam conversion, enhanced CO formation, CO yield, H₂ yield, corrected fuel flux, cold gas efficiency and 'volatiles' stoichiometry etc.) are within \pm 10%.

Measured parameters	Instrument details					
Mass loss rate of packed bed	30 kg capacity weighing balance with 1g					
	accuracy with RS-232 interface for data					
	logging					
Mass loss rate of single particle ex-	200 g capacity weighing balance with 1					
periments	mg accuracy with RS-232 interface for					
	data logging					
Volumetric flow rates of reactants	Alicat mass flow controllers, turn down					
	ratio: 100:1 and accuracy: 1%					
Peak bed temperatures	1.5 mm bead R Type thermocouples; ac-					
	curacy $\pm 2^{\circ}C$					
Gas composition measurement for	Perkin Claurus 680 GC; accuracy \pm 5%					
packed bed experiments						
Gas composition measurement for	Bhoomi gas analyser					
packed bed/single particle experi-						
ments						
Data acquisition	Agilent benchlink datalogger 34972A					
	model; frequency 3.3 Hz					

Table 2.3: Measured quantities and their corresponding instruments used

2.3 Summary

All the experimental techniques, tools, methods used and associated uncertainties of results are presented in this chapter. Table 2.3 summarizes the list of all the equipments, measured parameters used in the current study. The results from the experiments are presented and discussed in the subsequent chapters.

CHAPTER 3

GASIFICATION WITH O_2-CO₂ MIXTURES

In this chapter, experimental results from biomass gasification with O_2 -CO₂ mixtures and procedure to quantify the net carbon-di-oxide conversion are presented. The principal aim of the study is to determine the CO₂ conversion potential of biomass in downdraft flame propagation mode. Net CO₂ conversion (*NCC*, g/kg of biomass loaded) is defined by Eq. 3.1.

$$NCC = \frac{(m_{CO_2,v} + m_{CO_2,inlet} - m_{CO_2,outlet})}{m_b}$$
(3.1)

where, m_b is mass of biomass (kg), $m_{CO_{2,v}}$ is the mass of CO₂ (g) released through 'volatiles' oxidation, $m_{CO_{2,inlet}}$ is the mass of CO₂ in the O₂–CO₂ mixture supplied (g) and $m_{CO_{2,outlet}}$ is the mass of CO₂ in exit gas (g). It is important to note that even in air cases, CO₂ released from 'volatiles' oxidation participates in reduction reactions to produce CO and the amount is substantial (details later). For air and other O₂–N₂ cases, the second term on R.H.S of the equation is zero.

3.1 CO₂ conversion

In air gasification systems, the possible sources of CO are through (1) partial oxidation of 'volatiles' carbon and (2) reduction of CO₂ and other gases formed during 'volatiles' oxidation by char. In gasification with O₂–CO₂ mixtures, in addition to 'volatiles' CO₂ (i.e. $m_{CO_{2,v}}$) reduction with char, there is a possibility of inlet CO₂ reduction as well. This must be accounted in the *NCC* calculation (refer Eq. 3.1). Though focus is on gasification, experiments usually cover ϕ_v in the range of 3 to 0.8. In char oxidation regime (i.e. when $\phi_v < 1$), char will be inaccessible for reduction reactions. The general scheme of reaction is as follows - the fuel (volatiles, fuel moisture and char) reacts with oxidizer (either O₂–CO₂ or O₂–N₂ mixture) to give exit gases, water vapor, and char (if not fully reacted) as products. Ash is assumed to be non-reactive. General algorithm used for calculating the net CO_2 /steam conversion, CO yield, H₂ yield etc., is shown in Fig. 3.1. CHO mass of reactants is calculated from the amount of biomass loaded, its proximate and ultimate analysis and the amount of oxidizer supplied. The mass fraction of water vapor in the exit gas is calculated iteratively as shown in Fig. 3.1. The stopping criteria is based on atomic balance. Volatiles equilibrium calculation is performed with 'volatiles' biomass and oxidizer using NASA CEA SP - 273 CODE to find out the 'volatiles' oxidation products. A particular experimental case from P23C (O_2 flux of 31 g/m²s) is taken to outline the procedure for estimation of net CO_2 conversion (*NCC*).



Figure 3.1: Algorithm used for calculation

Relevant parameters for computation are listed in Table 2.3. Each cell value of Table 3.1 is referred by # numeric; for instance, #1 refers to the value of the first cell which is 2484 g of biomass loaded.

S.No	Details (inputs)	Values	S.No	Details(output)	Values
1	Biomass loaded (g)	2484	24	Final H ₂ mass (g)	51
2	Volatiles (g)	1639	25	Final CO ₂ mass (g)	4708
3	Moisture (g)	248	26	Final HHC mass (g)	7.3
4	Fixed carbon (g)	335	27	Final H ₂ O mass (g)	911
5	Ash (g)	248	28	C mass balance %	4.6
6	$O_2 - CO_2$ (%, by mass)	23/77	29	H mass balance %	7.9
7	Total reaction time (s)	4759	30	O mass balance %	-1.6
8	Total O_2 supplied (g)	1284	31	'Volatiles' formula	CH _{3.33} O _{1.49}
9	Total CO_2 supplied (g)	4118	32	Equivalence ratio ϕ	1.68
10	Biomass left at end of reaction (g)	278	33	'Volatiles' energy release (MJ)	25.2
11	Fixed carbon reacted (g)	305	34	ΔH_{fv} (kJ/mol)	-342
12	Total reactant/product mass (g)	7596	35	CEA temperature (K)	1480
13	Iterated H_2O fraction (final)	0.12	36	CEA CO mass (g)	1130
14	Dry product mass (g)	6684	37	CEA CO ₂ mass (g)	4864
15	C H O N S fractions	Table 2.1	38	CEA H ₂ mass (g)	25.6
16	$T_{pb}(K)$	1459	39	CEA H ₂ O mass (g)	1575
17	Oxidizer mass flux (g/m²s)	125.2	40	CO enhancement (g/kg)	270
18	Fuel mass flux (g/m²s)	56.3	41	CO ₂ conversion (g/kg)	63
19	LHV of biomass (kJ/g)	15	42	Total sensible energy (kJ)	12378
20	Heating value of carbon (kJ/g)	32	43	Total LHV (kJ)	26732
21	$h_b{}^0$ (kJ/mol)	-190	44	Enthalpy of formation of reactants (kJ)	-52790
22	Final CO mass (g) $[Y_{CO} * #14]$	1821	45	Enthalpy of formation of products (kJ)	-62680
23	Final CH ₄ mass (g)	41	46	Energy balance %	4.7

Table 3.1: Indicative data of P23C case at \dot{m}''_{ox} of 31 g/m²s

3.1.1 Mass balance

Of the 2484 g (#1) of agro residue based pellets loaded in the reactor, 1639 g is 'volatiles' (#2), 248 g is moisture (#3), 335 g is fixed carbon (#4) and 248 g is ash (#5). This is calculated from the proximate analysis of pellets given in Table 2.1. The oxidizer O_2 -CO₂ fraction is 23/77 in this case (#6) and the \dot{m}''_{ox} of the experiment is 31 g/m²s (which corresponds to 41.2 slpm at 298 K and 1 atm). The flaming mode duration is 4760 s (#7) and this corresponds to 1284 g of O_2 (#8) and 4118 g of CO_2 (#9) supplied in entire duration. Unreacted carbon left at the end of flaming mode is 278 g (#10) and hence the fixed carbon consumed in the reaction is 305 g [#11 = #4 - (#10 - #5)]. The total reactant mass (#12) is 7596 g (sum of #2, #3, #8, #9 and #11). The total product mass is equal to the reactant mass which is the mass of exit gases including water vapor and other condensable vapors (if any). Exit gas compositions on dry basis (measured by GC) and



Figure 3.2: Gas composition and T_{pb} variation with \dot{m}''_{ox} ; uncertainties in data smaller than marker size are not reported

 T_{pb} variation for P23C and C23C are shown in Fig. 3.2. The raw data of all other cases are reported in Appendix A. As \dot{m}''_{ox} increases, exit gas CO₂ concentration reduces and then increases, whereas CO follows exactly opposite trend of CO₂. Concentrations of H₂, CH₄ and HHC decreases with increasing \dot{m}''_{ox} . Fraction of water vapor in exit gases is not known, *a priori*. It is estimated using elemental balance.

3.1.2 CHO balance

Wet composition of exit gases on mass basis is required to calculate NCC. The total amount of water vapor produced is estimated from carbon, hydrogen and oxygen balance for the gasification reactions; the procedure is same as that used in Varunkumar et al. (2012). But unlike in Varunkumar et al. (2012), where the methane equivalent of HHC is estimated from atomic balance, data for HHC composition is available from GC analysis. Input carbon sources include carbon from 'volatiles', CO₂ and fixed carbon reacted. Ultimate analysis of the biomass on dry ash free basis (refer to Table 2.1, where C, H and O % by mass are given) is taken to calculate the amount of carbon from fuel i.e. 'volatiles' and fixed carbon reacted $[(\#1 - \#3 - \#5) \times 0.457 - (\#10 - \#5) = 878$ g of C]. Carbon from the oxidizer stream is estimated from the amount of input CO_2 $[#9 \times (12/44) = 1123$ g of C]. Summation of both gives the total input carbon of the reaction [878 g + 1123 g = 2001 g of C]. Hydrogen sources are from fuel and moisture i.e. $[(\#1 - \#3 - \#5) \times 0.0661 + \#3 \times (2/18)] = 159$ g of H. Oxygen in the input is from fuel, moisture and oxidizer $[(\#1 - \#3 - \#5) \times 0.46 + \#3 \times (16/18) + \#8 + \#9 \times (16/44)]$ = 5416 g of O. Dry composition of the exit gases from GC is converted to mass basis and the mass fractions (Y_i) are multiplied with #14 to get the mass of all gases in the exit stream on dry basis. The exit H₂O fraction is estimated by enforcing CHO balance. The carbon, hydrogen and oxygen error percentages after iteration for the example are 4.6, 7.9 and 1.6 % (#28, #29 and #30) respectively. For all the cases the CHO balance is within \pm 10%. Wet composition of the exit gas is now known (#22 to #27). Thus, from the above procedure mass of outlet CO_2 on wet basis i.e. the third term of R.H.S of Eq. 3.1 is known (#25).

3.1.3 'Volatiles' equilibrium calculations

Computation of 'volatiles' CO₂ (the first term in R.H.S of Eq. 3.1), requires composition of 'volatiles' oxidation products. This is calculated with NASA CEA SP-273 code. 'Volatiles' oxidation in gasification regime is diffusion controlled (Varunkumar, 2014), and hence equilibrium approach is appropriate to get the composition of 'volatiles' products. The inputs required for the calculation are 'volatiles' equivalence ratio (ϕ_v) and enthalpy of formation of 'volatiles' biomass (ΔH_{fv}). To calculate ϕ_v ,

the total C (difference between 'volatiles' and fixed carbon), H and O of 'volatiles' biomass consumed from the flaming mode are accounted and empirical formula is obtained ($CH_{3.33}O_{1.49}$, #31). It is important to note that, if the operating mode is very rich, some 'volatiles' will be left unburnt and hence the 'volatiles' formula will vary and the method developed accounts for this. Oxidizer for the current case is a mixture of O_2 -CO₂ and from this 'volatiles' stoichiometric F/O of 0.27 is computed. Actual F/O is the ratio of \dot{m}''_{f} (#18) and \dot{m}''_{ox} (#17) which are 56.3 and 125.3 g/m²s respectively and hence the actual F/O of 0.45 is obtained. Therefore, 'volatiles' equivalence ratio (ϕ_v) is 1.7. To calculate ΔH_{fv} , total input energy i.e. heat released by 'volatiles' biomass is computed considering 5% heat loss (Varunkumar, 2014) and the value is 25.2 MJ (#33 = (#19 \times #1 - #4 \times #20) \times 0.95). Molecular weight of the 'volatiles' biomass is 39.15 g/mol (from #31) and total 'volatiles' moles reacting is 47.7 from which ΔH_{fv} value of -342 kJ/mol is computed (#34). Equivalence ratio (ϕ_v) and enthalpy of formation of 'volatiles' ΔH_{fv} is now known. With these inputs, equilibrium calculation is done with NASA CEA software. Exit gas mass fractions are multiplied with total product mass (#12) and individual mass of each gas is obtained as listed from #36 to #39 of Table 3.1. The ratio of the net positive difference of #37 (sum of 'volatiles' CO₂ and inlet CO₂) and #25 (outlet CO_2) to #1 (biomass loaded) gives net grams of CO_2 converted per kg of biomass loaded (NCC), which is 63 g/kg (#41). CO enhancement (ECM, g/kg of biomass loaded) i.e. fraction of CO in excess with CEA calculation (see Eq. 3.2) which is attributed to Boudouard and water gas shift reaction route is 270 g/kg of biomass (#40).

$$ECM = \frac{(m_{CO,outlet} - m_{CO,v})}{m_b}$$
(3.2)

where, $m_{CO,outlet}$ is the mass of CO in exit gas and $m_{CO,v}$ is the mass of CO at the end of 'volatiles' oxidation. Maximum CO enhancement is thought to occur when the total fixed carbon is reacted with 'volatiles' oxidation products.

To obtain a theoretical limit for maximum CO, 'volatiles' oxidation products (#36 to #39) are equilibrated with total fixed carbon (#4) and compared with the experimental values. In experiments, CO is maximum near 'volatiles' stoichiometry and decreases on either side, CO_2 reaches minimum around the same point and increases on either side. Concentrations of H₂ is higher and H₂O is less as compared to equilibrium concentrations. A few cases show that the theoretical value is less than the actual (refer

S.No	\dot{m}''_{ox}	m_{CO}		m_{c}	m_{CO_2}		m_{H_2}		m_{H_2O}	
		eq*	exp*	eq	exp	eq	exp	eq	exp	
Units	(g/m^2s)	(g/kg of biomass)								
P19C case										
1	10	579	261	1700	1876	36	23	241	414	
2	17	734	498	2030	2205	27	15	380	412	
3	33	658	441	3080	3410	9	11	567	431	
4	50	562	720	5497	5539	6	11	727	509	
P23C	case									
5	12	519	227	1056	1127	32	12	165	394	
6	19	579	261	1700	1876	36	23	241	414	
7	31	791	725	1790	1895	28	20	448	397	
8	60	561	884	3169	2970	6	17	618	470	
9	89	584	513	5858	6061	7	7	709	573	
P32C	case									
10	16	374	235	743	710	31	13	154	384	
11	26	526	308	884	931	37	17	166	345	
12	41	674	453	1032	1113	39	20	256	379	
13	79	637	576	1824	1988	9	16	568	449	
P42C	P42C case									
14	20	329	129	574	624	31	7	139	340	
15	33	383	152	623	655	33	11	142	374	
16	66	593	333	750	818	41	20	184	346	
17	99	737	546	702	879	36	22	362	363	
18	149	627	570	896	952	13	20	399	383	

Table 3.2: Comparison of equilibrium results with experimental values

* eq - equilibrium ; exp - experiment

Table 3.2). This is because char reactions are generally rate limited and the system operates far from equilibrium.

3.1.4 Energy balance

Energy balance is used to crosscheck C, H and O balance as discussed earlier and also to calculate the cold gas efficiency of the system. Energy balance of any combustion/gasification packed bed system with any fuel is as given by Eq. 3.3.

$$m_{ox}[h_{ox}^{0} + h_{ox}^{s}] + m_{b}[h_{b}^{0} + h_{b}^{s}] = m_{char}[h_{c}^{0} + h_{c}^{s}] + \sum_{i=1}^{n} m_{i}[h_{i}^{0} + h_{i}^{s}]$$
(3.3)

L.H.S of the above equation is the total input energy of the reactants and R.H.S is the total output energy from products, where m_{ox} , m_b , m_{char} , m_i are mass of oxidizer, biomass, unreacted carbon and i^{th} component of exit gas, h_{ox}^{0} , h_b^{0} , h_c^{0} and h_i^{0} are the corresponding heat of formation at standard conditions (1 atm and 298 K), h_{ox}^{s} , h_b^{s} , h_c^{s} and h_i^{s} refers to sensible enthalpy of oxidizer, biomass, unburnt carbon and exit

gases respectively. Oxidizers used in the work are O_2-N_2/CO_2 out of which O_2 and N_2 have zero formation enthalpy. Also, the sensible enthalpies of the reactants are zero (as reactants are at standard conditions i.e. 1 atm and 298K). In product side, the enthalpy of formation of unreacted carbon h_c^0 is also zero. Moreover, the sensible enthalpy of unburnt carbon is small (less than 1% of total input energy) and hence neglected. Considering these factors, the above equation is simplified as given by Eq. 3.4.

$$m_{CO_2}h_{CO_2}^0 + m_b h_b^0 = \sum_{i=1}^n m_i [h_i^0 + h_i^s]$$
(3.4)

All the relevant properties are taken from JANAF thermo-chemical tables. Enthalpy of formation of biomass $(h_b^{\ 0})$ on as received basis (#21) is calculated (refer to Table 3.1) similar to the procedure described in subsection 3.1.3. The sensible enthalpies of all exit gases are calculated at corresponding T_{pb} (refer Fig. 3.3 to Fig. 3.4).



Figure 3.3: Bed temperature variation with \dot{m}''_{ox} - P23C case; uncertainty smaller than marker size.



Figure 3.4: Bed temperature variation with \dot{m}''_{ox} - P19C case; uncertainty smaller than marker size.

It is important to note that, T_{pb} of all O₂–N₂ (including air case) cases is higher than corresponding O₂–CO₂ case (refer Fig. 2.5) due to the higher heat capacity of CO₂ as compared to N₂ (Annamalai *et al.*, 2013; Bu *et al.*, 2017). The mass of CO₂, biomass and all exit gases for the illustrative case from P30C case at \dot{m}'_{ox} of 31 g/m²s are taken from Table 3.1. The difference between L.H.S (#44) and R.H.S (i.e. sum of #42 and #45) gives the percentage error in energy balance (#46). Energy is balanced within ± 5%. The ratio of LHV (#43) to sum of LHV (#43) and sensible enthalpy (#42) gives the cold gas efficiency. In this case the cold gas efficiency is 68.4% ((#43/(#42 + #43) × 100) = 68.4%).

Elemental and energy balance calculations are implemented in a spreadsheet (for case P23C at \dot{m}''_{ox} of 31 g/m²s the calculation sheet be downloaded from Jaganathan, 2018). The same procedure is used to calculate the net CO₂ conversion for all experiments (as listed in Table 2.2) of the current work.

3.2 Results and discussion

The results of NCC, ϕ_v and ECM variation with \dot{m}''_{ox} for all cases as listed in Table 2.2 are shown in Fig. 3.5 to Fig. 3.10.

Net CO₂ Conversion (*NCC*) for all cases is significantly higher around 'volatiles' stoichiometry ($\phi_v \approx 1$) i.e. the transition point of gasification to combustion as compared to either side of it. To elucidate the effect of oxidizer, the *NCC* of O₂–CO₂ cases is compared to the corresponding O₂–N₂ cases and the results are shown in Fig. 3.5 to Fig. 3.7.



Figure 3.5: *NCC* variation with \dot{m}''_{ox} for P23C, P33N, C23C and WP23C cases; uncertainty $\leq \pm 10\%$.


Figure 3.6: *NCC* variation with \dot{m}''_{ox} for P32C, P43N, P42C and C32C cases; uncertainty $\leq \pm 10\%$.



Figure 3.7: *NCC* variation with \dot{m}''_{ox} for PA, P19C, P28N, CA, C19C and WPA cases; uncertainty $\leq \pm 10\%$.

As seen, NCC of O_2-N_2 cases is less/negligible as compared to corresponding O_2-CO_2 cases. Air cases show significant NCC of around 200 - 300 g/kg of biomass near 'volatiles' stoichiometry which is still lesser than corresponding O_2-CO_2 cases. Also, ECM at 'volatiles' stoichiometry is a direct indicator of CO yield and it is found to be around 600–800 g/kg of biomass for most of the O_2-CO_2 cases reported in this study as shown in Fig. 3.8 to Fig. 3.10.



Figure 3.8: ECM variation with \dot{m}''_{ox} for P23C, P33N, C23C and WP23C cases; uncertainty $\leq \pm 10\%$.



Figure 3.9: ECM variation with \dot{m}''_{ox} for P32C, P43N, P42C and C32C cases; uncertainty $\leq \pm 10\%$.



Figure 3.10: *ECM* variation with \dot{m}''_{ox} for PA, P19C, P28N, CA, C19C and WPA cases; uncertainty $\leq \pm 10\%$.

High CO₂ concentration in O₂–CO₂ cases, promote reactions of char with CO₂, especially near 'volatiles' stoichiometry as this corresponds to reducing conditions with highest possible bed temperature. This argument is further supported by enhanced char conversion of O₂–CO₂ cases as compared to O₂–N₂ cases as seen from Fig. 3.11 to Fig. 3.13 and hence, higher *NCC* is observed in O₂–CO₂ than the corresponding O₂–N₂ cases.



Figure 3.11: Char conversion with \dot{m}''_{ox} in gasification regime of air and 19% O₂ cases; uncertainty smaller than marker size.



Figure 3.12: Char conversion with \dot{m}''_{ox} in gasification regime of 23% O₂ cases; uncertainty smaller than marker size.



Figure 3.13: Char conversion with \dot{m}''_{ox} in gasification regime of 32%, 42% and 43% O_2 cases; uncertainty smaller than marker size.

3.2.1 Gas residence time

To exhibit the char conversion behavior under gasification conditions, the exit gas residence time (t_g) is calculated by the following procedure. Total volumetric flow rate of the exit gas is calculated after correcting for density of the hot gas (around 0.5 kg/m³ for O₂–CO₂, air and O₂–N₂ cases). Representative char bed volume is taken to be that corresponding to one particle layer thick. Now, the char bed volume divided by the volumetric flow rate of exit gas gives t_g . The values of t_g for all the cases is given in Table A.1 to Table A.4 of Appendix A. The typical residence time of the 'volatiles' oxidation products with the upstream char layer varies from 6 - 80 ms for all the cases shown in the current work. From the char conversion results shown from Fig. 3.11 to Fig. 3.13, it is clear that as $\phi_v \rightarrow 1$, char conversion approaches 100%. Therefore, the char reactions are limited by residence time (and hence kinetic rate) under rich conditions and become limited by the available amount of char as $\phi_v \rightarrow 1$.

3.2.2 'Volatiles' stoichiometry (ϕ_v) and NCC

As mentioned earlier, 'volatiles' stoichiometry is a unifying parameter to analyze results from gasification experiments. For experiments with air cases and P28N case, 'volatiles' stoichiometry is attained in the range of \dot{m}_{ox}'' studied. Hence, the contribution of Boudouard reaction with char is more prominent due to highest possible bed temperatures as $\phi_v \rightarrow 1$ and CO₂ from 'volatiles' oxidation is converted to CO resulting in *NCC*. For other O₂–N₂ cases, $\phi_v > 1$, hence *NCC* is not observed. Also, for cases operated in combustion regime i.e. $\phi_v < 1$, *NCC* is not observed (refer Fig. 3.5, Fig. 3.7, Fig. 3.8 and Fig. 3.10). This is due to char participation in oxidation reactions.

In any particular case if \dot{m}''_{ox} increases, ϕ_v decreases i.e. the operational regime of the reactor shifts from gasification to char oxidation dominated zone and the reaction front gets thinner. As \dot{m}''_{ox} increases (i.e. shifting from gasification to char oxidation regime), the scatter in temperature measured by the thermocouples placed along the axial distance of reactor decreases. Refer PA and P30C cases in the Fig. 2.5 and Fig. 3.3 respectively (for PA from ±130 K to ±30 K and for P23C ±110 K to ±20 K). This implies that the operational regime of the reactor shift towards equilibrium (\dot{m}''_{ox} of 40 g/m²s for PA and 60 g/m²s for P23C), a similar observation made by Varunkumar (2014).

On the other hand, as discussed earlier, if the oxygen fraction is increased for same \dot{m}''_{ox} , \dot{m}''_{f} increases, which leads to fuel rich operation. Hence it is clear that the bed operates from lean to rich with increasing O₂ fraction for same \dot{m}''_{ox} . Similarly, rich to lean with increasing \dot{m}''_{ox} for any particular O₂ fraction (refer Fig. 3.14). This leads to steep slopes of ϕ_v for low O₂ fraction experiments (say air, 19% O₂, 23% O₂ cases) and shallow slopes of ϕ_v for high O₂ fraction experiments (32 and 42% O₂ cases). For low oxygen fraction experiments like P19C, C19C, P23C, and C23C $\phi_v \rightarrow 1$ at lower \dot{m}''_{ox} and peak *NCC* is observed as compared to higher O₂ fraction experiments like P32C, C32C and P42C (refer Fig. 3.6 and Fig. 3.14).



Figure 3.14: ϕ_v variation with \dot{m}''_{ox} ; uncertainty $\leq \pm 10\%$.

As discussed earlier, one another interconnected parameter with ϕ_v affecting *NCC* and *ECM* is T_{pb} . Reduction reactions of carbon with CO₂ are predominantly a high temperature pathway and well pronounced above 1000 K (Dasappa, 1999). High concentration of CO₂ promotes char reactions as compared to inert N₂ (refer section 1.2.1) and hence char conversion is more prominent in O₂–CO₂ cases than corresponding O₂–N₂ cases. 'Volatiles' oxidation reaction as discussed earlier is diffusion limited and hence, the char above flame front is available only for reduction reactions with 'volatiles' products in the gasification regime. In addition, the char conversion in all O₂–CO₂ cases, excluding coconut shell is complete before 'volatiles' stoichiometry, which implies that the char is only consumed by reduction reactions. Also, from experiments done by Dasappa (1999), it is shown that the char steam reaction is enhanced in CO₂ atmospheres. At low temperatures i.e. below 1500 K, CO produced, in turn, reacts with steam through water gas shift reactions and promotes the formation of CO₂ and H₂ whereas at high temperatures (1500 K or more) CO formation is enhanced as the equilibrium of water gas shift reaction shifts (CO + H₂O \rightleftharpoons CO₂ + H₂) towards the reactants along with Boudouard route. Hence, *NCC* is observed at $\phi_v \sim 1$ when the T_{pb} reaches 1500 ±100 K or more, and falls to zero on either side i.e $\phi_v > 1$ due to low bed temperatures and $\phi_v < 1$ due to char oxidation.

3.2.3 The case of coconut shells

Coconut shells do exhibit universal propagation behavior like pellets and NCC is observed. However, coconut shell exhibits different combustion characteristics like (1) high fuel flux than limiting value of 80 g/m²s with air (110 g/m²s against the maximum of 80 g/m²s for other biomass fuels with air), (2) high voidage as compared to pellets, (3) high methane and other higher hydrocarbons in exit gas and high cold gas efficiency (82% for C19C case at \dot{m}''_{ox} of 99 g/m²s), (4) flame jump is observed beyond 32% O₂ fraction and (5) poor carbon conversion. Some possible explanations are discussed in this section. High methane and HHC content with coconut shells is attributed to high 'volatiles' content and about 10% crude protein extractions and oil (Mukunda, 2011) in coconut shell reflected in higher heating value of around 18 - 20 MJ/kg as compared to pellets, which enhances 'volatiles' heat release rate and shows higher fuel flux. Also, the surface area of coconut shell particles is higher due to its flat and curved geometry which promotes heat transport. Single particle experiments done by Mahapatra and Dasappa (2014) on coconut shell also show similar behavior. Better heat transport, high heat release rate, high voidage of the bed (1.7 times higher than pellets) are the important interlinked factors responsible for enhanced burning rate of coconut shells. Otherwise, the other features of exhibiting universality in operational regimes like 'gasification' and 'char oxidation', NCC, ECM, char conversion are pertinent to

coconut shells also. Similar to pellets, char conversion is more in O_2 -CO₂ as compared to air case for coconut shell (refer Fig. 3.11, Fig. 3.12 and Fig. 3.13). The fixed carbon percentage on dry ash free basis is high for coconut shell (20%) and hence even with peak *NCC* of 406 g/m²s at \dot{m}''_{ox} of 120 g/m²s with C23C case, 10% of char is left unconverted. Further investigations are needed to understand the behavior of coconut shell in packed bed reactors and this will be addressed in future work.

3.2.4 Cold gas efficiency (η_g)

Cold gas efficiencies (η_g) of all the experiments done in the current work are plotted in Fig. 3.15 and Fig. 3.16.



Figure 3.15: η_g variation with \dot{m}''_{ox} of agro-residue pellet cases; uncertainty $\leq \pm 10\%$.



Figure 3.16: η_g variation with \dot{m}''_{ox} of a few other cases; uncertainty $\leq \pm 10\%$.

Cold gas efficiency is defined as the ratio of energy value of the exit cold gas to the input fuel. In conventional gasification with air, even with NCC the amount of CO_2 available for reduction is less as compared to O_2 – CO_2 cases and hence the cold gas efficiency of air cases is always lower than corresponding O_2 – CO_2 cases. At maximum ECM, CO concentration is more and hence η_g is also maximum at that point. As the bed operates in combustion regime, char gets oxidized and hence, fraction of combustibles in exit gas reduces leading to decrease in η_g (refer PA, P30C and CA cases). Also for coconut shell, as discussed earlier, η_g as high as 82% for C19C case is observed and this is due to the presence of methane and HHC along with enhanced CO formation.

3.3 Summary

Results of CO_2 conversion and CO yield enhancement of biomass in a canonical packed bed reactor are presented in this chapter. A new procedure for estimation of CO_2 conversion is developed. The salient features of this procedure are - (1) the importance of elemental and energy balance for accurate estimation of NCC are brought out, (2) the role of 'volatiles' CO₂ and its effect on estimated NCC is addressed for the first time and (3) char limited nature of CO₂ conversion as $\phi_v \rightarrow 1$ is brought out. Net CO₂ conversion is evident from the experiments for all O₂–CO₂ cases and is higher than corresponding air and O₂–N₂ cases. O₂–CO₂ cases show a maximum net CO₂ conversion around 400–600 g/kg of biomass and a maximum CO yield of 600–800 g/kg of biomass. Presence of CO₂ in the inlet stream promotes char reduction reactions and when the operation regime shifts to near 'volatiles' stoichiometry ($\phi_v \sim 1$), where T_{pb} is above 1500 K, significant NCC is observed. Increase in CO yield due to CO₂ conversion is observed in O₂–CO₂ cases as compared to air cases (2 – 2.5 times more). The gasification efficiency of all O₂–CO₂ cases are higher than corresponding air cases and this is due to the reactive contribution of CO₂ unlike inert N₂ in air and O₂–N₂ cases. However, the H₂ yield is comparable to air cases (around 10 - 20 g/kg of biomass) and strategies to improve H₂ yield are presented in chapter 5.

Before moving on to the problem of H_2 enhancement, a theoretical framework for understanding aspects of counter-current flame propagation that goes beyond the '*universal flame propagation model*' will be presented in the next chapter. While biomass fuels used in the current study generally exhibit universality in flame propagation dynamics, additional features associated with the use of O_2 – CO_2 and O_2 – N_2 mixtures with varying O_2 fractions, role of 'volatiles' stoichiometry, particle size effects and 'flame jump' etc, need further analysis. These aspects are discussed in chapter 4.

CHAPTER 4

NEW INSIGHTS IN TO COUNTER-CURRENT FLAME PROPAGATION IN PACKED BEDS

In this chapter, new insights from a theoretical analysis of the problem of countercurrent flame propagation in packed beds, that go beyond the *universal flame propagation model*, are presented.

The phenomenon of 'flame jump' was explained in the previous chapter. Particle size effects with air as oxidizer was investigated as a part of a study undertaken to optimize briquette fired grate furnaces used for steam generation in process industries. Single particle and packed bed experiments (in 500 mm reactor) were conducted to determine the optimum particle size and superficial velocity required for maximizing fuel flux and minimizing particulate carry over. Only parts relevant to the role of t_{ig} and t_v in flame propagation will be presented here. Other details can be found in Varunkumar *et al.* (2015).

Identification of conditions under which t_v becomes dominant is important for design of practical gasification systems. Also, establishing a theoretical framework for analyzing different zones of flame propagation as a function of particle size and oxidizer mass fraction and flux will enable identification of optimal conditions for gasification with O₂-steam mixtures. It is critical to avoid the issues identified here, especially 'flame jump', which is expected to be a more serious problem in gasification with O₂steam mixtures as the oxidizer will be preheated unlike in air and O₂-CO₂ cases.

4.1 Universal flame propagation (UFP) model

Under conditions of steady counter-current flame propagation in biomass packed beds with air as oxidizer and not too large particles (precise limiting sizes will be discussed later), variation of fuel consumption rate per unit area (corrected for ash and moisture content) with superficial velocity exhibits universality (Varunkumar *et al.*, 2013). This

is due to the particle density scaled ignition time being independent of biomass type, varying only with superficial velocity. Therefore, universality under steady propagation conditions is expected even when the oxidizer is changed from air to mixtures of O_2 - CO_2 and O_2 - N_2 .

4.1.1 Normalized Fuel Flux (NFF)

Raw data (not corrected for ash and moisture) showing the variation of \dot{m}''_f with \dot{m}''_{ox} for the cases of O₂–CO₂, O₂–N₂ and air experiments is shown in Fig. 4.1.



Figure 4.1: Uncorrected data of fuel mass flux variation with \dot{m}_{ox}'' ; uncertainty $\leq \pm 10\%$.

Similar to air gasification, the *gasification* and *char oxidation* flame propagation regimes are observed in O_2 – CO_2 and O_2 – N_2 cases too. In other words, the fuel flux increases with increase in oxidizer mass flux in the *gasification* regime and saturates in *char oxidation* regime. As brought out earlier, the transition can be identified using 'volatiles' stoichiometry. The fuel flux saturates in the char oxidation regime due to the following - as the oxygen mass flux increases, char layer gets oxidized and the increasing temperature is compensated by decreasing emissivity of the char-ash layer formed at the char surface which reduces the heat and mass transport process and hence, the \dot{m}_f' reaches saturation (Varunkumar *et al.*, 2013). Higher oxygen fraction (more than

40% of O_2 , by mass) shows enhanced fuel flux (as high as 208 g/m²s at a oxygen flux of 149 g/m²s of P42C case) due to increase of 'volatiles' heat release rate. Jaganathan and Varunkumar (2019) proposed a corrected fuel flux (*CFF*) given by Eq. 4.1.

$$CFF = \left(\frac{\dot{m}_{f_a}''}{\dot{m}_{f_{ref}}''}\right) \left(\frac{(HY_{ox}/s)_{ref}}{(HY_{ox}/s)_a}\right) \left(\frac{\rho_a}{\rho_{ref}}\right)$$
(4.1)

where, H, Y_{ox} , s and ρ represent heating value, oxidizer fraction, stoichiometric coefficient and bed density respectively. Suffixes (ref) and (a) represent reference and actual cases. Here agro residue based pellets with air as reactant was taken as the reference case. In Eq. 4.1, the s_a was calculated by using actual oxidizer to fuel ratio of particular experiment and ρ was taken to be bed density. Fuel like wood chips have calorific value comparable to pellets (around 16 MJ/kg) but, the bed density of such fuels is lesser like coconut shells. The fuel flux (\dot{m}''_f) variation with \dot{m}''_{ox} of wood chips is similar to that of pellets (Varunkumar, 2014). *CFF* calculated from Eq. 4.1 for such fuels will reduce further as compared to pellets. Also, the non-linear dependence of \dot{m}''_f with bed temperature is not captured in Eq. 4.1. Hence the Eq. 4.1 requires re-assessment. In the light of this, a modified equation was sought. The 'normalized fuel flux' as defined in Eq. 4.2 was found to be appropriate.

$$NFF = \left(\frac{\dot{m}_{f_a}''}{\dot{m}_{f_{ref}}''}\right) \left(\frac{(HY_{ox}/s)_{ref}}{(HY_{ox}/s)_a}\right)^2 \left(\frac{\epsilon_{b,act}}{\epsilon_{b,ref}}\right)$$
(4.2)

where, ϵ_b represent the bed voidage i.e. $1 - (\rho_b/\rho_p)$. In *NFF*, *s* is the stoichiometric coefficient which is invariant for a particular fuel with experimental conditions unlike s_a used in *CFF*. Bed voidage is taken as the reference in *NFF* unlike bed density used in *CFF* which can correct for the fuel shape and density effects effectively than density ratio as used in *CFF*. Also, exponent 2 for the second R.H.S term of Eq 4.2 captures the non-linear dependence of fuel flux enhancement due to bed temperature rise at higher O₂ fractions. A non-dimensional plot of *NFF* vs $\phi_v/(1 + \phi_v)$ is shown in Fig. 4.2 which takes into account all the required parameters of normalization. The term $\phi_v/(1 + \phi_v)$ is used in the plot to have a symmetric axis. The *NFF* plot clearly shows that, biomass as used in the current study do exhibit 'universal behavior' of fuel flux increase till *gasification* regime and saturation of fuel flux in *combustion* regime. Also, it is shown that the transition from *gasification* to *combustion* occurs at 'volatiles'

stoichiometry ($\phi_v \sim 1$).



Figure 4.2: Modified universal propagation behavior for different O₂–CO₂ cases with \dot{m}''_{ox} ; uncertainty $\leq \pm 10\%$.

4.1.2 Particle size effects

To explore the particle size effects on flame propagation, it was decided to study the single particle burning characteristics in the setup as described in section 2.2.2. Various sizes of GSB briquettes were made as shown in Fig. 2.1b for this purpose. Results from single particle experiments are shown in the Fig. 4.3. Predictions from a model to be discussed later is also included in Fig. 4.3. Model related aspects will be discussed later.



Figure 4.3: Variation of t_{ig} and t_v with d_p ; data points are from experiments and lines are for model predictions

As brought out earlier, when the particle size exceeds a critical value (i.e. $d_p > 20$ mm for air), t_{ig} becomes smaller as compared to t_v . Thus, beyond a critical size, t_v can be rate controlling. To validate this, experiments with larger particles in packed beds was carried out. Groundnut shell briquettes of various sizes were used for this purpose - diameter of the briquette is 100 mm and the length varied from 20 - 40 mm. Reference experiments were performed with agro-residue pellets (8 mm diameter and 15 - 20 mm in length) in a cylindrical furnace of 500 mm in diameter and 1200 mm in length made of SS310 insulated with high grade ceramic wool. Experiments were done at V_s of 18 cm/s and 30 cm/s for GSB and 18 cm/s for pellets. Propagation rate was calculated by two methods as described in Varunkumar (2014); method1 (M1): from mass loss rate measurement i.e. $\dot{m}''_f = \dot{m}/A_c$ and method 2 (M2): based on time - temperature data where, time taken for the axially placed thermocouples to reach flame temperature is used i.e $\dot{m}''_f = \rho_b \dot{r}$; where, \dot{m}''_f is the fuel flux in g/m²s, \dot{m} is the mass loss rate in g/s, A_c is the cross-sectional area in m², ρ_b is the bed density in kg/m³ and \dot{r} is the flame propagation speed in m/s. The results from the large reactor experiments measured using weighing balance (M1) and thermocouple data (M2) are shown in Fig. 4.4.



Figure 4.4: \dot{m}''_f variation with V_s in relation with universal propagation limits; reproduced from Jaganathan *et al.* (2017)

As expected from the UFP model, on dry ash free basis, there is very little variation in the fuel mass flux with superficial velocity beyond 18 cm/s. Though within the limits set by universal propagation model, the mass flux with briquettes is lower than that of pellets. This is consistent with the observations related to variation of relative magnitudes of ignition times (t_{ig}) and devolatilization times (t_v) with particle size described in Varunkumar *et al.* (2015). Deviation of the mass flux estimated from the temperature data compared to weighing scale method is also consistent with this observation indicating overlap of devolatilization in multiple layers as opposed to a single layer as assumed in the model. This clearly indicates that for larger particles ($d_p > 20$ mm for air) devolatilization becomes rate limiting.

To further elucidate the role of relative magnitudes of t_{ig} and t_v , the single particle model of Mukunda *et al.* (1984) is extended to predict t_{ig} . The extended version is called the 'unified ignition-devolatilization model'. This model is further extended to study the unsteady flame propagation characteristics like 'flame jump' in a packed bed.

4.2 Unified Ignition - Devolatalization (UID) model

Biomass combustion is a stage wise process of moisture evaporation, ignition, devolatilization and char combustion or heterogeneous combustion. As explained earlier, out of these, time for ignition and devolatilization can be rate controlling and a unified framework for estimating these quantities is required for accurate prediction of fuel burn rate and hence furnace design. The framework presented here is an extension of the devolatilization model developed by Mukunda *et al.* (1984) to capture the ignition process.

4.2.1 Ignition

A biomass particle exposed to an ignition source is considered ignited if a stable envelope diffusion flame is established around it. A quasi-1D approach (effective spherical symmetry) outlined in Mukunda *et al.* (1984) is used. A fresh biomass sphere of radius r_s at ambient temperature when suddenly exposed to a heat source, its surface temperature (T_s) starts to increase. This heating up time can be computed by solving transient heat conduction equation subjected to heat flux (\dot{q}''). Once the surface reaches the pyrolysis temperature (T_p), it starts releasing 'volatiles' and now the pyrolysis front (r_p) regresses towards the center. From mass conservation, mass flow rate at any radius is constant i.e. $G_p r_p^2 = G_s r_s^2$ where, G_p is fuel mass flux in kg/m²s at the pyrolysis front r_p , r_s is the surface radius. Using this, a gas phase convection-diffusion balance is established between r_s and r_p which is used to compute the temperature profile (see Eq. 4.3) inside pyrolysis front. More details on the derivation are given in Appendix B.

$$ln\left[\frac{\frac{H_d}{C_p} + \frac{\dot{q}''_w}{G_p C_p}}{T_s - T_p + \frac{H_d}{C_p} + \frac{\dot{q}''_w}{G_p C_p}}\right] = \frac{G_p r_p^2 C_p}{k} \left[\frac{1}{r_s} - \frac{1}{r_p}\right]$$
(4.3)

where, C_p is the specific heat at constant pressure, T_p , T_p , T_{∞} and are the surface, pyrolysis front and free stream temperatures respectively, H_d is the heat of pyrolysis and \dot{q}''_w is the heat flux into fresh biomass. Now, from Eq. 4.3, incorporating the surface heat flux boundary condition i.e. $k \frac{dT}{dr}$ which is equal to \dot{q}'' we get Eq. 4.4.

$$\frac{G_p r_p^2 C_p}{r_s^2} \left[T_s - T_p + \frac{H_d}{C_p} + \frac{\dot{q}''_w}{G_p C_p} \right] = \dot{q}''$$
(4.4)

By solving simultaneously, Eq. 4.3 and Eq. 4.4, the time required for 15% mass loss is calculated and taken as the ignition time. The criteria for ignition i.e. 15% mass loss comes from single particle experimental studies from the current work (refer section 2.2.2).

4.2.2 Devolatilization

In this unified approach, the ignition-to-devolatilization transition is accounted for by a switch from convective boundary condition to a thin flame boundary condition obtained from application of droplet combustion theory as given in Mukunda *et al.* (1984). As the flame engulfs the particle, surface receives heat from the flame and radiation effects from the particle surface can be dominant. To determine the heat transfered to the surface, temperature profile from the flame to surface has to be evaluated. In order to do the same, a conserved scalar approach is adopted and after incorporating necessary boundary conditions Eq. 4.5 is arrived at. More details on the derivation can be found in Appendix B.

$$\frac{G_p r_p^2 C_p}{r_s^2} \left\{ \frac{\frac{H_c Y_{o,\infty}}{s} + C_p (T_\infty - T_s)}{exp(\frac{G_p C_p r_p^2}{kr_s}) - 1} Nu - C_p (T_s - T_p) - H_d - \frac{\dot{q}_w''}{G_p} \right\} = \epsilon \sigma T_s^4 \quad (4.5)$$

$$\frac{\partial T}{\partial t} = \alpha \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial T}{\partial r} \right)$$
(4.6)

Equation 4.5 combined with the heat flux condition at the pyrolysis front (Eq. 4.3) and transient conduction equation (Eq. 4.6) is used to estimate the devolatilization time. A fixed pyrolysis front temperature of 473 K is assumed. The devolatilization rate obtained is used in Eq. 4.7 to track the pyrolysis front and the time taken for the interior radius i.e. $r_0 \sim 0$ to reach pyrolysis temperature is taken as the devolatilization time.

$$\frac{dr_p}{dt} = -\frac{G_p}{\rho_p} \tag{4.7}$$

where, H_c is the enthalpy of combustion of 'volatiles', $Y_{o,\infty}$ is the free stream oxygen mass fraction (0.232 for air), s is the stoichiometric A/F of 'volatiles' (1.53), k is the thermal conductivity of air (0.063 W/m-K), Nu is the Nusselt number and ρ_p is the particle density. The transient conduction solver is coded in Matlab[®] and the same is used to get the ignition temperature profile and heat flux into the fresh biomass (\dot{q}''_w) . Beyond the ignition time (t_{ig}) , the thin flame boundary condition (Eq. 4.5) is incorporated. Then equations from Eq. 4.5 to Eq. 4.7 are simultaneously solved for r_p , G_p and T_s using the value of \dot{q}''_w obtained from the solution of transient heat conduction equation. The iteration continues till mass is reduced to 25% of the initial mass. Thermodynamic and transport property values used in the model are taken from Mukunda *et al.* (1984).



Figure 4.5: Mass loss prediction with experiments

A typical mass loss plot obtained from the UID model for a single particle (10 mm diameter, agro-residue pellet) with convective boundary condition for ignition process is shown in the Fig. 4.5. Experiments were conducted for the same particle in similar conditions as explained in section 2.2.2. The experimental data is plotted along with predictions and the comparison is good. Also, match between predicted t_{ig} and t_v with experiments is excellent (within \pm 5% error) as shown in Fig. 4.5.

As discussed earlier, with increase in particle size, t_v becomes more than t_{ig} . UID model is used to predict the t_{ig} and t_v for various particle sizes as similar to the single particle experiments. Variation of t_{ig} and t_v (scaled with particle density ρ) with equivalent spherical diameter d_p is shown in Fig. 4.3. As inferred from Fig. 4.3, t_{ig} and t_v are comparable for particle size till 20 mm and above that the difference between the two becomes larger. When T_p is 600 K as given by Mukunda *et al.* (1984), the ignition times are higher than T_p =473 K since heating time goes up. However, the de-volatalization time also goes up and in this case it is over predicting t_v unlike the case of $T_p = 473$ K. During the initial stages of modeling, T_p of 600 K was taken, but, the comparison of t_{ig} and t_v from the model predictions and single particle experiments were not as good as with lower values of T_p . Hence, it was decided to crosscheck the pyrolysis temperature using TGA with agro-residue pellets used in the current study. The mass loss started at 473 K. Also, for a 10 mm particle, t_{ig} and t_v match from single particle experiments and UID model was better with $T_p = 473$ K compared to that with higher temperatures. Differences in values between model and experiment as shown in Fig. 4.3 is due to differences in ignition conditions and heat losses associated with experiments. However, the results from the UID model shows the relative magnitudes of variation between t_{ig} and t_v that is good enough to decide grate residence time, which ensures complete conversion of the fuel fed in the grate (refer Varunkumar et al., 2015, for more details).

4.2.3 Oxygen fraction and flame jump

The results discussed in the previous section were for the case with air as oxidizer. Effect of oxygen mass fraction in the oxidizer on t_{ig} and t_v and its role in steady propagation vs flame jump will be discussed in this section. Steady flame propagation is essential for any thermo–chemical packed bed biomass conversion systems. However, in experiments with O_2 – CO_2 and O_2 – N_2 it is observed that when the O_2 fraction is less than 15%, propagation ceases and on the other end, if the O_2 fraction is higher than 42% unsteady flame propagation phenomenon called 'flame jump' occurs. Here, the ignition front propagates upstream without complete conversion of 'volatiles'. Typical time-temperature data from P23C i.e O_2 – CO_2 experiment at a O_2 mass flux of 31 g/m²s is taken to elucidate steady flame propagation. Temperatures recorded by the thermo-couples T6 to T1 reach peak bed temperatures at constant time interval. The distance between the thermocouples is constant and hence the time interval (Δt) is constant as shown in the Fig. 4.6. It can be inferred from the plot that, the temperature profile is same at all time intervals. When the coordinate frame is fixed to the flame from (as

in the case of practical downdraft configuration, where the flame front is fixed and the biomass bed moves toward the flame front zone), the temperature profiles will be same at any instant of time. In other words the heat flux received by the fresh layer of biomass from the flame front is constant in steady propagation.



Figure 4.6: Temperature profile of a steady flame front across reactor length at different times - P23C case at \dot{m}'_f of 31 g/m²s

During 'flame jump', the ' Δt ' term becomes very small and no more a constant. This can be seen from Fig. 2.6 where, both steady and unsteady flame propagation are shown. For a steady flame, from UFP model, the surface energy balance of a fresh biomass particle upstream of a steady flame front is given as,

$$\frac{mC_p}{A_c}\frac{dT_p}{dt} = (f\epsilon\sigma(T_s^4 - T_p^4)) - h(T_p - T_0)$$
(4.8)

where, m, C_p , A_c , T_p , T_s and T_0 represent mass, specific heat, cross-sectional area, particle, surface and ambient temperature respectively (Varunkumar, 2014).

The total time required for the temperature of the fresh biomass particle to increase from ambient temperature (T_{∞}) to the ignition temperature (T_{ig}) is computed from the above equation and propagation rate \dot{r} is calculated as d_p/t_{ig} . An order of magnitude estimate of the L.H.S of Eq. 4.8 gives

$$\frac{mC_p}{A_c}\frac{dT_p}{dt} \sim \frac{mC_p(T_{ig} - T_\infty)}{A_c t_{ig}}$$
(4.9)

substituting t_{ig} as d_p/\dot{r} and replacing $m = \rho_b V$

$$\frac{mC_p}{A_c}\frac{dT_p}{dt} \sim \frac{\rho_b V \dot{r} C_p (T_{ig} - T_\infty)}{d_p A_c}$$
(4.10)

volume $V = \delta_{critical} A_c$ where, $\delta_{critical}$ is the critical thickness of the fresh biomass layer to be raised to the ignition temperature (T_{ig}) for flame propagation.

$$\frac{mC_p}{A_c}\frac{dT_p}{dt} \sim \frac{\rho_b \dot{r} C_p (T_{ig} - T_\infty)}{\frac{d_p}{\delta_{critical}}}$$
(4.11)

Substituting $\delta_{critical}/d_p$ as K, the Eq. 4.8 finally reduces into

$$K\frac{mC_p}{A_c}\frac{dT_p}{dt} \sim \rho_b \dot{r} C_p (T_{ig} - T_\infty)$$
(4.12)

where, factor K is to account for the critical mass of biomass to be raised to the ignition temperature and $\rho_b \dot{r}$ is the fuel flux (\dot{m}''_f) and the R.H.S of Eq. 4.12 becomes $\dot{m}''_f C_p (T_{ig} - T_0)$ which denotes the flux received by fresh biomass. The ignition time variation is dependent on incident flux which is a function of \dot{m}''_f of the flux term $\dot{m}''_f C_p (T_{ig} - T_0)$.

Steady propagation data for all the experiments with air, O_2-CO_2 and O_2-N_2 for different fuels are available. Taking T_{ig} as pyrolysis temperature i.e. 473 K, the ignition flux term $\dot{m}''_f C_p (T_{ig} - T_0)$ is calculated. Using UID model, replacing the ignition source term with $\dot{m}''_f C_p (T_{ig} - T_0)$, t_{ig} for all the cases is calculated.

A typical example of O_2-N_2 experiments with agro-residue pellets is taken to study the role of O_2 fraction in propagation. Fuel mass flux (\dot{m}''_f) obtained with same superficial velocity of 7.5 cm/s corresponding to O_2 fractions of 23, 28, 33 and 43 % (by mass) are taken. This is used to calculate the incident heat flux for a fresh biomass layer to be ignited (i.e. $\dot{q}'' = \dot{m}''_f C_p (T_{ig} - T_0)$). The variation of \dot{q}'' with O_2 fraction and results of t_{ig} and t_v calculated using UID model are shown in Fig. 4.7.



Figure 4.7: Variation of t_{ig} , t_v and \dot{q}''_w with increasing O₂ fraction

It can be seen from Fig. 4.7 that, t_{ig} is higher than t_v for air case (i.e. 23.2% O₂) and as the O₂ fraction is increased, the heat influx (\dot{q}'') increases, the ignition time becomes smaller than t_v and the ratio of t_v/t_{ig} increases from unity to around 2.3 at 43% till which steady propagation is observed. As seen from Fig. 4.7, with increase in O₂ fraction, t_v decrease is insignificant unlike t_{ig} . Increase in heat flux with increasing O₂ fraction enhances the volatile generation rate that prevent heat ingress due to what is termed 'blocking effect'. Due to this, the gas phase zone thickness is enhanced due to enhancement in flow from surface of the particle and hence, reduce the thermal gradients near the surface and convective heat transfer to the surface (Mukunda, 2011; Spalding, 1979). When O₂ fraction exceeds 43% the t_v/t_{ig} ratio goes beyond 2.3 and flame jump is observed. This is consistent with visual observation of flame jump in a transparent reactor by Varunkumar (2014) where flaming to ignition time ratio around 5 for thin wood chips and 2 for dense biomass like pellets is reported. In 'flame jump' zone UFP model is not applicable as the phenomenon become unsteady.

4.3 **Operational regimes**

It is clearly shown from O_2 -CO₂ experiments that 'volatiles' stoichiometry (i.e. $\phi_v \sim$ 1) is the transition point from gasification to combustion. Quantities of interest like *NCC*, *NSC*, CO and H₂ yield is of less or no relevance in combustion zone due to char oxidation. Hence, except for a few exploratory cases, most of the experiments aimed for gasification can be restricted till $\phi_v \sim$ 1. Insights from O₂-CO₂ experiments are applicable to O₂-steam cases too.

A plot of the ratio of ignition to devolatilization time versus 'volatiles' equivalence ratio is shown in Fig. 4.8 for all cases discussed so far. Based on this plot, the propagation regimes in a packed bed of biomass can be classified in to five zones.



Figure 4.8: Zones of operation of a packed bed of biomass

Some important flame characteristics of these zones are listed in the Table 4.1. In Zone I, oxidizer flux is low and fuel rich ($\phi_v > 2$). Hence, bed temperatures are less in this zone owing to low propagation rates (< 25 g/m²s). Also, here the time of ignition is very high as compared to devolatalization time. This effect is captured by $t_v/t_{ig} <$ 0.75. Zone II represents the optimum zone of operation with $2 \ge t_v/t_{ig} \ge 0.75$ and bed operation near 'volatiles' stoichiometry which enhances the bed temperature and

Zone characteristics							
Zones	t_v/t_{ig}	ϕ_v	Flame propagation	T_{pb} (K)	Char Conversion	CO yield	
Zone I	≤ 0.75	4 - 0.5	Slow/Propagation ceases	≤ 1000	Not complete	Low	
Zone II	0.75 - 2	2 - 1	Steady	1000 - 1500	Complete	High	
Zone III	0.75 - 5	≥ 2	Steady/Unsteady	≥ 1000	Not complete	Low	
Zone IV	2 - 5	2 - 1	Unsteady	1500 - 1800	Complete	Low	
Zone V	≥ 0.75	≤ 1	Steady/Unsteady	≥ 1500	Char oxidizes	Low	

Table 4.1: Characteristics of flame propagation zones of packed bed systems

favors net CO₂ conversion. Most of the cases which have shown steady propagation fall under this category. Zone III represents fuel rich zone where incomplete combustion of 'volatiles' is observed and the ratio t_v/t_{ig} is comparatively higher than Zone I and Zone II which shows tendency towards 'flame jump'. Zone IV represents the 'flame jump' zone (i.e. $t_v/t_{ig} > 2$). Except for coconut shell cases (which shows peculiar behavior of 'flame jump' around 32% O₂ fraction) P42C case fall in this zone where the O₂ fraction is more than 40%. It is also important to note that in this zone, the peak bed temperatures are high (1500 $\leq T_{pb} \leq$ 1800 K) which leads to melting of reactors and ash fusion problems. Zone V represents the char oxidation zone.

It can be seen from the Table 4.1 that Zone II is the optimum condition for steady flame propagation, moderate bed temperatures and better CO_2 conversion since operation is closer to 'volatiles' stoichiometry. Hence, for O_2 -steam experiments, Zone II is chosen for better steam conversion and high H_2 yield.

4.4 Summary

In this chapter, theoretical perspectives of packed bed biomass flame propagation that go beyond the limits of UFP model are presented. Normalization of fuel flux variations from different O_2 fractions is addressed through normalized fuel flux (*NFF*), which shows the regimes of 'gasification' and 'char oxidation' as a function of ϕ_v and also shows applicability of 'universal behavior' to all fuel – oxidizer combinations. Also, *NFF* shows necessity of including bed voidage for peculiar fuels like coconut shells which shows higher fuel fluxes even with air cases. However, enhanced burning characteristics of coconut shells as compared to pellets needs further exploration.

Limitations of predictive models from earlier studies for flame propagation rate for larger size particles where devolatalization is rate limiting is brought out through single particle and 500 mm reactor experiments. In light of this, a 'unified ignitiondevolatalization' model is developed from first principles to predict the ignition and devolatalization time of single particles. Predictions from the model is shown to agree well with experiments. In addition, from the model, it is shown that, 'flame jump' occurs when the ratio of flaming to ignition time (t_v/t_{ig}) exceeds 2. The idea is further extended to map different operational zones for packed bed biomass flame propagation systems. This map will be a useful tool for practitioners to choose operating conditions for various applications. The results from this chapter were used to make the following choices for gasification with O_2 -steam mixtures - (1) two varieties of biomass fuels are sufficient as inferred from 'universal flame propagation behavior' and O2-CO2 experiments, (2) operation can be restricted till 'volatiles' stoichiometry and should preferably be in Zone II and (3) oxygen fraction should be chosen between 20 - 40 % by mass to avoid 'flame jump', ash fusion and reactor melting issues. The results from O2-steam experiments are discussed in the next chapter.

CHAPTER 5

GASIFICATION WITH O₂-STEAM MIXTURES

Discussions from the previous chapters brought out the role of 'volatiles' stoichiometry and range of O_2 fractions in CO yield and *NCC*. These aspects are equally applicable to O_2 -steam mixtures as well since the phenomenon of conversion is similar. Also, as concluded from chapter 4, number of fuels for the study, appropriate oxidizer fractions, regime of operation can be planned *a priori*. As mentioned in chapter 1, the main aim of the current work is to explore the intrinsic hydrogen yield of biomass from a canonical packed bed configuration. Choice of experimental conditions, results from experiments are presented in this chapter.

5.1 Choice of experimental conditions

Earlier literature as discussed in chapter 1, clearly shows that fuel rich operation (i.e. $\phi_v > 2$) enhances the H₂ yield but leads to high tar fraction in syngas (Lv *et al.*, 2007). Studies reported by Sandeep and Dasappa (2013, 2014) use very high temperature steam (around 1100 K) to crack the tar and hence, the H₂ yield estimated from this study cannot be considered intrinsic. In this study steam temperature range is restricted between 120 - 150 °C. Lower limit to avoid condensation of steam when it comes in contact with low temperature biomass. Also, biomass is heated to around 60 - 70°C so that the bed upstream of the reaction zone is always maintained around 100 - 105 °C for the entire duration of the experiment. Oxygen fraction is restricted between 23 to 40% to avoid 'flame jump' as discussed earlier.

List of oxidizer fractions and notations used to refer to the experiments performed are listed in Table 5.1. Reference cases like WP23C and P42C (from O_2 -CO₂ experiments) were compared with the equivalent O_2 -steam cases. Experimental procedure and calculation method are already described in chapter 3. However, a sample spread sheet (for case WP30 at \dot{m}'_{ox} of 121 g/m²s) used for the calculation of results can be downloaded from Jaganathan (2019). It is important to note here that, the H₂ yield

S.No	Oxidizer	Experiments
1	Air**	WPA and PA
2	23% O ₂ -77% Steam	WP23
3	30% O ₂ -70% Steam	WP30
4	40% O ₂ -60% Steam	WP40
5	40% O ₂ -60% Steam	P40
6	23% O ₂ -77% CO ₂ **	WP23C
7	42% O ₂ –58% CO ₂ **	P42C

Table 5.1: Experimental nomenclature

* - all % on mass basis; ** - from chapter 3
WP - Wood pellet; P - Agro residue pellet

reported here does not account of H₂ content from methane and other higher hydrocarbons or in other words, intrinsic H₂ yield is reported in the current work. Results of fuel mass flux, 'volatiles' (ϕ_v) and overall (Φ) equivalence ratios, H₂ yield are presented and discussed in the following section.

5.2 Results and discussion

The measured fuel mass flux and the corresponding 'volatiles' equivalence ratio (ϕ_v) for different oxidizer compositions and fluxes are shown in Fig. 5.1.



Figure 5.1: ϕ_v variation with \dot{m}''_f ; uncertainty smaller than marker size.



Figure 5.2: ϕ_v variation with \dot{m}''_{ox} ; uncertainty smaller than marker size.

The amount of 'volatiles' consumed is estimated from the total biomass consumed and the proximate analysis (see chapter 3 for details). Since ϕ_v is going to be the primary variable of interest in the discussions that follow, fuel flux variation is shown as a function of ϕ_v in Fig. 5.1. The variation of ϕ_v with \dot{m}''_{ox} is shown in Fig. 5.2 for reference. With increase in \dot{m}''_{ox} , \dot{m}''_f increases till $\phi_v \to 1$ and then remains more or less constant - this behavior is consistent with the universal propagation phenomenon with air and O₂–CO₂ as oxidizers (Varunkumar *et al.*, 2013). Hence, ϕ_v is taken to be an indicator of operation regime ($\phi_v > 1$ corresponds to gasification regime and $\phi_v < 1$ corresponds to combustion regime). Figure 5.3 presents the variation of average peak bed temperature (T_{pb}) with ϕ_v .



Figure 5.3: T_{pb} variation with \dot{m}''_{f} ; uncertainty smaller than marker size.

Consistent with ϕ_v variation, T_{pb} increases as 'volatiles' stoichiometry is approached. Air cases show higher T_{pb} than WP23 and WP30 cases and this is due to the high heat capacity of steam than N₂ fraction present in air.

No ash fusion issues were found in the current study and this is mainly due to the following reasons, (1) the O₂ fractions were chosen from 23 - 40% and hence peak bed temperatures were below 1800 K unlike earlier O₂–CO₂ experiments where ash fusion occurred when O₂ fraction exceeded 40% (refer chapter 3) and (2) the char layer temperature is a few hundred degrees lesser than T_{pb} and hence below the ash fusion point of wood pellet which is around 1600 K (Holubcik *et al.*, 2015) and agro-residue pellet which is around 1500 K (Mukunda, 2011).

5.2.1 Char conversion and H₂ yield

Figure 5.4 shows the % char conversion as a function of 'volatiles' stoichiometry and it is observed that the char is almost completely converted before $\phi_v = 1$.



Figure 5.4: Char conversion with ϕ_v ; uncertainty $\leq \pm 10\%$.

In other words the char is consumed by reduction reactions like water gas (C + H₂O \rightarrow CO + H₂) and Boudouard (C + CO₂ \rightarrow 2CO) for all the cases. This argument is further supported by experiments of Dasappa (1999), indicating reactivity enhancement and shift towards diffusion limited conditions of char steam reaction at higher temperatures, which is the case here as $\phi_v \rightarrow 1$. Thus, operation near 'volatiles' stoichiometry enhances H₂ yield due to C +H₂O reaction; role of diffusion on the rate of this reaction is significantly higher at $\phi_v \sim 1$ ($T_{pb} \sim 1500$ K) as compared to lower temperatures at $\phi_v > 2$ ($T_{pb} \sim 1000$ K).

For the case of steam reaction with char, it is important to quantify the amount of steam getting converted. 'Volatiles' oxidation is diffusion limited (Varunkumar *et al.*, 2013; Porteiro *et al.*, 2010). Hence, 'volatiles' oxidation products are computed through equilibrium calculations with NASA CEA SP-273 code. Adopting a similar procedure as outlined in chapter 3, H_2 and CO yield (defined as mass of corresponding gas in grams per kg of biomass on wet basis) is determined. In addition to H_2 and CO yield, net steam conversion (*NSC*, g/kg of biomass) is calculated which is (similar to *NCC*)

from chapter 3) defined by Eq. 5.1.

$$NSC = \frac{(m_{H_2O,v} + m_{H_2O,inlet} - m_{H_2O,outlet})}{m_b}$$
(5.1)

where, $m_{H_2O,v}$ is the mass of steam released from 'volatiles' oxidation, $m_{H_2O,inlet}$ is the steam fed to the system, $m_{H_2O,outlet}$ is the mass of steam in the exit gas and m_b is the mass of biomass (refer Fig. 3.1 and chapter 3 for more details).

To elucidate the effect of ϕ_v on H₂ yield, a representative case with 30% O₂ and 70% steam is taken i.e WP30 case and the results are discussed in detail using Fig. 5.5.



Figure 5.5: Role of ϕ_v in H₂ yield - WP30 case; uncertainty $\leq \pm 10\%$.

In Fig. 5.5a, ϕ_v approaches unity and decreases further with increase in oxygen mass flux/oxidizer velocity. H₂ yield from equilibrium calculations decreases and reaches zero as $\phi_v \rightarrow 1$. At very rich condition i.e. $\phi_v = 2.04$, equilibrium H₂ yield is higher

than experimental yield; this is possibly due to fuel rich conditions i.e. from unburnt 'volatiles' and also due to gas phase reactions like reverse water - gas shift reaction which favors H₂ yield at temperatures below 1100 K (Callaghan, 2006). It is also important to note here that, under rich conditions the reaction is rate limited and hence, H₂ yield from equilibrium calculations are higher than actual yield. The H₂ yield from the experiment is nearly invariant till $\phi_v = 1$. This is mainly due to compensation of 'volatiles' H₂ with H₂ from reduction reaction of char with steam through water gas reaction (C + H₂O \rightarrow CO + H₂). Hence, CO as well as H₂ drops significantly after 'volatiles' stoichiometry due to char oxidation.

Consistent with this, net steam conversion (*NSC*) also increases and reaches peak value of about 320 g/kg of biomass around 'volatiles' stoichiometry for O₂-steam cases. Net CO₂ conversion (*NCC*) is in the range of 100 - 250 g/kg of biomass as against a range of 400 - 600 g/kg of biomass with O₂-CO₂ mixtures (chapter 3). This is mainly because biomass is the only source of CO₂ in O₂-steam cases and hence the CO₂ concentration in 'volatiles' oxidation products is lesser as compared to O₂-CO₂ cases. Also, since $T_{pb} < 1500$ K, CO₂ conversion due to Boudouard reaction is not significant as the temperatures of the char bed is a few hundred degrees lesser than T_{pb} (refer chapter 3). CO yield is still higher (around 450 g/kg of biomass) near $\phi_v = 1$, because, of char steam reaction. Also, near 'volatiles' stoichiometry the higher hydro carbons fraction is observed to be zero (details follow later), indicating very little or no tar i.e. better syngas quality. The cold gas efficiency (η_g) shows similar trend as that of H₂ yield and the values are always higher than corresponding air and O₂-CO₂ cases due to high concentration of CO and H₂ in the exit gas.

The results for the other cases listed in Table 2.1 are presented below. Variation of H₂ yield, CO yield, *NSC*, *NCC* and η_g with ϕ_v is shown from Fig. 5.6 to Fig. 5.11 respectively.

5.2.2 Intrinsic H₂ yield and NSC

The H₂ yield is in the range of 30–40 g/kg of biomass for all the O₂–steam cases over the entire gasification range (i.e. $2.1 \ge \phi_v \ge 1$) as shown in Fig. 5.6.





Figure 5.6: H₂ yield with ϕ_v ; uncertainty $\leq \pm 10\%$.





Figure 5.7: NSC variation with ϕ_v ; uncertainty $\leq \pm 10\%$.

It is important to note that all the cases in literature (Sandeep and Dasappa, 2013; Lv *et al.*, 2007) were restricted to fuel rich regime ($\phi_v > 2$), whereas the current work shows
that H₂ yield is invariant for $2.1 \ge \phi_v \ge 1$ which corresponds to an overall equivalence ratio of $3.4 \ge \Phi \ge 1.25$.

Interestingly, from the earlier works, it can be inferred that, the boundary of H₂ yield invariance is extended to very rich regime too i.e. $5.5 \ge \Phi \ge 2.1$ as reported in Cerone *et al.* (2016, 2017); Cerone and Zimbardi (2018). Under such highly fuel rich conditions, 'volatiles H₂' will dominate the H₂ yield; also, as the configuration used in Cerone *et al.* (2016, 2017); Cerone and Zimbardi (2018) is updraft, the role of char-steam reaction is limited. Lv *et al.* (2007) also observed similar yield with high tar generation due to fuel rich operation. Results of Sandeep and Dasappa (2013) show that the intrinsic component of H₂ yield, that is, after correcting for the contribution from methane (20 g/kg) and water gas shift reaction (36 g/kg), is 52 g/kg of biomass. This is slightly higher than that from other studies, perhaps due to the use of high temperature steam (1000 K).

5.2.3 Residence time

The important point to note is that, when operating at conditions with $\phi_v > 2$ (Cerone et al., 2016; Sandeep and Dasappa, 2013; Lv et al., 2007), the contribution from 'volatiles' is dominant and that from char-steam reaction is negligible (see Fig. 5.5a). As shown in the current study, char-steam reaction starts to dominate as $\phi_v \to 1$. This is due to the increase in temperature which in turn increases the rate of the reaction (Dasappa, 1999). The typical residence time of the 'volatiles' oxidation products with the upstream char layer (assuming one layer thick) is around 6 - 30 ms for all the cases shown in the current work (refer Table A.5). From the char conversion results shown Fig. 5.4, it is clear that as $\phi_v \to 1$, char conversion approaches 100%. Therefore, similar to O₂-CO₂ cases, the char reactions are limited by residence time (and hence kinetic rate) under rich conditions and become limited by the available amount of char as $\phi_v \to 1$. One more important observation is that, the intrinsic H₂ yield is almost same for variety of biomass in different reactor configurations as inferred from the results of Cerone et al. (2016, 2017); Cerone and Zimbardi (2018); Sandeep and Dasappa (2013); Lv et al. (2007). Also, current work shows that the catalytic role of ash, observed in TGA/DTA studies is not relevant in practical configurations. The role of ash is limited to that of an inert substance absorbing energy which might otherwise be available for de-volatilization.

5.2.4 Higher hydrocarbons and tar

It can be seen from the Fig. 5.6, that near 'volatiles' stoichiometry, for high O_2 fraction case like WP40 the H_2 yield is as high as 40 g/kg of biomass. Also, interestingly the higher hydrocarbons (like ethylene, acetylene, ethane and trace amounts of C_{6+}), which is also an indicator of tar in the exit gas is almost zero near 'volatiles' stoichiometry as shown in Fig. 5.8 for most of the cases.





Figure 5.8: HHC variation with ϕ_v ; uncertainty $\leq \pm 10\%$.

This is due to the 'close to complete oxidation of volatiles' and the associated high temperatures which aid tar cracking. In other words, operation of the bed near $\phi_v \approx 1$, enhances gas quality than fuel rich operation without much or no compromise in H₂ yield. Higher H₂ yield of 26 g/kg of biomass is observed for 42%O₂–58%CO₂ cases with agro residue pellets and this is due to very high peak bed temperatures around 1800 K which promotes H₂ yield. *NSC* reported for P42C is comparable to O₂–steam cases.

Carbon monoxide yield and NCC also follows the same trend like H_2 and the CO yield is lower for O_2 -steam cases (refer Fig. 5.9 and Fig. 5.10) as compared to O_2 -CO₂ and air cases as expected.





Figure 5.9: CO yield with ϕ_v ; uncertainty $\leq \pm 10\%$.





Figure 5.10: *NCC* variation with ϕ_v ; uncertainty $\leq \pm 10\%$.

5.2.5 Gasification Efficiency (η_q)

Cold gas efficiency (η_g) is defined as the ratio of energy content in the exit cold gas to the total energy contained in the biomass. Energy required for raising steam to 120 -150 °C is about 5 to 8 % of the total energy of the exit gas and this is not accounted for the calculation of the cold gas efficiency. The net steam conversion increases from zero and reaches maximum near 'volatiles' stoichiometry ($\phi_v = 1$) and falls off beyond that due to char oxidation for all the cases reported in the current work. *NCC* also follows similar trend as reported in chapter 3. Cold gas efficiency (η_g) as shown in Fig. 5.11 drops near 'volatiles' stoichiometry but still high as compared to air cases due to higher H₂ and CO content present in the syngas.



Figure 5.11: η_g with ϕ_v ; uncertainty $\leq \pm 10\%$.

Maximum cold gas efficiency of 70% is obtained for the case with 30% oxygen at ϕ_v around 1.5; the corresponding hydrogen yield is 38 g/kg of biomass. P42C case also shows similar η_g as that of other O₂-steam since the H₂ and CO content is high in the syngas because of very high T_{pb} of about 1800 K as compared to other O₂-CO₂ cases. In practice, operating close to 'volatiles' stoichiometry to ensure tar free exit gas with a slight compromise on cold gas efficiency will be preferable.

5.2.6 Operational zones of O₂–steam experiments

As explained in chapter 4, the operational zone of the current O_2 -steam experiments falls under Zone II and this ensures steady flame propagation as seen from Fig. 5.12 for most of the cases.



Figure 5.12: Zones of operation of O₂-steam experiments

5.3 Summary

Counter-current biomass packed bed reaction behavior with O_2 -steam mixtures has been the subject of exploration of this chapter. Novelty and important highlights from this chapter are as follows - (1) intrinsic H₂ yield potential of biomass is determined under self-sustained steady propagation conditions covering both gasification and combustion regimes, (2) minimum upstream bed temperature of 120 - 150 °C is used as against very high steam temperatures (> 800°C) reported in earlier works, permitting greater simplicity in the choice of reactants, (3) H₂ yield is invariant (around 30 -40 g/kg of biomass) with increasing mass flux of the oxidizer within the gasification regime and this is mainly due to additional H₂ generated from char steam reaction which is shown to compensate for the reduction in H₂ from 'volatiles', (4) near 'volatiles' stoichiometry, T_{pb} is higher and hence the higher hydrocarbons are zero and therefore better gas quality as compared to fuel rich operation, (5) increased CO and H₂ content increases the cold gas efficiency (maximum η_g of 70% is obtained for WP30 case at ϕ_v of 1.5) of O₂-steam cases as compared to air cases even at slightly rich conditions and (6) when 'volatiles' stoichiometry coupled with high T_{pb} , even with O₂-CO₂ cases, the H₂ yield (around 26 g/kg of biomass) is enhanced. These results can be used in the design of scaled up systems for continuous operation.

CHAPTER 6

CONCLUSIONS AND FUTURE WORK

This thesis has contributed to the fundamental understanding of counter-current flame propagation characteristics in a biomass packed bed system. Effects of different oxidizer combinations, namely, O_2 – CO_2 , O_2 – N_2 and O_2 –steam on propagation rate, CO and H₂ yield and HHC fraction in the exit gas are brought out. The important conclusions of the present work are summarized under the following titles, (1) role of 'volatiles' equivalence ratio, (2) gasification with O_2 – CO_2 mixtures, (3) insights from UID model and (4) gasification with O_2 –steam mixtures.

Role of 'Volatiles' equivalence ratio

A variety of biomass from earlier and current study is shown to exhibit *universal flame* propagation behavior. From the current study, 'volatiles equivalence ratio' emerges as an unifying parameter for analyzing thermo-chemical conversion of biomass in packed bed reactors. Variables including, fuel mass flux, CO and H₂ yield, char conversion and HHC fraction in exit gases share similar characteristics when expressed as functions of ϕ_v , irrespective of the oxidizer. These characteristics are as follows -

- 1. For all fuel and oxidizer combination, $\phi_v > 1$ in the *gasification* regime and $\phi_v < 1$ in the *char oxidation* regime, that is, transition from *gasification* to *char oxidation* occurs at $\phi_v = 1$.
- 2. Normalized fuel flux exhibits universality irrespective of the oxidizers and fuel type as a function of ϕ_v .
- 3. Syngas yield (CO and H₂) is found to be maximum around $\phi_v \rightarrow 1$ due to enhanced conversion of CO₂ and steam with char.
- 4. Complete char conversion is achieved at a slightly rich ϕ_v (usually around 1.5), indicating participation of char in reduction reactions.
- 5. In general, the HHC fractions are near zero around $\phi_v \sim 1$ which implies that the syngas is tar free.

Gasification with O₂–CO₂ mixtures

Some important outcomes from experiments with O₂–CO₂ mixtures are as follows,

- 1. Steady flame propagation is shown to be established with variety of fuels and O_2 fraction in the range of 19 40 %. Beyond O_2 fraction of 40%, *flame jump* is observed.
- 2. Net CO_2 conversion is quantified by invoking 'volatiles' equilibrium and enforcing elemental and energy balances. It is also important to state here that, this method also quantifies the *NCC* from air cases (maximum value is around 220 g/kg of biomass) which is a unique feature of this work.
- 3. Presence of CO₂ in the inlet stream promotes char reduction reactions and when the operation regime shifts to near 'volatiles' stoichiometry ($\phi_v \sim 1$), where T_{pb} is above 1500 K, significant NCC is observed.
- 4. Maximum net CO₂ conversion of 400–600 g/kg of biomass and CO yield around 600–800 g/kg of biomass are observed for O₂–CO₂ cases, which is 2–2.5 times higher than the corresponding air cases.
- 5. Char limited nature of CO₂ conversion as $\phi_v \rightarrow 1$ is brought out.
- The gasification efficiency of all O₂–CO₂ cases are higher than corresponding air cases and this is due to the reactive contribution of CO₂ unlike inert N₂ in air and O₂–N₂ cases.
- H₂ yield from O₂-CO₂ gasification is in the similar range as that of air gasification systems (around 10 - 20 g/kg of biomass).

Insights from UID model

Though under conditions of steady propagation, fuel flux exhibits universality with ϕ_v , explanation of unsteady propagation phenomenon namely, 'flame jump' needed exploration beyond the scope of *universal flame propagation model*. Also, single particle experiments have shown that the t_v becomes greater than t_{ig} beyond 20 mm with air as oxidizer and hence, t_v can limit the fuel flux. In the light of this, a *unified ignition-devolatalization* model is developed to predict t_v and t_{ig} and following are the main outcomes of UID model,

- 1. The relative magnitudes of t_v and t_{ig} as a function of particle size is brought out.
- 2. With air as oxidizer, beyond d_p of 20 mm $t_v >> t_{ig}$ and t_v influences the flame propagation. This is consistent with results of large reactor experiments using GSB.
- 3. 'Flame jump' is shown to occur when t_v/t_{ig} exceeds 2.

4. From UID model and experimental results, a non dimensional plot of t_v/t_{ig} vs ϕ_v showing different operational zones of biomass gasification systems is presented. Five zones are identified from this map, out of which zone II is identified as the optimum operating zone for gasification.

Gasification with O₂-steam mixtures

Understanding of the flame propagation behavior using 'UID' framework allows to choose experimental conditions for O_2 -steam experiments. Zone II is chosen for the study based on the insights from theoretical studies. O_2 fractions is chosen between 20 to 40% to avoid unsteady flame propagation zones. As inferred from 'universal flame propagation behavior' and O_2 -CO₂ experiments, biomass exhibits universality when corrected for ash and moisture. Hence, only two fuels (wood pellets and agro-residue pellets) are used for O_2 -steam experiments. Some important outcomes of O_2 -steam gasification study are listed below,

- 1. Intrinsic H_2 yield of 30 40 g/kg of biomass is observed in entire 'gasification' regime and this is 2-2.5 times higher than the corresponding air cases.
- 2. Demarcation between 'volatiles' H₂ at fuel rich conditions (i.e. $\phi_v > 2$) and H₂ from char-steam reaction at slightly fuel rich conditions ($2 \ge \phi_v \ge 1$) is clearly brought out.
- 3. As $\phi_v \rightarrow 1$, bed temperature increases and the char steam reaction dominates promoting H₂ yield and at the same time leads to tar free exit gas. This hitherto unknown result is reason why all the earlier works were focused on highly fuel rich conditions tolerating high tar content.
- 4. Like NCC, net steam conversion (NSC) is also quantified.
- 5. Char limited nature of char-steam reaction as $\phi_v \rightarrow 1$ is brought out.
- 6. Also, no flame jump, ash fusion and reactor melting issues were observed as the experiments were done in 'Zone II' as identified from Fig. 5.12 of chapter 5.

Studies with O_2 – CO_2 , O_2 – N_2 and O_2 –steam in practical configurations like fixed bed and fluidized bed in the literature, in general, reports the results of parametric studies. For instance, in O_2 steam gasification, steam to biomass ratio (SBR) is a commonly used parameter and the H₂ yield is reported at various SBR at different equivalence ratios and bed temperatures. Since SBR is interconnected with fuel flux, oxidizer mass flux and O_2 fraction, interpretation of results is not straight forward. On the other hand, when the reactor variables like normalized fuel flux, CO and H₂ yield are expressed as functions of 'volatiles' stoichiometry (though not an independent variable), the behavior shares similar characteristics as brought out here. This feature can be readily adopted by practitioners to choose operating conditions for a particular application.

6.1 Future work

Aspects requiring further exploration include,

- 1. Experiments in a continuous mode downdraft gasifier system with optimum O_2 -CO₂-steam ratio to generate syngas suitable for liquid fuel synthesis (i.e. with H₂/CO ratio > 2) and integrating the same with catalytic FT process.
- 2. The exit gas from the oxy-steam gasification system contains more than 50% of mass fraction of steam at a temperature of about 600 800 K. This is close to the operating conditions of high temperature water gas shift unit (HTS) with industrial Fe/Cr catalyst, which can enhance the production of H₂ further (Mehrabian *et al.*, 2012). This can be better strategy to improve the H₂ yield and will be pursued by the author.
- 3. To extend the UID model to predict the flame propagation rate of the packed bed gasification system.
- 4. To study and develop systems towards liquid fuel synthesis from syngas.

APPENDIX A

EXPERIMENTAL DATASET

								G	Gas Com	positio	on % (v.	/v)			
Experimental details	m_0 (g)	V_s (cm/s)	$\dot{m}_{ox}^{\prime\prime}$ (g/m ² s)	$\dot{m}_f^{\prime\prime}\left(\mathbf{g}/\mathbf{m}^2\mathbf{s} ight)$	$\mathbf{T}_{pb}\left(\mathbf{K}\right)$	ϕ_v	Φ	\mathbf{CH}_4	СО	\mathbf{H}_2	\mathbf{CO}_2	ннс	\mathbf{N}_2	t_g (ms)	% Char Conversion
Air	2539	5	12	35.4	1148	2.6	3.4	3.31	11.59	6.48	21.46	1.96	55.2	49	0
	2540	7.5	19	44.6	1289	2.35	2.8	2.18	17.84	7.09	17.4	0.85	54.6	33	18
	2526	15	37	59.6	1510	1.56	1.85	1.09	16.63	4.85	15.8	0.33	61.3	19	87
	2521	22.5	56	63.4	1580	1.1	1.3	0.5	10.1	1.5	11.9	0.2	75.8	14	92
23% O ₂ and 77% CO ₂	2651	7.5	29	47.5	1340	1.72	2.04	1.8	25.5	8.1	64.2	0.4	0	26	87
	2629	15	60	58.8	1493	1.04	1.23	0.1	20	3.2	76.8	0	0	15	100

Table A.1: Experimental data - air and O₂–CO₂ experiments with wood pellets

	Gas Composition % (v.								v/v)						
Experimental details	$m_0 \left(\mathbf{g} \right)$	V_s (cm/s	$\dot{m}_{ox}^{\prime\prime}$ (g/m ² s)	\dot{m}_f'' (g/m²s)	$\mathbf{T}_{pb}\left(\mathbf{K}\right)$	ϕ_v	Φ	CH ₄	CO	\mathbf{H}_2	\mathbf{CO}_2	ннс	\mathbf{N}_2	t_g (ms)	% Char Conversion
19% O ₂ and 81% CO ₂	2364	3	10	24.6	1028	2.18	2.86	2.4	15.5	10.4	70.9	0.7	0	58	0
	2059	5	17	31.7	1172	1.67	2.17	1.6	23.2	9.6	65.3	0.8	0	37	32
	2114	10	33	42.8	1452	1.15	1.49	1.1	15.8	5.2	77.8	0.1	0	21	100
	2346	15	50	44.2	1519	0.787	1.01	0.5	16.3	3.4	79.9	0	0	15	100
23% O ₂ and 77% CO ₂	2431	3	12	30	1114	2.19	2.92	2.9	19.7	14.4	62.1	0.8	0	55	0
	2474	5	19	40	1266	1.79	2.34	2.0	28.3	14.1	55.4	0.3	Ő	37	37
	2484	7.5	31	56	1459	1.68	2.19	1.3	32.2	12.7	53.6	0.1	Ő	24	91
	2552	15	60	65	1611	0.96	1.25	0.6	29.2	7.8	62.4	0	0	14	100
	2558	22.5	89	58	1542	0.55	0.727	0.2	11.5	2.3	86.1	0	0	9	100
32% O ₂ and 68% CO ₂	2414	3	16	54 3	1042	2.69	39	4	17.3	15.4	61.8	15	0	43	0
5270 02 und 0070 CO2	2302	5	26	70.6	1329	2.37	3.07	33	26	19.1	49.8	1.0	0	30	2
	2574	7.5	41	92.3	1493	2.03	2.63	2.4	30.6	18.7	47.9	0.5	Ő	20	32
	2392	15	79	100	1614	1.11	1.44	0.7	27.7	10.8	60.8	0	0	13	94
42% Q. and 58% CQ.	2271	3	20	85	1172	3.1	1 08	6.0	10.1	14.1	50	1.8	0	34	0
4270 O2 and 3670 CO2	2271	5	20	110	1204	27	3.93	47	19.1	10.3	5/3	1.0	0	24	0
	2404	10	55 66	161	1274	$\frac{2.7}{2.04}$	2.05	3.2	17.7 78.7	19.5 23.5	54.5 44	1.0	0	14	21
	2625	15	99	103	1500	2.04	2.0 2.25	17	37.8	25.5	387	0.3	0	11	77
	2025	22.5	149	208	1765	1.04	1.52	1.7	38.0	18.6	413	0.5	0	8	100
	2733	22.5	177	200	1705	1.02	1.52	1.2	50.9	10.0	т1.5	0	0		100

Table A.2: Experimental data - O_2 - CO_2 experiments with agro-residue pellets

								(Gas Cor	npositio	n % (v/	v)			
Experimental details	m_0 (g)	V_s (cm/s	$\dot{m}_{ox}^{\prime\prime}$ (g/m²s)	\dot{m}_f'' (g/m²s)	$\mathbf{T}_{pb}\left(\mathbf{K} ight)$	ϕ_v	Φ	CH ₄	СО	\mathbf{H}_2	\mathbf{CO}_2	ннс	\mathbf{N}_2	t_g (ms)	% Char Conversion
Air	2367	3	7	22.3	1001	2.38	3.09	2.7	12.7	6.7	21.2	1.2	55.5	81	8
	2369	5	12	31.2	1214	2	2.6	2.1	12.8	14.6	13.6	1	56	51	10
	2372	7.5	19	40.2	1342	1.68	2.17	1	16.3	11.5	14.8	0.4	56	34	21
	2469	15	37	56.6	1549	1.2	1.57	0.6	16.9	5.1	15.8	0.1	61.5	19	90
28% O. and 72% N.	2011	3	10	31.6	1060	27	37	3 35	8 12	14.06	24.07	1.2	/18	63	0
2070 O ₂ and 7270 N ₂	2011	75	25	54.7	1317	1.96	2.56	1.6	14 75	18.04	18 23	0.28	40	20	20
	2318	10	33	62.5	1517	1.90	2.50	1.0	20.2	16.04	15.25	0.28	47.1	23	55
	2390	15	49	75	1594	1.34	1.75	0.5	23.9	7.0	16.2	0.1	52.3	17	100
33% O ₂ and 67% N ₂	2345	3	12	41.8	1222	3.1	4.07	3.8	9.8	14.4	26.9	1.45	43.5	55	0
	2350	7.5	30	71.45	1398	1.8	2.35	1.47	9.9	13.9	13.6	0.19	60.8	26	0
	2446	15	59	100.8	1594	1.5	1.96	0.84	20.05	13.9	15.6	0.16	49.3	15	60
43% O ₂ and 57% N ₂	2300	3	16	74.2	1255	3.86	5.06	5	10 59	13 13	32.6	1 89	36.8	39	0
1576 O2 and 5776 N2	2300	75	40	120.3	1587	27	3 49	4 03	12.85	22.18	27.6	1.57	31.5	20	31.7
	2393	15	79	206	1627	2.3	2.98	2.7	24.3	21.9	20.18	0.25	30.6	11	94

Table A.3: Experimental data - air and O_2 - N_2 experiments with agro-residue pellets

$\begin{array}{cccc} 3 & 7\\ 7.5 & 19\\ 15 & 37\\ 22.5 & 56\\ 30 & 74\\ 37.5 & 93 \end{array}$	\dot{m}^2 s) \dot{m}''_f (g/m ² s) 26.7 49.45 74.7 91.69 96.86 102.5	T _{pb} (K) 1000 1181 1307 1465 1471	ϕ_v 3.3 2.44 1.88 1.54	Φ 4.16 3.05 2.35	CH ₄ 3.01 3.12	CO 8.7 12.32	H ₂ 5.68 7.8	CO ₂ 20.57	0.92	N ₂ 61.11	<i>t_g</i> (ms) 75	% Char Conversion
3 7 7.5 19 15 37 22.5 56 30 74 37.5 93	26.7 49.45 74.7 91.69 96.86 102.5	1000 1181 1307 1465 1471	3.3 2.44 1.88 1.54	4.16 3.05 2.35	3.01 3.12	8.7 12.32	5.68 7.8	20.57	0.92	61.11	75	0
7.5 19 15 37 22.5 56 30 74 37.5 93	49.45 74.7 91.69 96.86 102.5	1181 1307 1465 1471	2.44 1.88 1.54	3.05	3.12	12.32	7.8	18 36	1 22	1		
15 37 22.5 56 30 74 37.5 93	74.7 91.69 96.86 102.5	1307 1465 1471	1.88 1.54	2.35				10.50	1,22	57.1	32	30
22.5 56 30 74 37.5 93	91.69 96.86 102.5	1465 1471	1 54		2.56	13.4	8.38	16.29	1.04	58.33	18	37
30 74 37.5 93	96.86 102.5	1471	1.57	1.92	2.2	13.5	6.83	16.26	0.71	60.5	13	51
37.5 93	102.5		1.22	1.52	1.82	14.15	6.86	15.44	0.53	61.2	10	58
		1530	1.03	1.3	1.25	11.85	5.87	16.54	0.29	64.2	8	67
5 17	41.8	1098	2 67	3 35	3.03	13 49	7 46	74 97	1.05	0	34	12
10 33	62.2	1298	1.98	2.5	234	16 44	8 25	72 23	0.74	0	19	38
15 49	74 35	1252	1.50	1.98	2.32	14 27	5 89	76 74	0.71	0	14	72.5
22.5 74	. 88	1210	1.24	1.56	2.14	13.34	5.24	78.54	0.74	Ő	9	75.7
30 99	75.14	1418	0.79	0.99	1.88	14.19	5.1	78.16	0.67	0	8	91.6
3 12	38.06	1026	3 25	1 26	4.52	15 / 8	8 01	60.03	1 16	0	50	0
75 31	69.9	1235	2.25	3.03	4 15	18.17	9.32	66 27	1.10	0	22	8
15 60	96.4	1532	17	2.14	2.75	22.78	8.72	64 74	1.00	0	13	40
22.5 89	107.5	1469	1.25	1.58	2.71	21.66	7.58	67.25	0.8	Ő	9	75
30 11	9 104.5	1573	0.924	1.17	2.09	20.78	6.59	70.04	0.5	0	7	84
5 26	110.5	1092	37	56	4 97	19.12	6 76	67 74	1 41	0	24	0
15 79	203	1439	2.67	3.4	45	24.5	11.83	57.05	2.12	0	10	30
22.5 11	9 246	1415	2.17	2.8	4.43	22.12	12.04	59.2	2.21	Ő	7	35
30 15	8 215	1724	1.42	1.82	2.51	30.06	14.06	52.06	1.31	0	6	50
1 22 3 1 22 3	5 60 2.5 89 60 119 5 26 5 79 2.5 119 60 158	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$

Table A.4: Experimental data - air and O_2 -CO₂ experiments with coconut shells

								G	as Con	npositi	on % (v/v)			
Experimental details	m_0 (g)	$\dot{m}_{steam}^{\prime\prime}$ (g/m ² s)	$\dot{m}_{ox}^{\prime\prime}$ (g/m ² s)	$\dot{m}_f''\left(\mathbf{g}/\mathbf{m}^2\mathbf{s} ight)$	$\mathbf{T}_{pb}\left(\mathbf{K} ight)$	ϕ_v	Φ	\mathbf{CH}_4	CO	\mathbf{H}_2	\mathbf{CO}_2	ннс	\mathbf{N}_2	t_g (ms)	% Char Conversion
23% O_2 and 77% Steam	2552	54.6	16.3	39.09	1071	2.11	3.03	3.2	25.6	37.6	33.1	0.5	0	49	32.9
Wood pellets	2554	91.1	27.2	47.6	1137	1.54	2.2	3	27.9	35.5	33	0.7	0	33	78
	2537	127.5	38	46.4	1188	1.04	1.55	2.9	27.1	31.1	37.5	0.8	0	25	97
	2511	173.3	51.8	46.7	1368	0.87	1.14	2.8	26.2	25.3	45.4	0.3	0	20	99.8
$30\% \text{ O}_2$ and $70\% \text{ Steam}$	2552	54.6	23.4	54.15	1182	2.04	2.94	2.9	3.18	36.9	28	0.5	0	41	50.5
Wood pellets	2524	91	38.9	61.17	1301	1.42	2	3	32.5	33.8	30.1	0.6	0	28	87.3
1	2587	173	74.1	80.4	1394	0.94	1.25	1.6	29.1	27	42.3	0	0	16	99.8
$40\% \text{ O}_2$ and $60\% \text{ Steam}$	2495	54.6	36.4	82	1373	1.95	2.86	2.4	38.2	36.5	22.9	0.1	0	31	40.8
Wood pellets	2555	127	85	129	1625	1.35	1.93	1.6	43.3	32.2	22.8	0.1	0	16	97.7
	2537	182	121	128	1709	0.94	1.34	0.6	33.1	33.7	32.6	0	0	13	98
40% O ₂ and 60% Steam	2650	54.6	36.4	65 71	1446	12	2.06	36	26.4	36.7	34.3	0	0	34	60.2
Agro-residue pellets	2625	91.1	60.6	100	1516	1.05	1.88	2.7	20.4 39.8	33.2	23.5	0	0	21	90

Table A.5: Experimental data - O_2 -steam experiments with wood pellets and agro-residue pellets

APPENDIX B

UNIFIED IGNITION - DEVOLATALIZATION (UID) MODEL DERIVATION

In this section, analytical expressions with relevant boundary conditions used in section. 4.2 to understand the single particle burning are elucidated. As a dry particle heats up, volatiles are released from the particle after a critical temperature; called the pyrolysis temperature here; and a flame envelopes the particle. This flame resembles the steady flame of droplet combustion. The UID model is evolved on lines of the diffusion limited classical droplet theory.

As with Mukunda *et al.* (1984) four zones can be identified in the flaming region of the particle as shown in Fig.B.1.Region I constitutes virgin wood, region II shows the charred region,region III is the gas phase between the particle and flame, region IV shows the ambient. P shows the propagating pyrolysis front. Pyrolysis front is identified by the thin zone which at the pyrolysis temperature, which is assumed to be the minimum temperature at which volatiles are evolved. In order to describe the evolution of the particle when subjected to high temperatures, species and energy conservation equations are solved for all the four regions. Region I is dominated by transient conduction whereas the other three zones can be taken to be quasi-steady. This assumption is valid as the rate of movement of pyrolysis front is very small compared to gas velocities.The governing equations for different equations are given in B.1-B.3



Figure B.1: Basic elements of the model

Region I: $0 \le r \le r_p(t)$

$$\frac{\partial T}{\partial t} = \frac{\alpha_w}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial T}{\partial r} \right) \tag{B.1}$$

Region II,III,IV: $r_p(t) < r \leq \infty$

$$\frac{\dot{m}C_p}{4\pi r^2}\frac{\partial T}{\partial r} = \frac{k}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial T}{\partial r}\right) \tag{B.2}$$

$$\frac{\dot{m}C_p}{4\pi r^2}\frac{\partial Y_i}{\partial r} = \frac{k}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial Y_i}{\partial r}\right) \tag{B.3}$$

The interface and boundary conditions for the above are given in B.4-B.11

$$-k\frac{\partial T}{\partial r}\Big|_{r_s} = \dot{q}_s''(r_s, t) \tag{B.4}$$

$$T(r,0) = T_{\infty}, \quad T(\infty,t) = T_{\infty}$$
(B.5)

$$k\frac{\partial T}{\partial r}\Big|_{r_{p^+}}^{r_{p^-}} = H_d \dot{m} / 4\pi r_p^2 \tag{B.6}$$

$$k\frac{\partial T}{\partial r}\Big|_{r_{s^+}}^{r_{s^-}} = \sigma\epsilon_s T_s^{\ 4}, \quad \rho D\frac{\partial Y_f}{\partial r}\Big|_{r_{s^-}}^{r_{s^+}} = 0 \tag{B.7}$$

$$k\frac{\partial T}{\partial r}\Big|_{r_{f^+}}^{r_{f^-}} = \rho DH_v Y_f\Big|_{r_{f^-}}^{r_{f^+}}$$
(B.8)

$$\rho D \frac{\partial Y_f}{\partial r} \Big|_{r_{p^-}}^{r_{p^+}} = (1 - Y_{fp^+}) \dot{m} 4 \pi r_p^2$$
(B.9)

$$\rho D \frac{\partial Y_f}{\partial r} \Big|_{r_{f^-}}^{r_{f^+}} = \rho D \frac{\partial Y_O}{\partial r} \Big|_{r_{f^-}}^{r_{f^+}} / s \tag{B.10}$$

$$Y(\infty, t) = Y_{\infty}, T(\infty, t) = T_{\infty}$$
(B.11)

Integrating the transient heat conduction equation subject to the boundary conditions Eq.B.4-B.5 with numerical integration schemes yields the temperature profile in the particle. Substitute $\dot{m}/4\pi r_p^2 = G_{total}$, where G is the total flux. As for a droplet it can

be shown that $G_{total} = G_{volatiles} = G$. Mass balance says that the mass of volatiles at any radius should remain unchanged.

$$Gr^{2} = G_{p}r_{p}^{2} = G_{s}r_{s}^{2}$$
(B.12)

Region II: $r_p(t) < r \leq r_s(t)$

Integrating B.2 and making use of B.12 yields

$$Gr^{2}C_{p}T - r^{2}k\frac{\partial T}{\partial r} = G_{p}r_{p}^{2}C_{p}T_{p} - r_{p}^{2}k\frac{dT}{dr}\Big|_{r_{p}^{+}}$$
(B.13)

Since the temperature profile in the virgin wood particle can be completely determined with the boundary conditions specified, $k \frac{dT}{dr}\Big|_{r_p^-}$ can be evaluated. Let this be q_w ". Now expressing $\frac{dT}{dr}\Big|_{r_p^+}$ in terms of q_w " using B.6 yields

$$G_p r_p^2 C_p T - r^2 k \frac{\partial T}{\partial r} = G_p r_p^2 C_p T_p - r_p^2 (q_w'' + G_p H_d)$$
$$G_p r_p^2 C_p \left[(T - Tp) + \frac{H_d}{C_p} + \frac{q_w''}{G_p C_p} \right] = r^2 k \frac{dT}{dr}$$

Integrating again gives

$$ln\left[\frac{T - T_p + H_d/C_p + q_w''/G_pC_p}{T_s - T_p + H_d/C_p + q_w''/(GpCp)}\right] = \frac{G_pC_pr_p^2}{k}\left[\frac{1}{r_p} - \frac{1}{r}\right]$$
(B.14)

Substituting $T = T_s @ r = r_s$

$$ln\left[\frac{T_s - T_p + H_d/C_p + q_w''/(GpCp)}{H_d/C_p + q_w''/G_pC_p}\right] = \frac{G_pC_pr_p^2}{k}\left[\frac{1}{r_p} - \frac{1}{r_s}\right]$$
(B.15)

A particle is said to be ignited when $m/m_0=0.85$ (taken from experimental data).Before the particle is ignited and after the pyrolysis front has propagated into the particle, the surface receives heat from the ambient atmosphere giving:

$$k\frac{dT}{dr}\Big|_{r_s^+} = k\frac{dT}{dr}\Big|_{r_s^-} = h(T_s - T_\infty)$$
(B.16)

From B.14, $\frac{dT}{dr}$ can be evaluated:

$$\frac{dT}{dr} = \frac{G_p C_p r_p^2}{kr^2} \left(T - T_p + \frac{H_d}{C_p} + \frac{q_w}{(G_p C_p)} \right)$$

Equation B.16 then changes to

$$\frac{G_p C_p r_p^2}{r_s^2} \left(T_s - T_p + \frac{H_d}{C_p} + \frac{q_w''}{G_p C_p} \right) = h(T_s - T_\infty)$$
(B.17)

Equations B.15 and B.17 are solved simultaneously before flame envelopes a particle to get the flux G_p , surface temperature T_s and the temperature profile T(r, t) inside the particle. As flame engulfs the particle, surface receives heat from the flame and radiation effects from the particle surface can be dominant. To determine the heat transferred to the surface, temperature profile from the flame to surface has to be evaluated. In order to do the same, a conserved scalar approach is adopted.

From $r_p(t) < r \leq \infty$:

$$Gr^2 C_p T - r^2 k \frac{dT}{dr} = -\omega_f''' H_v$$
$$Gr^2 C_p Y_{ox} - r^2 \rho D \frac{dY_{ox}}{dr} = s \omega_f'''$$

 H_v is the heat of combustion of volatiles and s is the stoichiometric ratio.For Le=1, it is seen that by manipulating the above equations the source terms on the right hand side can be eliminated.

$$Gr^2\phi - r^2\frac{k}{C_p}\frac{d\phi}{dr} = 0$$

where ϕ is the conserved scalar given by $C_pT + H_vY_{ox}/s$. Integrating the above equation gives

$$G_p r_p^2 \phi - r^2 \frac{k}{C_p} \frac{d\phi}{dr} = G_p r_p^2 \phi_s - r^2 \frac{k}{C_p} \frac{d\phi}{dr} \Big|_{r_s + r_s}$$

Similar to the integration done above this yields,

$$\ln\left[\frac{\phi - \phi_s + \frac{kr_s^2}{G_p C_p r_p^2} \frac{d\phi}{dr}\Big|_{r_s^+}}{\phi_\infty - \phi_s + \frac{kr_s^2}{G_p C_p r_p^2} \frac{d\phi}{dr}\Big|_{r_s^+}}\right] = \frac{G_p C_p r_p^2}{k} \left(\frac{1}{-r}\right) \tag{B.18}$$

Evaluate ϕ at r_s and ∞

$$\phi_s = C_p T_s + \frac{H_v Y_{ox,s}}{s} = C_p T_s$$
$$\phi_\infty = C_p T_\infty + \frac{H_c Y_{ox,\infty}}{s}$$

Differentiating B.18 gives

$$\frac{d\phi}{dr} = C_p \frac{dT}{dr} + \frac{H_v}{s} \frac{dY_{ox}}{dr}$$
$$\frac{d\phi}{dr}\Big|_{r_s^+} = C_p \frac{dT}{dr}\Big|_{r_s^+}$$

$$k\frac{dT}{dr}\Big|_{r_{s}^{+}} = \frac{G_{p}r_{p}^{2}}{r_{s}^{2}} \left[\frac{C_{p}(T_{\infty} - Ts) + \frac{H_{v}Y_{ox,\infty}}{s}}{exp(\frac{G_{p}C_{p}r_{p}^{2}}{kr_{s}}) - 1}\right]$$
(B.19)

Using B.18 in B.7 yields

$$\frac{G_p r_p^2}{r_s^2} \left[\frac{C_p (T_\infty - Ts) + \frac{H_v Y_{ox,\infty}}{s}}{exp(\frac{G_p C_p r_p^2}{kr_s}) - 1} - (C_p (T_s - T_p) + H_d + q_w "'/G_p) \right] = \sigma \epsilon_s T_s^4$$
(B.20)

Solving Eqs.B.15 and B.20 simultaneously gives G_p , T_s and temperature profile inside the particle when the flame engulfs the particle. The time is taken from ignition to the center of the particle (r_0) to reach the pyrolysis temperature is termed as devolatalization time (t_v) in UID model.

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