UNIVERSITÀ DI PISA

Scuola di Dottorato in Ingegneria "Leonardo da Vinci"



Corso di Dottorato di Ricerca in Ingegneria Chimica e Scienza dei Materiali

Tesi di Dottorato di Ricerca

Development of Experimental Systems and Modelling Tools for Studying Biomass Gasification

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Sviluppo di Sistemi Sperimentali e Strumenti Modellistici per lo Studio della Gassificazione delle Biomasse

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da II Sistema Periodico, Primo Levi

SOMMARIO

Negli ultimi quaranta anni lo sfruttamento delle biomasse ha subito una crescente evoluzione. Durante la crisi petrolifera degli anni settanta si è assistito a un crescente interesse nei confronti delle biomasse, spinto dalla ricerca di fonti energetiche diverse da quelle fossili. Successivamente questo concetto è stato affiancato dalla necessità di utilizzare fonti rinnovabili e ridurre l'effetto serra. Ad oggi la nascita del concetto di bioraffineria considera la biomassa non solo un combustibile alternativo, ma anche materia prima per ottenere combustibili liquidi e gassosi, nonché chemicals. La gassificazione delle biomasse a partire dagli anni settanta si è sempre posta come una possibile risposta alle esigenze del momento. La gassificazione, potendo essere attuata in diverse condizioni operative e configurazioni reattoristiche, consente di convertire la biomassa in un gas di diversa composizione che può essere utilizzato per molteplici scopi, dalla produzione di energia elettrica alla sintesi di chemicals; inoltre, non essendo legata specifico tipo di biomassa. consente ad uno di utilizzare fonti di approvvigionamento diversificate. Tuttavia ad oggi la gassificazione delle biomasse non è una tecnologia matura, a causa della persistenza di alcune barriere tecnologiche, in particolare la formazione di catrami (tar) che costituiscono un problema per l'utilizzo finale del gas prodotto. Questa situazione di stallo può essere superata proponendo soluzioni alle barriere di natura tecnologica e fornendo esempi concreti di impianti di gassificazione funzionanti ed affidabili.

L'attività svolta nella presente tesi ha cercato di fornire delle risposte a queste esigenze. Data la complessità dell'argomento è stato adottato un approccio che affianca l'attività sperimentale a quella modellistica che sono applicate a problemi di diversa scala, da quella di laboratorio a quella pilota. Gran parte dell'attività svolta è in relazione alla recente nascita del CRIBE (Centro di Ricerca Inter-Universitario Biomasse da Energia); in particolare è stato seguito lo sviluppo, la messa a punto e il testing delle unità di pirolisi e gassificazione presenti nel centro. L'approccio multi-scala è partito dai fenomeni coinvolti nella gassificazione delle biomasse: in particolar modo lo step di pirolisi. A riguardo è stata messa a punto una procedura di valutazione di cinetiche di devolatilizzazione di biomasse ad alta velocità di riscaldamento, che integra una campagna sperimentale di prove di pirolisi con un Drop Tube Reactor e la relativa modellazione di questa apparecchiatura con un codice CFD. Lo studio della pirolisi delle biomasse è proseguito presso il CRIBE attraverso la messa a punto di un reattore di pirolisi a letto fisso finalizzata allo sviluppo di un sistema di campionamento dei catrami di pirolisi (tar) e la relativa procedura di caratterizzazione analitica, che va a integrare diverse tecniche di laboratorio, dall'analisi TG-FTIR alla GC-MS, Queste attività sono state propedeutiche alla fase successiva che è stata incentrata sullo studio e caratterizzazione di un impianto di gassificazione di biomasse di scala pilota. Lo studio è composto da una parte sperimentale nella quale sono stati condotti dei test di gassificazione di biomasse pellettizzate e una parte modellistica dove si è cercato di rappresentare il funzionamento del gassificatore attraverso un codice di flow-sheeting. Dallo studio sperimentale si è potuto valutare i parametri di processo più importanti e valutare le prestazioni del processo di gassificazione, attraverso misure e campionamenti. Lo studio modellistico ha consentito di dare un'interpretazione fenomenologica del funzionamento del gassificatore.

ABSTRACT

In the last forty year biomass exploitation has evolved. Dating back to the seventies biomass were recognized as an alternative source of energy to fossil fuels in the scenario of the oil crisis. Subsequently the interest in biomass increased driven by the search of renewable and carbon dioxide neutral fuels. Nowadays biomass is not just an alternative fuel but a source of liquid and gaseous bio-fuels as well as the raw material for chemicals production, within the framework of a bio-refinery.

Starting from the seventies biomass gasification has always been recognized as a potential solution to the aforementioned issues. Biomass gasification can be carried out in different operating conditions and reactors, allowing controlling the composition of the syngas. As a consequence it is possible to use the gas for different purposes, from power generation to chemicals synthesis. Moreover biomass gasification is not biomass specific, spreading the range of feedstock sources.

Despite these capabilities, biomass gasification is not an established technology. The reason is related to some technological barriers; in particular biomass tar still represents a big issue for the final use of the syngas.

In order to overcome this situation it is necessary to promote solutions to the technological barriers and provide reference of operating and reliable gasification plants.

The activity carried out in this Thesis was focused on these needs.

Recognizing the complexity of the topic, a methodology that integrates modelling and experimental activities was adopted and applied both to laboratory and pilot scale studies. This Thesis is linked to newly born CRIBE (a research centre devoted to the study of energy biomass), dealing with the development, setup and testing of the pyrolysis and gasification units installed in the centre.

The first part of the work was focused on the phenomena involved in biomass gasification, in particular biomass devolatilization. A procedure for the evaluation of high heating rate biomass devolatilization kinetics was developed, integrating an experimental campaign on a Drop Tube Reactor with a modelling activity of this laboratory device by means of a CFD code.

The study of biomass pyrolysis was further carried out at CRIBE. An experimental campaign on a batch pyrolysis reactor was carried out both to test the capabilities of a tar sampling system and asses a tar characterization methodology which integrates different laboratory techniques (from TG-FTIR to GC-MS).

These activities provided the basis for the following phase, which focused on the study and characterization of a pilot scale gasification plant. This activity was carried out integrating an experimental campaign and a modelling study. The experimental campaign was focused on the gasification of pelletized biomass, evaluating the most important parameters as well as the performance of the gasification process, based on process measures and samplings. The modelling study was carried out with a flow-sheeting code and aided the phenomenological description of the gasifier behaviour.

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LIST OF SYMBOLS AND ABBREVIATIONS

Chapter 1

Nomenclature

- CC carbon conversion, -
- CGE cold gas efficiency, -
- ER equivalence ratio, -
- FC fixed carbon, %
- LHV lower heating value, MJ m⁻³_n
- M_{bio} biomass loading rate, kg of dry biomass h⁻¹
- PS specific gas production, $m_n^3 kg^{-1}$ of dry biomass
- Q_{gas} gas flow-rate, m³_n h⁻¹
- R_j^{gauge} reaction-j, kg s⁻¹
- VM volatile matter, %
- X biomass conversion, -
- x_i mass fraction of component i, -
- y_i molar fraction of component i, -

Subscripts

- c carbon
- c combustion
- G gasification
- MR methane reforming
- P1 primary pyrolysis
- TC tar cracking
- ws water gas-shift

Superscripts

bio biomass

- BFB bubbling fluidized bed
- CFB circulating fluidized bed
- CHP combined heat and power
- IC internal combustion
- IGCC integrated gasification combined cycle
- PCFB pressurized circulating fluidized bed

Nomenclature

pre-exponential factor, s⁻¹ Α particle area. m² A_{n} Ċ drag coefficient, specific heat at constant pressure, cal kg⁻¹ K⁻¹ C_P d characteristic system dimension, m d_p particle diameter, m D₃₂ Sauter mean diameter, m activation energy, cal mol⁻¹ Ε particle emissivity, m **e**_p f_i mass fraction of the i-th particle dimensional class, gravitational constant, m s⁻² g convective heat exchange coefficient, cal s⁻¹m⁻²K⁻¹ h radiating flux to the particle surface, cal s⁻¹ 1 first order kinetic constant. s⁻¹ k thermal conductivity of the fluid, cal s⁻¹m⁻¹K⁻¹ **K**f mass, kg т n fluid refraction index, -Nusselt number, $Nu = \frac{dh}{k_c}$ Nu particle perimeter, m p_p Prandtl number, $\Pr = \frac{C_p \mu}{k_c}$ Pr convective heat flow, cal s⁻¹ Q_c mass heat flow, cal s⁻¹ Q_m radiating heat flow, cal s⁻¹ Q_c ideal gas constant, cal mol⁻¹ K⁻¹ R particle Reynolds number, $\operatorname{Re}_{p} = \frac{d_{p} |u_{g} - u_{d}| \rho_{g}}{u}$ Re_n gas Reynolds number, Re = $\frac{du_g \rho_g}{u}$ Re Roundness factor, $RF = \frac{4p_p}{A}$ RF t time, s particle relaxation time, s $t_{pr} = \frac{\rho_p d_p^2}{18\mu}$ tpr Т particle temperature, K T_{g} gas temperature, K Т'n electric heater nominal temperature, K

- u_q gas velocity, m s⁻¹
- u_p particle velocity, m s⁻¹
- V volatiles mass released, -
- V° maximum volatile mass released, -
- x_i pyrolysis conversion for the i-th particle dimensional class, -
- X_{ash} ash mass fraction, -
- z axial coordinate from the DTR entrance downwards, m

Greek letters

- α stoichiometric coefficient related to volatiles, -
- β stoichiometric coefficient related to char, -
- δ mass fraction of a dimensional class, -
- ρ_{g} gas density, kg m⁻³
- $\rho_{\rm p}$ particle density, kg m⁻³
- μ gas dynamic viscosity, kg m⁻¹ s⁻¹
- ΔH_m specific enthalpy variation associated to mass transfer, cal kg⁻¹
- σ Stefan Boltzmann constant, cal s⁻¹ m⁻² K⁻⁴
- τ residence time, s
- χ global pyrolysis conversion for a single run, -

Subscripts

- p particle
- g gas
- *i* index
- r relaxation
- 1, 2, 3 indexes
- lowT low temperature interval
- highT high temperature interval

- DD size distribution of diameter
- MD mono-dimensional class
- DTR Drop Tube Reactor
- CFD Computational Fluid Dynamics
- KIN kinetics

Nomenclature

FC fixed carbon, %

VM volatile matter, %

- Bf before feeding
- CFB circulating fluidized bed
- dTG derivative thermo-gravimetric
- ECN Energy Centre of the Netherlands
- F1 fraction 1
- F2A fraction 2A
- F2B fraction 2B
- F3 fraction 3
- FID Flame Ionization Detector
- FTIR Fourier Transformed InfraRed
- GC Gas Chromatography
- HPLC High Pressure Liquid Chromatography
- IEA International Enery Agency
- *LIF* Laser Induced Fluorescence
- MBMS Molecular Beam Mass Spectrometry
- MS Mass Spectrometry
- NMR Nuclear Magnetic Resonance
- PAH Policyclic aromatic compounds
- PID Photo Ionization Detector
- TC1 thermocouple 1
- TC2 thermocouple 2
- TC3 thermocouple 3
- TCD Thermo Conducibility Detector
- TGA Thermogravimetric Analysis
- TD Thermo Desorption
- RSD Reference Standard Deviation
- SPA Solid Phase Adsorption
- UA Ultimate Analysis

Nomenclature

- bed cross section, m² A_h
- permeability, m² b
- L_b bed depth, m
- bed void fraction, е
- gas flow-rate, $m_{n}^{3'} h^{-1}$ Q
- CGE cold gas efficiency, -
- ER equivalence ratio, -
- equivalent spherical diameter, -ESD
- LHV lower heating value
- biomass loading rate, kg h⁻¹ Mhio
- char production rate, kg h⁻¹ M_{char}
- air flow-rate, kg h⁻¹ Mair
- syngas production rate, kg h⁻¹ $M_{\rm s}$
- wastewater production rate, kg h⁻¹ M_{w}
- P_q depression in the gasifier jacket, mmH₂O
- Pn PS depression at the nozzle outlet, mmH₂O
- specific gas production, $m_n^3 kg^{-1}$ of dry biomass
- Х biomass conversion, -
- mass fraction of component i, -Xi
- molar fraction of component i, -Уi

Greek letters

- gas dynamic viscosity, kg m⁻¹ s⁻¹ μ_a
- Φ particle sphericity, -
- ΔP_{cond} pressure drop in the condenser, mmH₂O
- pressure drop in the raw-filter, mmH₂O ΔP_{f1}
- ΔP_{f2} pressure drop in the fine-filter, mmH₂O
- pressure drop in the safety-filter, mmH₂O ΔP_{f2}

Subscripts

- bed b gas g particle р
- sensible sens
- chem chemical

- Ar as received
- B1 balance 1, involving gasification tests 1,2 and 3
- B2 balance 2, involving gasification tests 4 and 5
- Bf before feeding
- BED solid sample collected from the gasifier bed

- C1 charry residue collected from the collection tank after test 1
- C3 charry residue collected from the collection tank after test 1
- C5 charry residue collected from the collection tank after test 1
- FTIR Fourier Transformed InfraRed
- GC Gas Chromatograph
- HFR high resistance to flow
- IC internal combustion
- LFR low resistance to flow
- *LPG* liquid propane gas
- *MIX* mixture of wood sawdust and sunflower residue pellets
- MS Mass Spectroscopy
- PA Particulate collected at the bottom of the tank below the cyclone
- PAH Polycyclic aromatic compounds
- PB Particulate collected in on the wall of the tank below the cyclone
- PC Particulate collected in on the wall of the pipe at the gasifier outlet
- PLC Programmable Logic Controller
- SRP Sunflower Residue Pellet
- TC0 Thermocouple 0 (gasifier outlet)
- TC1 Thermocouple 1 (cyclone outlet)
- TC2 Thermocouple 2 (scrubber outlet)
- TC3 Thermocouple 3 (blower outlet)
- TCD Thermo Conducibility Detector
- TOC Total Organic Carbon
- WSP Wood Sawdust Pellet

Nomenclature

- A pre-exponential factor, (depends on the reaction rate expression)
- a_s specific volumetric area, m² m⁻³
- C_i concentration, kmol m⁻³
- c_p specific heat, J kmol⁻¹ K⁻¹
- d_{ρ} particle diameter, m
- d_{po} initial particle diameter, m
- D_{reat} reactor diameter, m
- D_m diffusivity, m² s⁻¹
- *E* activation energy, J kmol⁻¹
- ER equivalence ratio, -
- f corrective function for heterogeneous reactions, -
- *h* convective heat transfer coefficient, J kmol⁻¹ K^{-1} m⁻²
- I^+ radiation intensity in the positive direction, W m⁻²
- *I* radiation intensity in the negative direction, W m⁻²
- I_b black body radiation intensity, W m⁻²
- k_i kinetic constant, (depends on the reaction rate expression)
- k_m mass transfer coefficient, m s⁻¹
- h_i specific enthalpy, J kmol⁻¹
- m moisture release rate, kg h⁻¹
- n_c char pyrolysis yield, -

$$\begin{array}{ll} n_{g} & \text{gas pyrolysis yield, -} \\ n_{t} & \text{tar pyrolysis yield, -} \\ Nu & \text{Nusselt number, } Nu = \frac{d_{p}h_{sg}}{\lambda_{g}} \\ q & \text{heat flux, J m}^{-3} \text{ s}^{-1} \\ P & \text{pressure, atm} \\ Pr & \text{Prandtl number, } \Pr = \frac{C_{p}\mu_{g}}{\lambda_{g}} \\ PS & \text{specific gas production, m}^{3}_{n} \text{ kg}^{-1} \text{ of dry biomass} \\ R & \text{ideal gas constant, atm L mol}^{-1} \text{ K}^{-1} \\ R_{j} & \text{reaction rate, kmol m}^{-3} \text{ s}^{-1} \\ Re & \text{Reynolds number, } \operatorname{Re} = \frac{d_{p}U_{g}C_{g}}{\mu_{g}} \\ Sc & \text{Schmidt number, } Sc = \frac{\mu_{g}}{\mu_{g}} \\ Sh & \text{Sherwood number, } Sh = \frac{k_{m}d_{p}}{D_{m}} \\ t & \text{time, s} \\ T & \text{temperature, K} \\ T_{0} & \text{reference temperature, K} \\ U_{g} & \text{gas velocity, m s}^{-1} \\ U_{s} & \text{solid velocity, m s}^{-1} \\ U_{so} & \text{initial solid velocity, m s}^{-1} \\ z & \text{axial coordinate, m} \end{array}$$

Greek letters

- α assigned multiplicative factor in f, -
- Δh_j heat of reaction, J kmol⁻¹
- ε void fraction, -
- κ absorption coefficient, -
- λ_g gas thermal conductivity, W K⁻¹ m⁻¹
- λ_s bed thermal conductivity, W K⁻¹ m⁻¹
- μ_g gas dynamic viscosity, kg m⁻¹ s⁻¹
- v stochiometric coefficient, -
- ρ_i bulk density, kg m⁻³
- ρ_{char0} constant char bulk density, kg m⁻³
- σ Stefan-Boltzmann constant, W m⁻² K⁻⁴
- τ optical coordinate, m

Subscripts

bio	biomass
С	combustion
cond	conductive
ev	evaporation
g	gas
G	gasification
j	reaction index
т	mass
moi	moisture
MR	methane reforming
р	particle
P1	primary pyrolysis
rad	radiative
S	solid
тс	tar cracking
WS	water gas-shift
W	wall

Abbreviations

PFR Plug Flow Reactor WSP Wood Sawdust Pellet

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INED WITH $D_{32} =$
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62
EXPERIMENTAL
63
EXPERIMENTAL
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CHAPTER 1. BIOMASS GASIFICATION: STATE OF THE ART AND TECHNOLOGICAL BARRIERS

The economic and environmental sustainability of the planet relies on the identification and use of renewable sources and the exploitation of wastes for energy and materials production. Biomass fuels represent a renewable energy source and may be abundant in specific local areas. The possibility to substitute fossil fuels with biomass is becoming more and more attractive, since it is possible to consider this material not just as a solid fuel but also as a source of chemicals. hydrogen and liquid bio-fuels [1]. The biorefinery concept has been developing in the last ten years and it is the evolution of the traditional oil refinery. Biomass gasification, among other technologies, is an option for exploiting biomass and can be considered the core of the biorefinery, since all the residues deriving from other platforms can be used to produce power, chemicals and hydrogen with this process. Biomass gasification is a thermo-chemical process that converts the solid biomass into a gaseous fuel, mainly composed of CO, H₂, CH₄, CO₂, N₂. This gas is often named Syngas (underlining its use as reagent for chemical synthesis); however different names can be found in the literature such as wood-gas or producer-gas. For biomass gasification to occur high temperature and a gasifying agent (e.g. oxygen) are required. The gasification of solid fuels has been studied since the 18th century and the first applications to coal date back to the early 19th century. Biomass gasification has become important during the Second World War due to the fuel shortage for transportation. In the last decades the interest in biomass gasification has been floating, starting from the 70s until about 1987, biomass gasification is considered as a response to the oil crisis [2]. Subsequently the number of published papers and patent decreased until the late 1990s when concerns about the climate change started a new season of studies in Europe [2]. After 2000, Japan, China and India emerged as important players in this field.

The main driver to choose biomass gasification as a technology for biomass exploitation is its potential flexibility for the input as well as for output. Different sources can be used as feedstock for a biomass gasifier such as dedicated energy crops, forest and agricultural residues, by-products and wastes of the pulp and paper industry, food industry and specialties industry. As aforementioned, different products can be produced starting from syngas, since, depending on the final destination, the gasification step can be carried out in different operating conditions to generate syngas with different heating value or hydrogen content. This flexibility allows combining biomass gasification with several end-users such as heat and power generation, chemicals synthesis and hydrogen production.

1.1 Biomass gasification basics

The aim of this Paragraph is to highlights the main phenomena involved in biomass gasification, the steps that operate in a gasification plant and the main properties and applications of the syngas.

1.1.1 Gasification chemistry and phenomena

The gasification process is based on the partial oxidation of a solid fuel due to a gasifying agent, usually air, oxygen and steam. The partial oxidation provides heat for the endothermic reactions and phenomena of the process (drying, devolatilization, reduction reactions). Fig. 1.1 represents the main steps involved in a gasification process and Tab. 1.1 reports the reactions of the gasification process.



Figure 1.1 - Main reactions and heat transfer phenomena in a gasifier.

As a biomass particle enters a gasifier it starts to heat up, as a consequence the biomass particle releases its moisture content and subsequently begins the devolatilization process (reaction R_{p1}). The biomass devolatilization generates three macro-products: gas, tar and char. The devolatilization gas is usually composed of carbon monoxide, carbon dioxide, hydrogen, methane and water and light hydrocarbons. Tar represents a broad range of organic compounds which are vapours at the gasifier temperature (more than 400°C) but liquid at room temperature. Char is the solid residue of the biomass. As oxygen contacts the combustible volatiles and the char both homogeneous and heterogeneous oxidation reactions can take place. Volatiles and tar combustion produces carbon dioxide and water trough reactions R_{c1} , R_{c2} , R_{c3} , R_{c4} . Char undergoes oxidation trough the heterogeneous reaction R_{c_1} this reaction generates both carbon monoxide and carbon dioxide, the mutual proportion are function of the temperature, the oxygen availability and ash content of the char. These combustion reactions provide the heat for biomass drying and devolatilization and for the other

reactions involved in the process, the heat is transferred trough convection, mass transfer, conduction and radiation. In the gaseous phase tar and methane are subjected to steam reforming (R_{TR} and R_{MR}), generating carbon monoxide and hydrogen. Tar can also decompose as a consequence of high temperature due to thermal cracking (R_{TC}), generating lighter gases such as carbon monoxide, carbon dioxide, hydrogen and methane. In addition the equilibrium of the water gas-shift reaction (R_{WS}) affects the concentration of carbon monoxide, water, carbon dioxide and hydrogen according to the temperature of the system. The char can be converted into gas at high temperature (more than 600°C) to carbon monoxide, hydrogen and methane due to heterogeneous reactions with carbon dioxide (R_{G1}), steam (R_{G2}) and hydrogen (R_{G3}).

	<u>acc g</u>	aomodilom
biomass \rightarrow char + volatiles (tar + gas)	R_{P1}	DEVOLATILIZATION
$C + \phi O_{2(g)} \rightarrow 2(1-\phi)CO + (2\phi-1)CO_2$ (Oxidation)	R _c	
$C + CO_{2(q)} \rightarrow 2CO$ (Boduard)	R_{G1}	HETEROGENEOUS
$C + H_2O_{(q)} \rightarrow CO + H_2$	R_{G2}	REACTIONS
$C + 2H_{2(g)} \rightarrow CH_4$	R_{G3}	
$CO + H_2O(g) \leftrightarrow CO_2 + H_2$ (water/gas shift reaction)	R_{ws}	
TAR + $O_2 \rightarrow CO + H_2O$	R _{c1}	
TAR + $H_2O \rightarrow CO + H_2O$ (Tar reforming)	R_{TR}	
$TAR \rightarrow CO + CO_2 + CH_4 + H_2$ (Tar cracking)	R_{TC}	Homogeneous
CH_4 + 1.5 $O_2 \rightarrow CO$ + 2 H_2O	R_{c2}	REACTIONS
$CH_4 + H_2O \leftrightarrow CO + 3H_2$ (Reforming-Methanation)	R_{MR}	
$CO + 0.5O_2 \rightarrow CO_2$	R _{c3}	
$H_2 + 0.5O_2 \rightarrow H_2O$	R _{c4}	

Table 1.1 - Main reactions involved in biomass gasification.

It is worthy to note that devolatilization and heterogeneous reactions are greatly influenced by the operating conditions such as temperature, heating rate, particle size distribution and pressure. As far as devolatilization is concerned it is widely recognized that operating conditions affects the reaction rate, the macro-products distribution [3], the gas species composition [4], the tar composition [5] and the composition as well as the morphological properties of the char [6,7]. These latter properties along with the ash content of the char have a great influence on the heterogeneous reactions favouring or limiting the reaction rate. The gasification system is characterized by the solid motion and behaviour, the particle size and motion depend on the gasifier configuration, the particles can move very slowly or being transport in fast jet of gas. The particles can break up due to several phenomena such as comminution, fragmentation and abrasion, depending on the flow regime in the gasifier. Since different flow regimes can be achieved in different gasifiers, the gas can experience from laminar to highly turbulent flows; in addition according to the gasifier geometry and solid distribution the gas flow may encounter different degree of mixing from very low axial and radial dispersion to perfectly stirred condition.

As a consequence, despite the chemical reactions are the same in every gasifier, the geometry and the operating conditions generate completely different systems.

1.1.2 Biomass gasification steps

Three different steps can be recognized in a biomass gasification plant (Fig. 1.2): biomass conditioning, biomass gasification and syngas clean-up. Biomass conditioning groups all the pre-treatment that are required to meet the biomass properties specified for a gasifier, for instance drying can be a conditioning step to bring the biomass moisture content below the limit specified for a certain type of gasifier. Biomass gasification can be operated in several gasifier types and operating conditions that will be object of the following Paragraphs. The gasification step produces a charry residue (namely charcoal) and the desired product, the syngas. The last step before the end-user is the syngas clean-up, here different gas treatment can be performed to let the gas meet the end-user specifications. For instance, a cyclone is the clean-up required to reduce the particulate content.

From a logical point of view the design of a gasification plant depends on the enduser. Once the end-user is defined the most suitable gasification technology and operating conditions have to be chosen. The choice of a certain gasifier provides, along with the feedstock properties (biomass) and end-user specifications, the information for the design of the conditioning and the clean-up steps, respectively.

The main properties of the syngas are the LHV, the gas species composition, the TAR and particulates contents. Tab. 1.2 reports the relevant syngas properties according to the end-user. For instance, the only need for re-burning in coal power plants is an adequate lower heating value of the gas (LHV). In this case air gasification is a suitable option and the gas clean-up is not a major issue. As the end-user becomes more sophisticate, higher syngas properties are required, as a consequence the gasifier and clean-up systems choice become critical issues. For instance, the syngas preparation for chemicals synthesis via Fischer-Tropsch reaction requires very high hydrogen and carbon monoxide contents. Thus it is necessary to operate gasification with steam and oxygen, in order to avoid the nitrogen removal step, as well as very low tar, particulate and sulphur content to avoid catalyst poisoning.



Figure 1.2 - Basic scheme of a gasification plant.

End-User	Syngas properties
Co-firing in coal furnace	LHV > 2.5 MJ $m_n^{-3}_{gas}$
Steam cycle	
Turbo-gas	LHV > 2.5 MJ $m_n^{-3}_{gas}$ Low tar content
IC-Engine CHP	Low particulate matter content
Liquid bio-fuels synthesis Hydrogen production	LHV > 10 MJ m _n ⁻³ gas Very low tar content Very low particulate content Nitrogen removal

1.2 Biomass gasification technologies

As mentioned in Paragraph 1.1 the gasifier setup is, along with the operating conditions, the main choice to satisfy the requirements of the end-user. Different gasification technologies lead to different gasification behaviour and issues [8]. The aim of this Paragraph is to provide a brief description of the available gasification technologies. Two major gasification categories can be identified: fixed bed gasifier and fluid bed gasifier. As aforementioned, the choice of the gasifier is related to the end-user; however the affordability of a technology relies on the size of the plant and the feedstock input.

1.2.1 Fixed bed gasifiers

Fixed bed (or moving bed) gasifiers are thick bed of biomass supported on a grate, the biomass is typically charged from the top of the gasifier. Fixed bed gasifiers can be classified according to the geometry and gasifying agent distribution in two groups: Updraft and Downdraft. These gasifiers operate under slight vacuum conditions, are usually relatively simple and are suitable for small-medium scale applications (up to few MWth). In the updraft gasifier the gasifying agent enters from the bottom of the gasifier and moves upward, the biomass is loaded from the top and moves downward. The biomass is ignited over the grate, generating high temperature in this zone which becomes the oxidation zone. The low oxygen hot gas moves upward providing heat for the other zones; consequently as the biomass enters from top experiences drying, devolatilization and gasification reactions and, finally, oxidation. Due to this configuration the syngas outlet temperature is low and the tar content is pretty high, since the gas does not experience high temperature zones where tar could be converted through reactions R_{TR} and R_{TC} . As far as concern downdraft gasifiers, different configurations can be identified, the most documented configuration is throated gasifiers. In throated gasifiers the air enters through several radial nozzles in a zone with a restricted cross section, positioned in the middle of the gasifier. The biomass is ignited in the restricted area generating the oxidation zone, as the biomass gets closer is heated up and drying and devolatilization takes place. After the oxidation zone both the gas and the biomass move downward, given the lack of oxygen and the high temperature gasification reactions (R_{g1}, R_{g2}, R_{g3}) occur, this latter zone is often called reduction zone. The tar content in this gasifier is low, due to tar cracking (R_{rc}) that can occur in the throat of the gasifier. A disadvantage of this technology is high gas outlet temperature, which is likely to contain alkaline vapour and particulates. Several other fixed bed gasifiers are described in the literature such as cross draft gasifier and open-top gasifiers. It is worthy to note that different geometries can be identified in the literature, depending on the design of the gasifier manufacturer.

1.2.2 Fluid bed gasifiers

In fluid bed gasifiers fuel particles of specified size and mixed with another solid are suspended due to the gas flowing from the bottom of the gasifier. Concerning biomass gasification, the two most common configurations are bubbling fluidized bed and circulating fluidized bed. Heat can be provided directly, with air or oxygen
injection in the bed, or indirectly by means of internal heat exchanger, or with the fluidization medium acting as a heat carrier between two reactors.

These gasifiers are specific for stationary processes, therefore are usually suitable from medium to large scale installations and are usually complex to be managed. These gasifiers usually produce gas with high particulates content; therefore a cyclone is usually a component of the installation. The gas temperature at the outlet is relatively high, containing alkaline vapours. These gasifiers are meant to produce more tar than downdraft gasifiers but less than updraft gasifiers. Two phases can be recognized in a bubbling bed gasifier: a dense phase (with a high solid content), located at the bottom of the reactor, and a diluted phase in the riser. In the lower zone gas bubbles formation and implosion generate high turbulence. thus favouring an intimate mixing of the solid components; the higher zone is much more likely to be represented as a plug flow reactor. In circulating bed the gas velocity is high enough to transport pneumatically all the solid, thus achieving higher degree of mixing, turbulence and heat transfer. This gasifier is suitable for large scale applications, a well documented application [9] is the pressurized circulating fluid bed (PCFB) coupled with gas turbine in an integrated gasification combined cycle (IGCC).

1.2.3 Comparative analysis

The evaluation of a gasification technology is strictly related to the end-user, the plant size and feedstock availability. Tab. 1.3 reports a comparison of some gasification technologies, highlighting their advantages and disadvantages. Fixed beds are pretty easy in the design, this leads to simple operating procedures and low realization costs; therefore they are suitable for small scale applications, but, as the plant capacity increase they should be avoided, since this design cannot cope with high biomass load. As a consequence [10] states that downdraft gasifiers are suitable for applications up to 1 MWth and Updraft gasifiers up to 10 MWth (Fig. 1.3). Updraft gasifiers compared to downdraft are more flexible, they can operate with biomass with higher moisture content, since the steam produced in the drying zone does not reach the oxidation zone, and with smaller particle size since there is no restriction in the cross section. Another advantage is the lower gas outlet temperature. On the other hand Updraft gasifiers produce syngas with higher tar and water content. Fluid bed gasifiers are more complex than fixed beds, thus requiring higher investment and management costs. They require tight specifications of fuel size and are very sensible to ash melting phenomena, leading to bed agglomeration and loss of fluidization. On the other hand these reactors are more flexible in terms of feedstock, allow reaching higher throughput and can be coupled (as in the case of PCFB) to gas-turbine. Finally, it can be stated that the higher the plant capacity, the higher the flexibility in terms of feedstock, but the higher the system complexity and costs.



Table 1.3 - Biomass gasification technologies comparison.



Figure 1.3 - Suitable biomass gasifiers for a given thermal input [10].

1.2.3.1 Documented applications

Here a brief list of documented biomass gasification applications is reported. Broad database about gasifier manufacturers and reported applications can be found elsewhere [11, 12].

Tab. 1.4 lists some of the most cited applications that can be found in the World Wide Web. Notably the case studies reported are not from scientific articles rather from company reports or research and development centres. With the exception of Güssing, all the documented applications operate with air as gasifying agent. The small scale applications range from 300 kWth to 3 MWth, most of them are based on a downdraft gasifier and the syngas end-user is combustion in an internal combustion engine for combined heat and power (CHP) production. With the only exception of Güssing, medium and large scale applications are devoted to produce syngas for co-combustion in a coal furnace. Notably large scale fluid bed can operate even with very high moisture content (up to 60%); however this leads to a reduction in the gas LHV. To the author knowledge, with the exception of Güssing and Varnamo, the most common applications is air gasification in fixed bed gasifier for very small scale to small scale applications, these are not widely reported and for instance are spread in the rural areas of India [13]. Medium to large scale applications are usually demonstrative project coupled with "simple" end-user such as re-burning or co-combustion in coal power station. No high level applications such as Fischer & Tropsch synthesis are documented at such scale, and this is a consequence of the poor diffusion and the scarce reliability that biomass gasification has encountered in the past years.

Use	СНР	СНР	СНР	СНР	CHP	CHP	СНР	22	8	S
η_{tot} %	ı	80	93	ı	75		80		95	91
η_{el}	ı	24	27	ı	32	30	25	c	r	c
LHV Gas (MJ m _n ⁻³)	ŗ	4-4.8	5.5-6.5	4.5-5.5	ı	5-6	12-14	2.5-5	·	2-3.5
Th. Out. (MW)	0.18	0.16		0.7	ı	0	4.5	5-13		
EI. Out. (MW)	0.1	0.13	0.2	0.5		٢	2	Ľ	r	ч
Th. In. (MW)	0.3	0.5	0.68	N	3.125	3.5	8	10	50	60
GA.	Air	Air	Air	Air	Air	Air	Air Steam	Air	Air	Air
т	DD	QQ	7S	DD	QQ	D	CFB	CFB	CFB	CFB
% M	·	15	35-45	ı	ı	30-55	ı	30-60		20-60
Bio	·	Wood residues	Wood chips	Wood chips	ı	Wood chips	Wood chips	Wood chips, bark, sawdust	sawdust	Wood chips, bark, sawdust
Location	Boughton (UK)	Hogild (DK)	- -	Neustad (A)	- 'DK)	Harboore (DK)	Gussing (A)	Zwelteg (A)	Rouien (B)	Lathi (FIN)

Table 1.4 - Gasification applications reported in Internet. [W: moisture; T: technology; GA: gasifying agent; Th. In: thermal input; El. Out.: electric output; Th. Out.: thermal output; η_{el} electric efficiency; η_{tot} total energy efficiency; DD: downdraft; UD: updraft; TS: double-stage; CFB: circulating fluidized bed.]

1.2.3.2 Performance Indicators

The aim of biomass gasifiers is to convert the solid fuel into a gaseous fuel which can be used for several purposes. Consequently the efficiency of a gasifier can be defined as its ability to convert the solid fuel and its energy content into a gas. Different indicators can be used to evaluate the biomass conversion; here a brief list is presented.

The specific gas production is the rate between the gas flow-rate (in $m_n^3 h^{-1}$) and the biomass fed to the gasifier (in kg h^{-1}):

$$PS = \frac{Q_{gas}}{M_{gas}} \tag{1}$$

This parameter can be defined in several ways, depending on the gas (wet gas or dry gas) and biomass (wet, dry or daf) properties, respectively.

The carbon conversion is the rate between the carbon leaving the gasifier in the gas (as CO, CO_2 etc.) and the carbon entering the system:

$$CC = \frac{Q_{gas} \cdot \sum_{i=1}^{n} y_c^i}{M_{gas} \cdot x_c}$$
(2)

An equivalent definition of the carbon conversion is the rate between the carbon leaving the system as carbonaceous residues and the carbon entering the system. Another representation of the biomass conversion is the overall biomass conversion, which is defined according to the ash-tracer method:

$$X = 1 - \frac{x_{ash}^{bio}}{x_{ash}^{char}}$$
(3)

The energy content of the syngas is usually can be expressed with its lower heating value (LHV) as the heat (in MJ) generated from the combustion of one m_n^3 of syngas. By taking into account the specific gas production and the energy content of the biomass, it is possible to define the cold gas efficiency as the ratio between the chemical energy leaving the system associated to the cold and tar-free syngas and the chemical energy entering the system associated to the biomass:

$$CGE = \frac{Q_{gas} \cdot LHV_{gas}}{M_{bio} \cdot LHV_{bio}} \tag{4}$$

Where LHV_{gas} and LHV_{bio} are the lower heating values of the syngas and the biomass (in MJ m_n^{3} ⁻¹), respectively. Obviously, the higher CGE the more efficient is the gasifier. It is worthy to note that this definition is suitable for standard applications where the gas is cooled prior to combustion, for instance in an internal combustion engine. When different applications are to be considered the definition can be adapted. For instance, if the syngas is to be used as a re-burning fuel in a coal furnace, there is no need for gas quenching and gas removal, thus the gas sensible heat, the water latent heat and the chemical energy associated to tar have to be considered.

Except for parameters related to the material and energy balance of the gasifier, the most important performance indicator is the contaminants content of the syngas, the main contaminants are:

- gases such as H₂S, SO₂, NO_x, HCI and other chlorinated compounds;
- tar;
- heavy metals (Hg, Cd, etc.);
- alkali and particulates.

These contaminants may cause erosion, rusting and plugging, and their presence often determine, along with the end-user specifications, the gas clean-up strategy and plant emissions. Tab. 1.5 reports a comparison of literature values of the listed performance indicators for different gasifiers. Fixed bed gasifiers are likely to achieve higher conversion values than fluid beds. This can be related to the higher biomass residence time. CGE and LHV_{gas} cannot be related to the gasifier design. Fixed bed gasifiers produce a syngas with lower particulates content than fluid bed gasifiers, due to lower gas velocity and attrition. As aforementioned downdraft gasifier are likely to generate the lowest tar content, while updraft gasifiers the highest.

Table 1.5 - Typical performance indicators for different gasification technologies.					
	Units	Updraft	Downdraft	BFB	CFB
PS	$m_{n gas}^{3} kg_{bio}^{-1}$	-	2-3.3 ^c	1.9-2.46 ^{d,e}	2.50-2.65 [†]
CC	%	-	91-98 ^c	76-91 ^{d,e}	86-97 ^f
LHV _{gas}	MJ m _n -3	5.0-6.0 ^ª	4.2-5.7 ^c	3.3-5.3 ^{d,e}	3.6-4.0 ^f
CGE	%	40-60 ^ª	52.2-65 [°]	50-60 ^{d,e}	46-66 [†]
Tar	g m _n -3	20-100 ^b	0.1-1.2 ^b	1-15 [♭]	1-15 ^b
Particulate	g m _{n gas}	0.1-10 ^b	0.1-0.2 ^b	2-20 ^b	10-35 ^b

a:[14]; b:[15]; c:[16]; d:[17];e:[18];f:[19]

1.3 Syngas properties and operating conditions

The syngas composition relies on three main operating conditions:

- gasifying agent;
- equivalence ratio;
- temperature;

The effect of the equivalence ratio and temperature are widely assessed in the scientific literature, in particular for air gasification. The effect of pressure is less relevant for biomass gasification; the only application is PCFBs in IGCC which are very complex systems. Here a brief review of the operating conditions effect is presented.

1.3.1 Gasifying agent

The gasifying agent influences both the gas composition and the gas heating value. Tab. 1.6 reports an indicative variation of the syngas composition as a function of the gasifying agent. Air gasification is the most simple and economic technology thus is suitable for small scale applications, it generates a low LHV syngas due to the high nitrogen content. Oxygen gasification increase the LHV due to the nitrogen removal and it is an option for producing high carbon sequestration and storage. The use of oxygen dramatically increases the plant operating costs and complexity due to the necessity air separation unit and the storage and distribution systems. Steam gasification produces a high quality syngas (high hydrogen content and high LHV) but it is necessary to provide heat, so it is usually performed with steam/oxygen mixtures. The use of oxygen is gaining attention at small scale with low air enrichment level to overcome some of the issues and increase the gasifier flexibility.

	GASIFYING AGENT			
Composition [%vol]	AIR	OXYGEN	STEAM	
CO	12-15	30-37	32-41	
CO ₂	14-17	25-29	17-19	
H ₂	9-10	30-34	24-26	
CH ₄	2-4	4-6	1.4	
C_2H_4	0.2-1	0.7	2.5	
N ₂	56-59	2-5	2.5	
Gas LHV[MJ m _{n⁻³gas}]	3.8-4.6	10	12-13	

Table 1.6 - Syngas composition with different gasifying agents [20].

1.3.2 Equivalence ratio

Equivalence ratio is probably the main operating parameter in biomass gasification. This index relates (in the case of air gasification) the ratio between the mass of air and mass of biomass (daf) in the real conditions to the same ratio in stoichiometric conditions:

$$ER = \frac{\left(\frac{M_{air}}{M_{bio}}\right)_{real}}{\left(\frac{M_{air}}{M_{bio}}\right)_{stoich}}$$

(5)

When ER is equal to zero there is no oxidant in the system (for instance pyrolysis), ER equal to one represents stoichiometric combustion. When ER is larger than one then combustion in fuel lean conditions occurs, finally when ER is less than one fuel rich combustion occurs. Gasification is a fuel rich combustion, typically ER ranges between 0.2 and 0.4. The equivalence ratio strongly affects the gasification process; it determines the temperature of the system, the oxygen availability, the gas vield, the gas composition and heating value, as well as the tar content. Fig. 4a and Fig. 4b reports the results of some authors about the effect of ER on the specific gas production and the gas LHV, respectively. The higher the ER the higher the PS and the lower the gas LHV, this is due to higher oxidation of the fuel which leads to higher conversion into gas, higher carbon dioxide concentration and lower hydrocarbon contents (see Fig. 5a), thus reducing the gas LHV. As a consequence there is a trade-off between PS and LHV, and it is necessary to identify the optimal ER (maximizing CGE) for each gasification system. The equivalence ratio affects the tar concentration in the raw-gas. Fig. 5b reports a picture from the work of [17] showing the tar concentration plotted against the ER for two hydrogen to carbon ratio. The higher ER the lower the tar content in the fuel, this is due to higher temperature (R_{TC}) and higher oxygen availability (R_{C1}).



Figure 1.4 - Effect of ER on gas (A) yield and (B) LHV reported by some authors



Figure 1.5 - Effect of ER on (a) light hydrocarbons and (b) tar contents reported by [16] and [17], respectively.

1.3.3 Temperature

Temperature has deep impact on the devolatilization step of the biomass [23]; it modifies the macro-products (char, tar, gas) distribution as well as the gaseous species distribution. In addition temperature affects the several equilibrium reactions involved in a gasification system (for instance the water gas shift reaction, the Boduard reaction, the carbon oxidation to carbon monoxide or carbon dioxide etc.). From the gasifier point of view various authors [17,18] reported an increase in the gas production and the reduction of the tar content (see Fig. 6) for increasing temperatures. This can be explained considering that high temperature promotes R_{TC} , generating light gases such as carbon monoxide, carbon dioxide and methane. It is worthy to note that temperature is an operating parameter at laboratory scale but in a real system cannot be controlled a priori and it is a function of equivalence ratio, gas and solid flow-rates and thermal dispersions



Figure 1.6 - Effect of the reactor temperature on tar concentration in the raw gas, taken from [17].

1.4 Technological barriers

Despite the great interest in this technology the market diffusion of biomass gasification is slow. This technology is close to a commercial status [24] but there are some issues that have to be addressed. Except for politic-economic reasons, there exist some technological problems which make investment in this process risky. The aim of this Paragraph is to provide a review of technological problems related to biomass gasification. These issues can be divided in two groups. The first one is related to the feedstock specifications required by a gasifier, such specifications usually involve the biomass moisture and ash content as well as the particle size distribution; in addition specifications related to the biomass composition and morphology may be required. The second group involves the specifications usually involves the particulate and tar content of the syngas and are often pretty hard to be achieved.

1.4.1 Feedstock specifications

Tab 1.7 reports a comparison of the properties of woodchips derived from the maintenance of a natural reserve and the feedstock specifications for a downdraft gasifier provided by the manufacturer. As can be seen the biomass needs to be further processed in order to meet the gasifier specification. In addition it is not always possible to feed the same biomass to a gasifier, so multiple feedstock may be used. In this Paragraph some issues related to the feedstock availability, conditioning and specifications are discussed.

	Unit	As received woodchips	Gasifier spec
Moisture Ash LHV	% %dry MJ kg⁻¹	55 2 8.5	<20 <3 >17.5
Bulk Density	Kg m⁻³	220	>150 <450
Size		>50 mm 2.3% 5-50 mm 90% 1-5 mm 4.2% <1mm 3.5%	63-100 mm <2% 8-63 mm 88-100% 3.15-8 mm 0-10% <3.15 mm 0-2%

Table 1.7 - Comparison of the main properties of woodchips produced from the maintenance of a natural reserve and the limits to use them as feedstock for a downdraft gasifier provided by the manufacturer.

1.4.1.1 Variability of biomass properties

The composition of biomass fuels depends on the plant type and part (for instance bark and branches of woody biomass have a higher ash content than the tree trunk, thus representing a less valuable feedstock) and on the cultural techniques employed (for instance poplar trees deriving from three years rotation crops exhibit a higher trunk to branches yield than two years rotation crops).

Tab. 1.8 reports proximate analysis of some biomass materials. Lignocellulosic biomasses have a higher volatile matter content and lower ash content than agricultural and industrial residues. On the other hand gasifiers, especially those on a large scale requiring large input of feedstock, must deal with different kind of biomass. As a consequence operating conditions have to be adapted to ensure the specified performance of the gasifier. The easiest solution is to keep a biomass in large concentration while adding relatively small quantities of other materials and making the feedstock homogeneous through a mechanic device. The plants which are less sensitive to this problem are fluid bed, where the inert material ensures uniform conditions thus leading to a higher flexibility of the gasifier in processing different kind of biomass.

· · · · · · · · · · · · · · · · · · ·					
Biomass	VM	FC	ASH		
Willow	81.72	16.15	2.13		
Pinus Pinaster	82.00	16.50	1.50		
Eucalyptus	81.19	17.75	1.06		
Cacao shells	67.84	21.66	10.50		
Rice husks	66.40	13.60	20.00		
Switch Grass	65.1	17.30	17.60		

Table 1.8 - Proximate analysis of biomass materials (dry basis).

1.4.1.2 Moisture content

The biomass moisture content (which can be up to 70% in the natural state) affects strongly the conversion of biomass in energy products. High moisture levels make the combustion of the biomass difficult to be self-sustained and decrease the heating value of the gas and, consequently, the energetic efficiency of the process. In addition the high moisture content reduces the oxidation temperature leading to an incomplete cracking of hydrocarbons formed during pyrolysis. Tab. 1.4 reports the moisture content of some biomass used as feedstock in different existing gasifiers; over these levels it is necessary to pre-dry the feedstock. Notably this limit depends on the gasifier type. The gasifiers located in Zeltweg and Lathi are circulating fluid beds. They allow to process biomass with high moisture contents (up to 60%) even if this influences the energetic efficiency of the process (for instance the Lahti gasifier is designed for a range of thermal input 45-70 MW [25]), but the plant operation is not compromised. Among fixed beds, downdraft gasifiers (such that located in Hogild) are more sensitive to moisture than updraft gasifiers, the tolerable biomass moisture limit are 15% and 55%, respectively. In the first case the steam produced in the drying zone reaches the combustion zone producing low oxidation temperatures. When required, biomass drying represents a heavy cost both in terms of capital expenditure and heat export potential [26]. The choice of the drier depends on the plant capacity, the biomass size and type [27].

Several drying technologies are available in the market (a broad review is reported in [28] but this can be rather expensive, especially when small scale applications are considered. In addition, the drying step increases the plant complexity and involves safety and pollution issues [27]. Waste heat such as hot flue gases from an internal combustion engine can be used as heating medium, also with partial mixing with air; however this solution increase the plant complexity.

1.4.1.3 Solid Handling

Biomass is a solid fuel which can be very different in terms of shape and size but has to respect some specifications to be used as feedstock for gasification. Consequently it is mandatory to operate conditioning treatments of the raw material. Before entering the gasifier the biomass feedstock is purified from metallic and non-metallic (such as silica from the soil) impurities which can be an additional source of ash in the process. Subsequently the biomass has to be milled and sieved to the particle size required from the plant. These values depend on the gasifier type, some dimensional range are reported in Tab. 1.3. Fluid bed gasifiers require the smallest particle size and a narrow dimensional range, thus they imply demanding solid pre-treatments. Particle size reduction is usually performed with chippers or hammer-mills. The particle size distribution after chipping or milling has to be controlled and refined trough sieving by means of mechanical sieving or flotation. In small scale applications too fine particles cannot be fed to the plant thus generating a waste that has to be disposed or exploited. Pelletizing of biomass and residues is a common pre-treatment, which allows to increase the biomass density and the energy content and to produce a shape suitable to form the bed without packing it. However, depending on the pellet properties, this material is likely to break up in the gasifier and produce a finer particle size distribution that may compromise the gasifier operation, especially in fixed bed gasifier. It is worthy to note that all these mechanical steps require electricity or fuel which involving additional energy and economic costs. In a plant biomass is transported and fed to the gasifier through conveyor belts and screw conveyors. In the latter system the presence of coarse particles can block it. A typical problem related to packed bed of solid materials is bridging. Bridging is defined as the formation of a "bridge" of particles over an outlet which stops the flow of the solid material [29]. This condition may arise in downdraft gasifiers over the restriction called throat where air is inserted. In this case the flow of the solid material is blocked over the combustion zone. This situation can be avoided by changing the design of gasifier geometry. Another problem occurring in downdraft gasifier is channelling. Channelling is the formation of a "channel" below the throat where gas and tar enter without being in contact with the burning char bed, affecting the gasifier performance, in particular tar cracking reactions. Notably downdraft gasifiers are less flexible than updraft gasifiers and fluid bed gasifiers to variation of the biomass feedstock.

1.4.4 End-user specifications

Tab 1.9 reports a comparison of the properties of a syngas produced by a downdraft gasifier and the specifications reported by the manufacturer [30] for the use of the syngas in an internal combustion engine. As can be seen there is need for gas clean-up in order to meet the tight specifications. In this Paragraph some issues related to the gas clean-up are discussed. It is worthy to note that there is a discrepancy between the information provided by the engine manufacturer and those required to set up a clean-up system. For instance tar is often not reported and its content has to be induced from other parameters.

Table 1.9 - Tar and particulate contents at the outlet of a downdraft gasifier and limits specified by the manufacturer for safe and reliable IC-Engine operation*.

	Unit	Gasifier	End-user
		outlet	spec
Particulate	mg m _n -3	200	7
Tar	mg m _n ⁻³	1200	0.7**

* Assuming a gas LHV of 5 MJ m_n^{-3} .

**Referred as oil in the manufacturer list.

1.4.4.1 Ash and particulate

Ash is usually a source of problems in thermal treatments of solid fuels [31, 32]. Tab. 1.8 reports the ash content of some biomass. Notably lignocellulosic materials have ash content (1-2 %) which is lower than agro-industrial residuals (> 10 %). As a matter of fact most of the gasification applications use lignocellulosic biomass. The main troubles associated to ash are:

- 1) Particulates formation.
- 2) Fouling of surfaces.
- 3) Packing and de-fluidisation of the bed.

Ash is the major source of particulates but also the un-reacted carbon and the inert material in fluid bed contribute to overcome the emission limit. In addition the inorganic particulate can severely damage devices positioned after the gasifier through abrasion and corrosion phenomena. The particulate concentrations allowed in the gas exiting the gasifier depend on the final use. For instance [33] reported that in gas-engine applications the particulate level must be below 50 mg m_n^{-3} , while in gas-turbine applications it must be kept below 15 mg m_n^{-3} . Noteworthy these values are different from Table 1.9, highlighting the fact that is not easy to identify a definitive reference for these values.

The primary types of gas cleaning systems include cyclonic filters, barrier filters, electrostatic filters and wet scrubbers. The effect of biomass ash depends not only on its quantity but also on its composition. The composition determines physical properties of ash such as the melting point and the boiling point. Tab. 1.10 reports the ash composition of some biomass. Notably biomass fuels can contain high quantities of alkaline compounds such as potassium. This element is required in the plants growth and its concentration can be extremely high in fast growth

species. The high content of alkaline compounds can originate problems. Sodium and potassium salts in the ash can form eutectics which vaporize at moderate temperatures (about 700 °C). The aforementioned filters can just remove solid particulates but do not separate these alkaline vapours which remain in the hot gas. Such vapours start to condense at nearly 650 °C, therefore when the gas reaches "cold" surfaces located after the gasifier (for instance heat exchangers, blades of turbines etc.) the salts start to accumulate damaging the components of the plant. The importance of the presence of alkaline vapours in the gas depends on the end-use. The problem of formation and deposition of alkaline vapours is extremely critical in systems where the gas is used without a significant cooling. A moderate cooling of the gas before the particulate removal system can provide a good clean up for an end-use which allows a moderate ash deposition. In different applications (such as high speed gas-turbine) the gas clean up must be almost complete. However also in systems not very sensitive to ash deposit alkaline salts can generate problems like corrosion of metallic surfaces and inactivation of catalysts such as those used for tar cracking. The formation of low-melting point alkaline compounds in fluid bed can lead to agglomeration of the inert material. This situation may cause severe problems due to the loss of fluidization conditions of the bed and as consequence the shutdown of the plant operation. Alkaline vapours can be removed in conventional filters as small particles (such as bag filters) after a significant cooling of the gas exiting from the gasifier. Unfortunately this technique leads to a great loss of sensible heat and therefore the overall system energy efficiency is reduced.

A promising way to remove alkaline vapours at high temperatures is the alkali getter. In this system the hot gas flows through a ceramic filter and then through a packed filter charged with activated bauxite or emathlite. The results of [34] show a reduction in the concentration of potassium and sodium in vapours higher than 90% due to this system. It is worthy to note that this technology it is not already applied in real plants and it is an open search subject.

Table 1.10 - Ash composition of some biomass (dry basis) [33].						
Biomass	Poplar wood	Pine wood	Switch grass			
CaO	47.2	49.2	4.8			
K ₂ O	20.0	2.6	15.0			
P_2O_5	5.0	0.3	2.6			
MgO	4.4	0.4	2.6			
Na ₂ O	0.2	0.4	0.1			
SiO ₂	2.6	32.5	69.9			
SO ₃	2.7	2.5	1.9			
Other	17.9	12.1	3.1			

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1.4.4.2 Tar

The aforementioned barriers are typical either of biomass combustion and gasification. Instead, the presence of tar in the gas is a specific problem of biomass gasification (and pyrolysis). [35] offers the following insight as to his experience to date:

While a great deal of time and money has been spent on biomass gasification in the last two decades, there are very few truly commercial gasifiers, operating without government support or subsidies, day in, day out, generating useful gas from biomass. The typical project starts with new ideas, announcements at meetings, construction of the new gasifier. Then it is found that the gas contains 0.1-10% 'tars.' The rest of the time and money is spent trying to solve this problem. Most of the gasifier projects then quietly disappear. In some cases the cost of cleaning up the experimental site exceeds the cost of the project! Thus 'tars' can be considered the Achilles heel of biomass gasification. (In the gasification of coal, a more mature technology, the 'tars' (benzene, toluene, xylene, coal tar) are useful fuels and chemicals. The oxygenated 'tars' from biomass have only minor use. With current environmental and health concerns, we can no longer afford to relegate 'tars' to the nearest dump or stream.

Tar has been operationally defined in gasification works as the material in the product stream that is condensable in the gasifier or in downstream processing steps or conversion devices. However, this general usage is insufficient for modern gasification technology development because it loses the distinction between classes of compounds that originate under various reaction regimes, such as the primary pyrolysis products that may be in the gasifier effluent because of low-temperature operation or process upsets, and high molecular weight polynuclear aromatic hydrocarbons (PAHs), which are produced under high gas-phase reaction severity and are precursors of particulate matter "soot".

The NREL report [36] used the following biomass tar definition:

The organics produced under thermal or partial-oxidation regimes (gasification) of any organic material are called "tars" and are generally assumed to be largely aromatic.

However the same authors point out that some applications, such as fuel cells, may be affected by non-condensable species (for instance ethylene, cyclopentadiene, and benzene). As a consequence the tar definition is related to the syngas end-user specifications.

Another common definition of biomass is:

A complex mixture of oxygenated organic compounds and hydrocarbons condensable at room temperature.

Tab. 1.11 reports a typical tar composition. It includes polycyclic aromatic hydrocarbons which can lead to toxic properties of the tar; noteworthy these authors included toluene and benzene in their tar characterization. As can be seen from Tab. 1.11 and Tab. 1.12 several compounds can be identified in tar, thus the physical properties of tar are very complex. The tar classification is a hard matter, which is still not standardized; different classifications can be found in the scientific literature, for instance the one reported in [37] (see Tab. 1.11).

[38, 39] suggested a systematic approach to classifying pyrolysis products as primary, secondary, and tertiary to compare products from the various reactors that are used for pyrolysis and gasification.

Four major product classes were identified as a result of gas-phase thermal cracking reactions:

- 1. Primary products: characterized by cellulose-derived products such as levoglucosan, hydroxyacetaldehyde, and furfurals; analogous hemicellulose-derived products; and lignin-derived methoxyphenols;
- 2. Secondary products: characterized by phenolics and olefins;
- 3. Alkyl tertiary products: include methyl derivatives of aromatics, such as methyl acenaphthylene, methylnaphthalene, toluene, and indene;
- 4. Condensed tertiary products: show the PAH series without substituents: benzene, naphthalene, acenaphthylene, anthracene/phenanthrene, pyrene.

In the study of [38] it was found that the primary and tertiary products were mutually exclusive. That is, the primary products are destroyed before the tertiary products appear. The tertiary aromatics can be formed from cellulose and lignin, although higher molecular weight aromatics were formed faster from the lignin-derived products [38, 39]. Notably the [38] approach is slightly different from the one reported in Tab. 1.12.

	erennaee gaemea
Benzene	37.9%wt
Toluene	14.3%wt
Other Single-ring aromatic hydrocarbons	13.9%wt
Naphthalene	9.6%wt
Other two-ring aromatic hydrocarbons	7.8%wt
Three-ring aromatic hydrocarbons	3.6%wt
Four-ring aromatic hydrocarbons	0.8%wt
Phenolic compounds	4.6%wt
Heterocyclic compounds	6.5%wt
Others	1.0%wt

Table 1.11 - Typical composition of tar derived from biomass gasification [40].

Class	Name	Properties	Main compounds
1	GC-undetectable	Very heavy tars, cannot be detected by GC	Determined by subtracting the GC- detectable tar fraction from the total gravimetric tar
2	Heterocyclic aromatics	Tars containing hetero atoms; highly water soluble compounds	Pyridine, phenol, cresols, quinoline, isoquinoline, dibenzophenol
3	Light aromatic (1 ring)	Usually light hydrocarbons with single ring; do not pose a problem regarding condensability and solubility	Toluene, ethylbenzene, xylenes, styrene
4	Light PAH compounds (2-3 rings)	2 and 3 rings compounds; condense at low temperature even at very low concentration	Indene, naphthalene, methylnaphthalene, biphenyl, acenaphthalene, fluorene, phenanthrene, anthracene
5	Heavy PAH compounds (4 – 7 rings)	Larger than 3-ring, these components condense at high-temperatures at low concentrations	Fluoranthene, pyrene, chrysene, perylene, coronene

Table 1.12 - Tar classification reported in [37].

Mixed	Phenolic	Alkyl	Heterocyclic		Larger
Oxygenates	Ethers	Phenolics	Ethers	PAH	PAH
400 °C	500 °C	600 °C	700 °C	800 °C	900 °C

Figure 1.7 - Tar maturation scheme proposed by [41].

The tar formation mechanisms are based on several phenomena which are investigated to a certain extent in literature [5, 41, 42]. Fig. 1.7 reports the scheme proposed by [41]. The scheme highlights the transition of the tar composition as a function of process temperature from primary products to phenolic compounds to aromatic hydrocarbons. In addition the tar composition depends largely on the operating conditions of the process, for instance the temperature (and heating rate conditions) as reported in Fig. 1.7. Other operating conditions affecting the tar formation and composition are the oxygen and steam content in the gas, pressure and gas distribution in the gasifier.

As a consequence of the aforementioned observations it can be stated that the tar formation and composition depend on the biomass and the gasifier type. As a raw indication [43] the tar content is 100 g m_n^{-3} in the gas produced from updraft gasifiers, 10 g m_n^{-3} from fluid beds and 1 g m_n^{-3} from downdraft gasifiers. As a general rule it can be stated that: the higher the temperature the lower the tar yield [36]. As far as the tar formation and composition is concerned in different gasifier types, it useful to report the considerations of [35]:

In updraft (counterflow) gasification air/oxygen/steam contacts charcoal on a grate, generating gas temperatures of 1000-1400°C. This hot gas rises through the downcoming biomass, pyrolysing it at successively lower temperatures and eventually drying it. All of the types of tar [....] occur in the final gas, with primary tars dominating, typically at a level of 10-20%. Updraft gasifiers are useful for producing gases to be burned at temperature, but the high tar level makes them difficult to clean for other purposes.

In downdraft (coflow) gasification air/oxygen and fuel enter the reaction zone from above and burn most of the tars to pyrolyse the fuel, in a process called "flaming pyrolysis." The flame temperatures are 1000-1400°C, but the flame occurs in the interstices of the pyrolysing particles whose temperatures are 500-700°C, so that about 0.1% of the primary tars are converted to secondary tars and the rest are burned to supply the energy for pyrolysis and char gasification. Very few of the compounds found in downdraft gasification are found in updraft tars and viceversa. The low tar levels of downdraft gasifiers make them more suitable for uses requiring clean gas.

In *fluidized bed* gasifiers air/oxygen/steam levitate the incoming particles which recirculate through the bed. Some of the oxidant contacts biomass and burns the tars as they are produced as in a downdraft gasifier; some of the oxidant contacts charcoal as in an updraft gasifier. Thus the tar level is intermediate between updraft and downdraft, typically 1-5%.

One of the main properties of tar which affects the gasifier operation is the condensation temperature. The tar condensation relies on its compositions; each component contributes to the overall vapour pressure. As the tar vapour pressure overcomes the saturation condition (dew point) condensation begins according to the Raoult law. Hence, in condensation related issues, the tar dew point is a powerful parameter to evaluate the performance of gas cleaning systems. It is believed that, when the dew point of tar is reduced to levels below the lowest

expected temperature, fouling related problems by condensation or tar aerosols are solved. An illustration of the relation between the tar dew point and tar concentration is summarized by [44] and shown in Fig. 1.8. Condensation curves are given for the individual tar classes reported in Tab. 1.11, e.g. the dew point curve for class 5 is calculated including only class 5 tars. Furthermore, each tar component is contributes equal to the total concentration on mass basis. The dew point calculation excludes tar class 1, as the components are not known. For a CFB gasifier it is believed that tars that belong to class 1 start to condense around 300–350 °C. Even at low class 5 tar concentration of nearly 0.1 mg m³, the corresponding dew point (°C) exceeds the dew point valid for high concentration of class 2, 3, and class 4 tar (e.g. 1000 mg m_n^{-3}). It can be derived from Fig. 1.8 that class 5 tars dominate the dew point of tar. Even for very low concentrations of class 5 tars (e.g. <1 mg m_0^{-3}) a dew point below 100 °C can be obtained. The graph clearly points out that, dependent on the concentration in the syngas, classes 2 and 4 need to be partially removed for a proper tar dew point of about 25 °C. The class 3 tar compounds do not condense at concentration as high as 10,000 mg m_n^{-3} , and play an unimportant role in this matter.

The problems related to tar depend on the end-use of the gas. In co-combustion the gas produced from the gasifier is burned with pulverized coal in a furnace, so the tar calorific value is used without causing any problems to the plant. On the other hand when the gas is destined to an engine or when it is cooled down or pressurized the tar can lead to deposits, fouling and plugging; over 400 °C the condensed tar can form char blocking dramatically the pipelines of the plan. Reference values for acceptable tar contents in syngas are reported by [45] for IC-Engine (< 100 mg m_n⁻³) applications.



Figure 1.8 - Tar dew point of different tar classes plotted against the tar concentration in the gas [44].

The simplest system for tar abatement is water scrubbing. This solution cools down the gas and removes tar and particulates and is usually adopted at the gasifier exit. This operation is guite common but can lead to the production of wastewater with high concentrations of toxic compounds. As a consequence it is not easy to treat such wastewaters with biological processes [46]. In addition water scrubbing damages the energetic efficiency of the process cooling down the gas and reducing the calorific value of the gas due to the loss of the tar. Another option for tar abatement is tar cracking. This operation transforms the tar in gas, without a significant cooling of the gas, and thus allows obtaining higher energetic efficiency of the process [47]. This solution can be further classified in thermal tar cracking and catalytic tar cracking. In thermal tar cracking the gas produced from the gasifier is brought to high temperatures to break the molecular bonds and transform the tar compounds in gaseous compounds and char, thus increasing the tar and char yields. This treatment is usually operated in tubular reactors operating at temperatures in the range 500-900 °C and residence times in the order of some seconds (0.5-4s). The onset temperature of the tar thermal cracking depends on the tar composition while the gas residence time in the reactor depends on the tar composition and the desired conversion. The research in the field of tar thermal cracking aims to define optimal operating conditions and to predict the gas yield and composition in the gas leaving the process. Kinetic studies are carried out through experimental tests where the tar is either simulated (with toluene or naphthalene) or produced from gasification and pyrolysis processes. The main products of tar thermal cracking are CO, CO₂, CH₄, H₂. In tar catalytic cracking the gas produced from the gasifier is brought at high temperatures in a catalytic medium. The aim of this treatment is to enhance the transformation of tar in gaseous compounds. The catalytic cracking has the potential advantage of breaking very stable aromatic compounds (which can polymerize and form soot) which the tar thermal cracking cannot dissociate even at 900 °C. Many catalysts look suitable to be applied in tar decomposition, among others the most promising are Ni-based catalysts [48]. These catalysts are very active but are expensive and can be deactivated through coke formation. The research in this field aims to develop very efficient catalysts, optimal temperatures and residence times and to address the effect of the catalyst on the composition of tar processed gas stream.

1.4.6 Discussion

Five barriers to the commercial diffusion of biomass gasifiers have been presented: the variability of biomass properties, the biomass moisture content, the handling of solid materials and problems related to ash and tar in the produced gas. The design of the gasifier as well as a specific conditioning of the biomass can avoid problems 1, 2 and 3. Noteworthy if the efficiency of the gasification process can be enhanced the cost of conditioning processes could be reduced. The main technological innovations are expected in the field of the gas clean up. The most common treatment to remove particulates, alkaline vapours and tar is water scrubbing. This technique produces some disadvantages such as the loss of the calorific value associated to tar and the production of contaminated wastewater. The most promising technological solutions are "alkali getters" to remove alkaline vapours and tar cracking reactors (thermal or catalytic). These techniques allow cleaning up the gas produced from the gasifier at high temperatures thus leading to efficiencies gasification high energetic of the process.

1.5 Summary

In this Chapter biomass gasification has been briefly presented in order to introduce several basic concepts and issues that will be discussed in the forthcoming Chapters. It is worthy to note that from the discussion above biomass gasification emerges as a very flexible process that, in particular, allows producing several products and serving several different end-users. However this lack of specificity, as reported by [2], may be the cause for the slow progress of the technology. Since there is not a single way to approach the process, it is not clear which investor should be more interested in. In addition, despite the process flexibility, there are tight specifications both for the gasifier feedstock and the syngas properties. This partially compromises the flexibility of the technology, since ancillary equipments for the feedstock conditioning and the gas clean-up are required. As matter of fact the ancillary equipments can be more expensive or complex than the gasifier it-self or add very high costs to the whole system.

1.6 Research needs in biomass gasification

The discussion provided in this Chapter leads to the identification of the major research needs involved in biomass gasification. Fig. 1.9 reports a pictorial overview of various research subjects for each step of the gasification process.

Biomass is the feedstock for the process and a proper characterization of the biomass is of basic importance for understanding the gasifier behaviour. Biomass characterization involves both experimental data and modelling activities. Experimental data should be provided both with standard procedures to provide a comparable fingerprinting but also with peculiar experiments in operating conditions similar to those used in practical applications. These last type of data are important both for a direct comprehension of the phenomenology of the process and for the validation of numerical model, which may help the interpretation and prediction of biomass gasifier. Paragraph 1.3.1 has highlighted the importance of the feedstock conditioning, research should be carried out in order to simplify as much as possible these treatment through energy saving techniques and investigating suitable alternative practice (for instance biomass mixing). The effect of the gasifying agent is usually assessed in completely different conditions, for instance air compared with oxygen/steam mixtures, which leads to completely different process; slight changes in the gasifying agent (for instance very low oxygen enrichment of air) could be interesting subjects that may help to increase the flexibility of gasifiers. The gasifier is the core of the plant, academic investigation on lab-scale devices may help understanding the effect of operating variables; however it is not possible to improve the biomass gasification process regardless of the gasification technology. Thus experimental and modelling activities on pilot scale gasifiers are of basic importance in order to assess critical issues and suggest possible developments. In the last fifteen years many studies have been devoted to evaluate the performance and develop gas clean-up systems. Tar is maybe the major concern and tar sampling and tar cracking are the most investigated subjects. Several works are also devoted to assess the syngas use in internal combustion engines and Fischer & Tropsch synthesis reactors; however it seems that once the syngas meets the end-user specifications, technology are rather mature for its utilization. Finally a very important branch of the research related to biomass gasification is the treatment, exploitation and disposal of wastes. Major concerns are related to the use of the so called bio-char, depending on the local legislation this by-product has different definition, it can be used for combustion but many studies are dedicated to assess its use as a soil amendant in order to increase the carbon dioxide capture from the process. Other concerns are also related to the disposal of the wastes produced from the syngas clean-up. Hot gas clean up may avoid them but further studies and practical applications are required, in a short-term a deep analysis and possible treatment of the wastewater produced could be a precious information.



Figure 1.9 - Research needs in biomass gasification.

CHAPTER 2. THESIS APPROACH AND METHODOLOGY

The aim of this Thesis is to develop systems that may support the development of biomass gasification. As pointed out in Chapter 1, biomass gasification is a technology which is not completely established and requires several research needs to overcome some technological barriers. This Thesis is focused on the core of the gasification plant: the biomass gasifier. It is believed that a deeper understanding of the gasifier behaviour may help developing the technology thus enhancing the flexibility and performance of the process, without requiring demanding feedstock preparation and gas cleaning steps. A biomass gasifier is a complex system that involves several chemical and physical phenomena; in addition the description and the spatial and time scale of such phenomena change significantly according to the gasifier setup. To build the guidelines for the work a problem decomposition approach is developed (represented schematically in Fig. 2.1). The analysis of the biomass gasifier is decomposed in several sub-problems. A hierarchical classification of the problems is defined on the basis of the physical scale of the sub-problems.

The apex of the pyramid is the full system, the biomass gasifier. As we move down we encounter coupled problems such as the gas and solid temperatures which are derived from other phenomena of lower complexity such as the flow through porous media (at the unit scale) or heat and mass transfer phenomena (at the molecular scale). All the "bricks" that form the pyramid require detailed investigation in order to be able to properly describe the full system.



Problem decomposition

Figure 2.1 - Problem decomposition applied to a gasifier.

As a consequence a multi-scale approach is required. This involves carrying out both experimental studies and modelling studies, which should be properly integrated to enhance the quality of the information and data. Experimental studies, especially at small scale, should be performed focusing on model validation. On the other hand the modelling activity should be used with as much as possible integration with the experimental work in order to improve the reliability of the results and act both as an interpretative tool and as an aid for filling the gaps of the experimental work.

2.1 Steps of the work

The activities reported in this Thesis follows the aforementioned approach for the study of biomass gasifiers. As a consequence both experimental and modelling activities were carried out at different scales. Obviously, it is not the aim of this Thesis to fill all the knowledge gaps or solve all the technological issues involved in biomass gasification. This Thesis would rather give a significant contribution to some of the bricks of Fig.1 by developing experimental systems and modelling tools. The phases of the work are here briefly presented.

2.1.1 Selection of the working subjects

Once the biomass gasifier problem is decomposed according to the hierarchical approach it is necessary to decide which of the bricks should be investigated according to the scientific and technological urgency and the capabilities of our research group.

The following subjects were selected:

- Evaluation of the effects of high heating rate on biomass devolatilization, especially kinetics;
- Tar sampling and characterization, paying attention to the integration of different experimental techniques to provide useful data for modelling activity;
- Development of a pilot scale gasification facility, focusing on the characterization of the gasifier behaviour;
- Testing non conventional fuels in order to assess limit and capabilities of a pilot scale gasification system;
- Development of a model of the gasification facility.

2.1.2 High heating rate devolatilization kinetics

A procedure coupling an experimental characterization and Computational Fluid Dynamics (CFD) was developed for providing valuable global kinetic parameters to large applications of biomass fuels (fast pyrolysis, co-combustion and gasification). This is based on an advanced lab-scale apparatus (Drop Tube Reactor), reproducing high heating rates and low residence times at different nominal temperatures (400-800 °C) for particle size of practical interest. Although the relative simplicity of the operation, a detailed and accurate evaluation of the particle residence time and effective thermal history is needed to elaborate suitable global devolatilization kinetics, which differ significantly from low heating rate kinetics (for instance in thermogravimetric balance) and also from those obtained assuming

strong hypotheses (e.g. constant particle temperature in the reactor). The developed procedure gives kinetic parameters which are not the intrinsic devolatilization kinetics but global kinetics at high heating rates. These global kinetic parameters are useful to simulate practical systems (characterised by high heating rate) with comprehensive codes (CFD), since detailed particle kinetics require additional sub-models (e.g. of external and internal heat transfer) which may be time consuming and need many data, often known only with uncertainty. CFD is used as both diagnostic and predictive tool.

2.1.3 Tar sampling and characterization

Gas and char sampling and analysis are somewhat well addressed techniques. Tar, instead, still deserve investigations. A tar sampling system was developed and characterized both with simple test cases and pyrolysis tests. The innovative peculiarity of the system is that it is possible to select a different temperature, by means of temperature controllers ranging from -15°C up to 200°C, for each component. This allows fractionating the condensable species (tar and water) into four samples, which are related to different boiling temperature ranges, and guarantee the repeatability of the sampling. This sampling does not involve the use of solvents, therefore there is no need for extraction to obtain the final sample and a direct measure of the condensate quantity can be obtained by weighting. Four different analytical techniques were applied to the tar samples in order to develop an integrated characterization methodology.

2.1.4 Development and testing of a pilot scale gasification facility

A pilot scale gasification plant was developed within the framework of the CRIBE (Centro di Ricerca Inter-Universitario Biomasse da Energia). The pilot scale plant involves a biomass gasification facility equipped with wet gas clean-up, a batch drier and a tar cracking system. The core of the plant is the biomass gasifier, a 200 kWth downdraft throated gasifier using air as gasifying agent. The plant has been developed specifically for increasing the knowledge of the gasification process; therefore this commercial plant has been upgraded with several sampling and measurements devices. Case study tests were carried out with the purpose of assessing the gasifier behaviour. This aim was pursued evaluating the gas flowrates and pressure drops across the bed, temperature in the throat and at the outlet, gas composition and samples characterization, providing useful data for models validation. Pelletized fuels were chosen as reference to investigate the limit and capabilities of the plant, as well as addressing the fluid-dynamics characteristics of the bed. In addition biomass mixture (wood pellets/sunflower seeds residues pellets) were tested, in order to propose mixing as an option to broad the range of fuels for this technology. The process performance was evaluated according to the parameters defined in Chapter 1.

2.1.5 Modelling study of the downdraft gasifier

A modelling activity of the downdraft gasifier was carried out by means of the commercial software gPROMS. The model is based on a 1-D representation of the gasifier geometry and takes into account the relevant phenomena occurring during gasification, already discussed in Chapter 1. The first part of the work consisted in a broad literature review of the description of the phenomena and reactions, in particular devoted to compare different kinetics and resume the original sources

and thus the operating conditions in which were obtained; large discrepancy in kinetic parameters can be found in the literature. In addition the reliability of some sub-models was tested and it was found that at this stage the use of simple sub-models improves the simplicity of the comprehensive gasifier model, which has to take into account many phenomena, without compromising its reliability. The model is applied to the downdraft gasifier of the CRIBE and its experimental data are used for validation. The purpose of developing such a model is producing a tool to support the interpretation of the experimental data and suggest possible new measures and development of the plants to increase the amount of information.

CHAPTER 3. EVALUATION OF HIGH HEATING RATE BIOMASS DEVOLATILIZATION KINETICS

The main steps of biomass gasification are described in Chapter 1. One of this is biomass devolatilization. As already pointed out this step has a large impact on the whole gasification process and it is demonstrated that operating conditions greatly affect the devolatilization parameters [1, 2].

Conventional analysis (e.g. thermogravimetry) on lab-scale can give only a fingerprinting of the fuel, because the thermal conditions are far from those of practical applications. For instance, pyrolysis kinetics change substantially when varying the heating rate (see among others Wiktorsson et al. [3]). Therefore, advanced experimental facilities and elaboration procedures should be developed to provide fundamental data under operating conditions similar to those of the industrial scale.

A Drop Tube Reactor (DTR) is a relatively simple apparatus to study the fast pyrolysis of biomass fuels. High heating rates (on the order of 10⁴ °C/s) and low residence times (0.1-1 s) can be reproduced [4-7], while different analyses can be carried out on the gaseous products (speciation) and solid residues (char properties) [8-11]. However, most literature works are limited to the determination of particle conversion in different conditions, only few being actually devoted to elaborate kinetics. This is because the effective thermal history of the fuel particles in the DTR is difficult to be measured. A direct characterization would require sophisticated and intrusive experimental techniques, e.g. Particle Image Velocimetry, and optical accesses to the DTR interior, which are hardly practicable. Letho [5] provided measurements of particle velocity and position in the outlet section of a DTR by means of optical techniques and used these information to extrapolate data on the residence time in the whole DTR. Alternatively, the effective thermal history may be deduced from either simple hypothesis or theoretical models on the particle behaviour. The easiest hypothesis is to assume a constant particle temperature equal to the DTR nominal temperature [7], but significant errors may arise from this procedure.

Therefore, detailed models of the particle behaviour in the DTR are required and to this purpose Computational Fluid Dynamics can be taken into consideration. Indeed most of the commercial CFD codes allow treating multi-phase and reactive flows, so that the CFD poses itself a less expensive and time demanding tool for the investigation of biomass/coal pyrolysis devices. In addition, it can be adapted to full-scale plants, while extensive experiments are not always feasible in industrial devices.

Brown et al. [6] used CFD to model the gas and particles flow in a laminar entrained flow reactor. The CFD model did not account for reactions on the particles, which were assumed to be non reactive. The simulated particle trajectories, temperature and time were used in a bespoke spreadsheet where reactions were integrated appropriately. Consequently, in the procedure it was assumed that the impact of solid particles and product gases on the flow and temperature of the bulk flow is negligible; this makes sense when the flow of the solid fuel is significantly lower than that of the bulk flow. Fletcher et al. [12] investigated numerically through CFD an entrained flow gasifier, the fuel injections generating a swirl flow. The authors highlighted the complexity of the model, due to the numerous equations involved and the need of validation with experimental results. Meesri and Moghtadieri [13] evaluated the capability of a CFD code to predict sawdust combustion conversions. They developed a model by introducing global kinetic parameters obtained through experiments. The agreement between predicted and experimental results was good but data were obtained only for very high conversions. Ballester and Jimenez [14] proposed a methodology for measuring the oxidation parameters for pulverised coal from drop-tube and thermal histories obtained with CFD; they pointed out that the consideration of a particle-size distribution instead of a single representative diameter is effective in reducing the error of the CFD conversion predictions.

This Chapter reports

- experiments on biomass pyrolysis performed on a lab-scale Drop Tube Reactor;
- an Eulerian/Lagragian CFD model of the apparatus used as a diagnostic tool for obtaining the effective thermal history of the particles;
- the development of a procedure to elaborate global kinetics by combining experiments, direct characterization of the apparatus and CFD model results.

The use of CFD is discussed also as a predictive tool, as it poses difficulties and modelling choices to be addressed for the particular application, requiring the use of a combined approach between experiments and modelling.

3.1 Methodology

The methodology used in this activity is illustrated in the scheme of Fig. 3.1. Details will be provided in the forthcoming Paragraphs. Pyrolysis tests are performed by varying the reactor temperature and length in order to consider a sufficiently wide range of conditions. The fuel characterization as well as the conversion of the DTR residues is determined by conventional ThermoGravimetric Analysis (TGA). Fuel dimension and morphology are determined by SEM analysis. Moreover specific experiments are performed to directly characterize the apparatus. The gas thermal profiles along the DTR are measured as they allowed evaluating the boundary conditions to be set at the DTR walls. The CFD model was used as both diagnostic and predictive tool. In the first case, it provides the solid particle thermal histories for all runs. These data are needed to integrate a Single First Order Reaction (SFOR) model in a separate routine to obtain the kinetic parameters. All reactions are modelled with a SFOR model:

$$\frac{dV}{dt} = k(V - V^{\infty}) \tag{1}$$

where V is the volatile matter released during the run, V^{∞} the maximum volatile matter released, while k is defined as:

$$k = A \cdot \exp\left(-\frac{E}{RT}\right) \tag{2}$$



Figure 3.1 - Work procedure (coupling experiments and simulations).

A recursive procedure is developed to improve the kinetic analysis adopting more realistic hypotheses. In particular:

- step 1. The preliminary CFD model assumes the biomass to be mono-dimensional with a diameter equal to the Sauter mean diameter of the real size distribution. Low HR kinetics (KIN_0) are used in the initial step to obtain the thermal history of the particles. Subsequently kinetics are recalculated (KIN_1) by the kinetic routine which evaluates SFOR parameters A and E minimizing the sum of errors between experimental and model conversions for all runs (i.e. for all temperatures and reactor lengths).
- step 2. The second step of the recursive procedure consists in computing new thermal histories by adopting the high HR kinetics of the previous step (KIN_1) and introducing a discrete particle size distribution in the CFD model. The kinetic routine provides the second set of kinetics, KIN_2.
- step 3. The third step, as will be elucidated better in the results section, consists in splitting the entire range of temperature of interest into two intervals over which the kinetic routine is applied separately to give two couples of kinetic parameters, KIN_3lowT and KIN_3highT, respectively.

Finally, the different sets of kinetics obtained are introduced in the CFD model to evaluate its capability in predicting particle conversion for fast pyrolysis runs. To this purpose global biomass conversions estimated from CFD simulations are compared with experimental data.

3.2 Experimental section

The core of the experimental system (Fig. 3.2) is a Drop Tube Reactor which consists of an Inconel 600 tube (length = 1200 mm - ID = 54 mm) inserted in a vertical electric heater formed of three independent resistances (total heated length 914 mm). The temperature of each electric resistance is measured by an S type thermocouple and controlled to set the nominal temperature.

Two nitrogen streams are fed to the reactor through a water cooled head: the primary gas transports pneumatically the biomass particles through a small tube (ID = 1 mm) coaxially fixed to the DTR axis by a flow straightener, which reduces also the radial component of the secondary gas velocity.

The reactor length is varied by inserting a water-cooled collector probe at different heights. The collector probe cools down the gas and the solid residue, thus allowing tests with different particle residence times. The gas stream is separated from the solid residue through a glass fibre filter. The gas thermal profiles along the DTR axis are measured at different electric heater settings, maintaining constant the gas flow rate (1 and 2 L_n min⁻¹ for primary and secondary gas, respectively) and in absence of solid particles.

The same nominal temperature is set for the second and the third resistances, while the first resistance is switched off in all cases to avoid damage of the small feeding tube and the gaskets.



Figure 3.2 - Scheme of the experimental system.

5 nominal temperatures (400-800 °C) are tested with a K thermocouple regulated at different heights of the DTR and shielded by a ceramic material to avoid the radiant effects of the tube walls. In general, all profiles exhibit a wide isothermal range and a nearly symmetric shape (see the examples reported in Fig. 3.3 for two nominal temperatures).



Figure 3.3 - DTR experimental (symbols) and predicted (solid lines) thermal profiles at Tn = 600 °C and 700 °C.

A biomass fuel (cacao shells: C 47, H 6.0, N 2.6, S 0.23% wt dry and ash free basis; VM 71.05, FC 20.0, ash 8.95% wt dry basis) is milled and sieved and the dimensional range 90 - 150 um is used for the pyrolysis runs. SEM analysis is performed to quantify the biomass dimensional distribution and the shape factor RF (roundness) according to the procedure reported in Biagini et al. 2008 [15]. Results are shown in the distributions of Fig. 3.4a and Fig. 3.4b. The mean values of the equivalent spherical diameter and roundness are 93 µm and 1.6, respectively. In the model development, the Sauter mean diameter is actually needed, as mentioned in the previous section. It results 110 um. As for the shape factor, the observed roundness values indicate quite spherical particles. Moreover, solid residues collected after pyrolysis in different conditions have a roundness factor even closer to unity and, thus, the spherical shape is maintained during the runs. The pyrolysis tests are performed at five nominal temperatures (from 400 to 800 °C) and three collector probe positions, namely Z1, Z2 and Z3 (i.e. for a total reactor length of 254, 464 and 827 mm, respectively), to evaluate the effect of temperature and residence time on the solid fuel conversion. The gas flow rate of both streams is maintained at the values reported above, while the solid flow rate is 1.5 mg/s. Each test is prolonged for at least 15 minutes to ensure stationary conditions and recovery a sufficient amount of solid residue after the run. The DTR solid residues are oxidized in a thermogravimetric balance (a detailed description of the instrument is reported in Chapter 4) to obtain the devolatilization conversion.

of the instrument is reported in Chapter 4) to obtain the devolatilization conversion. 5 mg of each sample is oxidized in air (100 ml/min) in constant heating rate (20 °C min⁻¹) runs from 100 to 800 °C.



Figure 3.4 - (a) Dimensional distribution and (b) roundness factor of cacao shells and DTR residues.

The pyrolysis conversions (referred to the initial organic content of the biomass) are determined by the "ash tracer" method (e.g. [7]), thus assuming constant the ash mass, so that the volatile matter conversion can be calculated as:

$$\chi = 1 - \frac{X_{ash0}}{X_{ash1}} \tag{3}$$

where X_{ash0} and X_{ash1} are the ash mass fractions (determined with TGA) of the biomass and DTR residues, respectively. The use of the ash tracer has long been an issue in investigations on biomass thermal processes, since many materials contain volatile ash components and there is scepticism about the viability of the ash tracer method to calculate the pyrolysis conversion. In this study, preliminary tests on cacao shells were carried out to compare the ash yield at 550 and 800°C. The results showed that the difference in the cacao shells ash content is negligible. Therefore, the ash tracer method (applied in tests in which the maximum temperature achieved by the particle is 800°C) can be acceptable in this work.

3.3 Numerical model

The model is developed with the CFD code CFX 5.7 by Ansys Inc. The computational domain represents the DTR region extending from the bottom section of the injection tube downwards. Considering the axial symmetry of the problem, just a 5° angular sector of the reaction tube is modelled in order to decrease the computational cost. Three different computational domains are defined, depending on the three collector probe positions in the reaction tube. The grids are structured, the number of grid elements ranges from 90000 to 110000 as the domain length increased. Grid independency study was preliminarily carried out by halving and doubling the number of grid elements and assessing that results obtained with the grid were equal to those obtained with a more refined grid. Fig. 3.5 shows the computational domain, which is reflected with respect to the DTR axis for clarity of representation. The temperature of the primary flow in the inlet section is an unknown boundary condition. A simple CFD model of the injection tube was therefore developed independently from the main model to evaluate such a temperature, by considering both the effects of the DTR cooled head and the upper part of the reacting tube.

The effective wall temperature on the DTR surface, corresponding to a certain nominal temperature in the controller, is also unknown but is fundamental for defining the thermal domain. This was pointed out also by Brown et al. (2001) [6] who used temperature measurements on the walls to set the appropriate boundary conditions to the CFD model. In this work a preliminary CFD study was carried out to define the most suitable boundary conditions. The temperatures of the domain walls were optimized to reproduce the gas thermal profiles measured experimentally on the DTR axis. A good agreement is obtained comparing the results of this fitting procedure with the experimental measurements (see Fig. 3.3). Since the low volumetric fraction of the dispersed phase, an Eulerian/Lagrangian approach is chosen to describe the gas phase flow and the solid particles' motion. The gas (nitrogen) phase is solved in an Eulerian reference frame, by solving equations for mass conservation, chemical species transport, momentum transport and energy balance. The biomass particles are solved in a Lagrangian reference frame, by solving mass, force and energy balances on the particles. A fullvcoupled method is needed to take into account the interactions (through chemical species, momentum and heat) between the gas and solid phases.



Figure 3.5 - Computational domain of the DTR.

As far as the gas phase is concerned, it is worth noting the laminar regime of the flow (Reynolds number of approximately 1500) and hence the Eulerian equations are solved without any further hypothesis. In particular, there is no need for a turbulence model to close the equations. Radiation is taken into account through the P1 model [16] in the energy equation. The gas phase is assumed to behave as a grey gas, so that the radiation properties are not dependent on the wavelength.

The equation of motion is solved for the solid particles by assuming that the particles behave as hard spheres and particle-particle interaction is negligible. The former hypothesis is substantiated by near unity roundness factor of the parent material (see Fig. 3.4b). The latter hypothesis is motivated by the low volumetric fraction of the solid fuel in the DTR. Unsteady forces (virtual mass and Basset history), pressure gradient and lift forces are considered negligible, thus the only forces acting on the particles are due to drag and gravity.

The resulting equation is:

$$\frac{\pi d_{p}^{3} \rho_{p}}{6} \frac{d\vec{u}_{p}}{dt} = \frac{1}{8} \pi \rho_{g} d_{p}^{2} C_{D} \left| \vec{u}_{g} - \vec{u}_{p} \right| \left(\vec{u}_{g} - \vec{u}_{p} \right) + \frac{1}{6} \pi d_{p}^{3} (\rho_{p} - \rho_{g}) \vec{g}$$
(4)

where C_D is the drag coefficient, which is evaluated as a function of the particle Reynolds number Re_p through the Schiller-Naumann equation:

$$C_D = \frac{24}{\text{Re}_p} (1 + 0.15 \,\text{Re}_p^{0.687})$$
(5)

Particles are numerically introduced in the fluid domain every 5 iterations of the continuous phase. They are injected from 50 equally-spaced injection positions of the inlet section, assuming that they move at the same velocity of the primary gas. In the first simulations, a mono-dimensional size is assumed with a fixed diameter equal to the Sauter mean diameter D_{32} . It is calculated considering the mass of the particles and, thus, is more representative for evaluating the global conversion than the equivalent spherical diameter. Subsequently (step 2 and 3 in the methodology section), a discrete diameter distribution (made of 6 bins as in Fig. 3.4a) is extrapolated from the SEM results and fed to the numerical model, to better represent the real conditions. The global conversion to be compared with the experimental data is calculated as the weighted average of each particle size.

$$\chi = \sum_{i=1}^{j} f_i \cdot x_i \tag{6}$$

where χ is the global conversion for a single run, f_i and x_i are the mass fraction and conversion of the i-th particle dimensional class, respectively.

The solid particles are represented by three components: biomass, ash and char. The initial fraction of char in the biomass is zero. The ash content is derived from TGA analysis, while the biomass is assumed to follow one (KIN_1, KIN_2, KIN_3) or two (KIN_0) parallel devolatilization reactions. In the latter case (corresponding to step 1 in the methodology section), the scheme is the following:

$$biomass \rightarrow \frac{\alpha_1 volatiles + \beta_1 char}{\alpha_2 volatiles + \beta_2 char}$$

(7
Stechiometric coefficients (α_1 , α_2 , β_1 and β_2) and kinetic parameters for both reactions are derived from low HR runs in the TG balance [17]. In the other cases, single reactions are assumed.

The particle energy balance considers the convective and radiation heat flows as well as that associated with the mass transfer:

$$\sum_{i} \left(m_i c_{pi} \frac{dT_i}{dt} \right) = Q_C + Q_M + Q_R \tag{8}$$

where the *i*-th index refers to the *i*-th component in the particle.

The convective heat is:

$$Q_c = \pi d \cdot k_f \cdot N u \cdot \left(T_g - T\right) \tag{9}$$

where the Nusselt number is evaluated through the Ranz-Marshall correlation (1952) [18] for force convection:

$$Nu = 2 + 0.6 \operatorname{Re}_{p}^{0.5} \operatorname{Pr}^{0.33}$$
(10)

The heat flow associated to the mass transfer is:

$$Q_M = \sum_i \left(\frac{dm_i}{dt} \cdot \Delta H_{m_i} \right) \tag{11}$$

Finally, the radiation heat flow to the particle is

$$Q_{R} = \frac{1}{4} e_{p} \pi d_{p}^{2} \left(I - \sigma n T^{4} \right)$$
(12)

Particles are assumed opaque, i.e. $e_p = 1$.

3.4 Results

3.4.1 Experimental results

The solid residues obtained from pyrolysis tests in the DTR are oxidized in air in the thermogravimetric balance. Fig. 3.6 shows TGA curves of direct oxidation in air for cacao shells and three solid residues obtained from pyrolysis in the DTR in position Z2 and three nominal temperatures. The curve of the parent fuel exhibits two macro-steps of weight loss, the first between 200 and 400 °C corresponding to the devolatilization, the second between 400 and 550 °C imputed to char oxidation. Also, cacao residues at DTR nominal temperature 400 and 600 °C exhibit two macro-steps even though the relative weight loss is different: the weight loss due to devolatilization decreases, while that of char oxidation increases as the DTR temperature increases. The DTR residue at the highest temperature (800 °C) shows a single step in the weight loss, imputable to char oxidation. Actually, significant changes in characteristic temperatures can be observed. More details and implications on char properties can be found elsewhere [11].



Figure 3.6 - TG curves of oxidation in air of cacao shells and 3 solid residues (obtained from pyrolysis test in the DTR in position Z2 and 3 nominal temperatures).

The ash content in the solid residues is also derived from this analysis and it is used to calculate conversions according to the method described above. The biomass conversions at three reactor lengths are shown in Fig. 3.7 for all temperatures. At the lowest temperature (Tn = 400 °C) the conversion increases significantly with the reactor length. The minimum conversion observed is above 50%. The higher the nominal temperature, the higher the conversion. The conversion is above 70% for nominal temperatures higher than 500 °C for all reactor lengths. However, in these cases a slighter increase of the conversion with the reactor length can be observed. The run under the most severe conditions (Tn = 800 °C, maximum reactor length) is used to evaluate the maximum volatile matter released V° (see eq. 5), which corresponds to a conversion of 80.8%.



Figure 3.7 - Cacao shells conversion at different reactor lengths and nominal temperature conditions.

3.4.2 CFD model results

In this section the results of the CFD model used as a diagnostic tool are reported and discussed. In particular the effect of the operating conditions (reactor length and nominal temperature) on particle residence time and effective thermal history of biomass particles is evaluated.

In general, for all cases studied, the gas flow is dominated by the high speed of the primary gas jet in the region close to the injection tube, while the flow becomes fully developed in the far field where the jet momentum is lost. The gas velocity vectors show the gas flow moving downward along the tube axis, while the gas close to the tube walls moves upward due to higher temperatures. In addition, entrainment due to the primary gas jet leads to the formation of a recirculation region near the injection tube.

The fuel particles follow the gas jet behaviour, their velocity decreasing with the jet losing momentum. Consequently, the particles' residence time in the upper part of the DTR is much lower than that in the remainder of the DTR. This behaviour has to be expected because the particle relaxation time (t_{pr}) is very low, approximately ranging from 0.01 to 0.02 s, so that particles are very sensitive to gas flow variations. In addition, the fuel particles follow closely the DTR axis, due to the absence of turbulence effects. This finding is also accepted by other authors (e.g. Xiu et al., 2006) [7] and has been demonstrated by using particle tracking velocimetry techniques (Letho, 2007) [5].

In the bottom part of the DTR, the gas is cooled down and consequently the gas density increases, so that both gas and particle velocities decrease.

Although different hypotheses are assumed for deriving the thermal histories of fuel particles, a general discussion of CFD results can be drawn. In particular, the case of a mono-dimensional feed is considered. Fig. 3.8a reports the particle temperature as function of time for the same nominal temperature (Tn = 800 °C) but different reactor lengths. The particle residence time passes from 0.02 to 0.6 s from a reactor length Z1 to Z3. However, only for Z2 and Z3 the maximum

temperature is close to the nominal temperature, while the particle achieves significantly lower temperatures for Z1. The three curves overlap in the first instants: this indicates that the particle heating rate does not depend on the collector probe position for the investigated cases.

Fig. 3.8b shows the temperature of a cacao shell particle in the reactor, in three nominal temperature conditions for a fixed reactor length. In general, both particle heating rate and maximum temperature increase with increasing the nominal temperature. After the fuel particle has reached the peak temperature, it is cooled down gradually by of about 30-100°C and subsequently dramatically quenched. The gas stream moves slower as getting colder, thus it spends a longer time in the cool region; in this manner the quenching is effective, stopping the devolatilization reactions and ensuring temperatures below 30°C in the outlet section.

Similar observations can be drawn for the temperature-time vectors of all runs in different nominal temperatures and reactor lengths. Quantitative results are listed in Tab. 3.1, which reports characteristic values of the thermal histories, i.e. particle peak temperature T_{max} , maximum heating rate HR_{max} and time needed to reach the peak temperature τ_{Tmax} . This latter gives an idea of the fast heating of the particle: in all cases the values are less than 0.1 s. The heating rates vary between 1.6 and 4.3×10^4 °C/s, which are typical values of drop tube reactors [6, 7, 19]. These operating conditions are similar to those used in industrial power plants for fast pyrolysis or as the initial steps of combustion or gasification processes.



Figure 3.8 - CFD predictions of particle thermal histories for: (a) nominal temperature Tn = 800 °C at different reactor lengths; (b) reactor length Z3 and three nominal temperature conditions (particle diameter D_{32} = 110 µm, KIN_0).

	032 110		1011001
Run	T _{max}	$HR_{max} \times 10^{-4}$	τ _{Tmax} [S]
	[°C]	[°C/s]	
400Z1	372	1.64	0.039
400Z2	404	1.64	0.061
400Z3	408	1.63	0.073
500Z1	446	2.46	0.036
500Z2	493	2.48	0.062
500Z3	500	2.44	0.076
600Z1	522	3.34	0.033
600Z2	588	3.37	0.053
600Z3	598	3.30	0.074
700Z1	591	3.76	0.033
700Z2	693	3.80	0.061
700Z3	710	3.72	0.078
800Z1	643	4.25	0.031
800Z2	798	4.30	0.058
800Z3	822	4.23	0.078

Table 3.1 - Simulated results of characteristic values of thermal history determined with $D_{32} = 110 \,\mu m$ and KIN_0 kinetics.

The introduction of different kinetics in the CFD model negligibly affects the thermal histories of the particles. Vice versa, the particle size has a strong effect on the residence time as well as the effective particle temperature in the DTR. Fig. 3.9 shows thermal histories for 90 and 150 µm particles as well as for the D₃₂ =110 µm particle used in the mono-dimensional hypothesis. In general, notable differences in the thermal histories of particles with different diameter are observed, peak temperature for the largest particles being lower by of almost 50°C than that for the smallest particles. Also the heating rate is strongly dependent on the particle size: for instance, at Tn = 700°C with the collector probe in position Z2 it passes from 5.2 to 2.7 x10⁴ °C/s for 90 and 150 µm particles, respectively. Similar reductions are observed in the other cases.

Consequently, such a variation is expected to be a source of errors when comparing the experimental conversions (obtained for a distribution of diameters) with the model conversion assuming a mono-dimensional particle size or a discrete distribution.



Figure 3.9 - CFD predictions of particle thermal histories for different particle sizes $(dp = 90, 110 \text{ and } 150 \ \mu\text{m})$ for two experimental conditions $(Tn = 400^{\circ}\text{C}, \text{ reactor length } Z2; Tn = 700^{\circ}\text{C}, \text{ reactor length } Z2)$ (KIN_0).

3.4.3 Kinetic Analysis

As proved from the particle thermal history reported in the previous section, each single test is far from being conducted in isothermal conditions.

To evidence the importance of evaluating the effective thermal profile of particles inside the DTR with the CFD analysis, kinetic parameters KIN_Isot were preliminarily determined by assuming a strong hypothesis, i.e. constant particle temperature and equal to the DTR nominal temperature. Resulting kinetics are shown in the Arrhenius plot of Fig. 3.10. This hypothesis allows to easy calculation, but kinetics obtained by this way are hardly suitable. As observed above, the effective thermal history of particles differs significantly from isothermal conditions and the nominal temperature is reached only for few instants.

Table 3.2 - Kinetic	parameters for	or different S	SFOR calcu	ılations.
Parameter	KIN 1	KIN 2	KI	N_3
i didifictor			low T	high T
A [s ⁻¹]	10300	950	33300	625
E [kJ/mol]	37.9	25.5	43.9	20.4

The first step of the recursive procedure reported in Fig. 3.1 assumes that the biomass follows two parallel devolatilization reactions (according to eq.4). These kinetics are called KIN_0 and represented in Fig. 3.10. The parameters obtained from the best fit procedure applied to the integration of SFOR 1 are listed in Tab. 3.2 and represent the set KIN_1 (A₁ = 10300 s⁻¹ and E₁ = 37.9 kJ/mol). They are high HR kinetics but derived from CFD thermal histories of mono-dimensional solid particles with d_p = D₃₂ and low HR devolatilization kinetics.

Tab. 3.3 compares the experimental conversions with those predicted from SFOR_1 in different runs. The conversions are overestimated in some cases, especially at high conversions. KIN_1 kinetics are compared in the Arrhenius plot of Fig. 3.10 with the other kinetics: KIN_1 indicates more reactive biomass particles than with either KIN_0 low HR kinetics (which actually assumed two parallel reactions) or KIN_Isot derived from the strong hypotheses reported above, that is isothermal runs. The large discrepancy between KIN_1 and KIN_Isot suggests that attention should be paid when elaborating the information of DTR experiments. In the specific case, rough assumptions on the particle thermal history lead to a large underestimation of the biomass reactivity.

In the subsequent step (which will give KIN_2) two arguable hypotheses are removed:

- the CFD model tracks a discrete particle size distribution of biomass particles
- the particles undergo devolatilization with high HR kinetic (KIN_1)

Conversion	Exp	SFOR_1	SFOR_2	SFC)R_3
				Low T	High T
Size model		MD	DD	DD	DD
Kinetic parameters		KIN_1	KIN_2	KIN_3 lowT	KIN_3 highT
Run					
400Z2	61.6	58.2	61.9	61.6	-
400Z3	65.1	67.9	66.9	72.1	-
500Z3	72.2	79.2	69.8	79.7	-
600Z1	74.9	68.5	79.9	69.5	-
600Z3	75.9	80.8	79.9	80.8	80.4
700Z1	75.5	75.5	65.9	75	75.4
700Z3	78.4	80.8	80.6	-	80.8
800Z1	76.1	78.3	68.1	-	76.1
800Z2	79.3	80.8	79.5	-	80.5

Table 3.3 - Comparison of biomass conversion values (% wt dry) obtained from experimental tests and predicted by the SFOR kinetic.

MD: mono-dimensional class (D_{32}) , DD: size distribution of diameter

The best fit results are $A_2 = 950 \text{ s}^{-1}$ and $E_2 = 25.5 \text{ kJ/mol}$, thus different from those previously calculated. However, the difference between KIN_1 and KIN_2 is not pronounced when compared in an Arrhenius plot, as shown in Fig. 3.10. As pointed out in the introduction, this procedure gives global parameters rather than intrinsic kinetic parameters, as discussed below

The predictions of SFOR_2 kinetics can be observed from Tab. 3.3: the agreement with the experimental conversions at low nominal temperatures is improved with respect to SFOR_1. However, two runs at high nominal temperatures (both with Z1 reactor length) show a larger error.

The difference in thermal histories obtained by considering the simulations with different kinetics KIN_1 and KIN_2 but the same diameter is practically negligible. Vice versa, the schematization of particle size (discrete distribution or monodimensional feed) plays a major role in the kinetic determination because the difference in the thermal histories is significant (as reported in the previous section). This is in agreement with Ballester and Jimenez [14] who addressed diameter effects on the evaluation of kinetics for char oxidation in an entrained flow reactor. Although the authors used a relatively narrow size distribution, they claimed that the size distribution is one of the major sources of errors in the kinetic parameters derivation.

In the third step the entire range of temperature is split in two intervals (400-600 °C low temperature and 700-800 °C high temperature, respectively), over which the kinetic routine SFOR_3 is applied separately, to obtain two couples of kinetic parameters, called KIN_3lowT and KIN_3highT, respectively. These are $A3_{lowT} = 33300 \text{ s}^{-1} - \text{E}_{3lowT} = 43.9 \text{ kJ/mol}$ and $A_{3highT} = 625 \text{ s}^{-1} - \text{E}_{3highT} = 20.4 \text{ kJ/mol}$ for low and high nominal temperature, respectively.



Figure 3.10 - Arrhenius plot of different set of kinetics (see Tab. 3.2).

This step reduces the errors between model and experimental conversions (see Tab. 3.3). This is reasonable as the set of experimental data is fitted more accurately by two curves instead of just one curve. In fact, the representation of the pyrolysis with multiple temperature intervals facilitates the description of the relevant phenomena as the release of volatile products is influenced by the operating conditions [20,21], competitive kinetic paths taking place, as in the decomposition of cellulose [22].

Conversion errors associated with SFOR_3 are similar to those of SFOR_2 in the low temperature range, while errors of SFOR_3 are much lower than those of SFOR_2 in the high temperature range. Both KIN3_lowT and KIN3_highT kinetics showed a higher reactivity than KIN_0 and KIN_lsot, but are comparable with KIN_1 and KIN_2 kinetics (Fig. 3.10).

The activation energies reported in Tab. 3.2 are low compared with typical intrinsic kinetics of biomass pyrolysis, which are generally obtained in low HR runs, where the thermal transfer is not a controlling step. When high HR runs are studied, the intrinsic chemistry and the heat transfer can be hardly separated. In the conditions of this work, the particles are thermally thin (Bi <0.2 on the basis of Bryden's classification [23]) and this implies that the internal heat transfer resistance is negligible compared to the external heat transfer, thus the particle can be assumed isothermal. On the other hand the devolatilization reaction is limited by external heat transfer (Py' < 5). Therefore the developed procedure gives kinetic parameters which are not the intrinsic devolatilization kinetics but global kinetics at high heating rates. These global kinetic parameters are useful to simulate practical systems (characterised by high heating rate) with comprehensive codes (CFD), since detailed particle kinetics require additional sub-models (e.g. of external and internal heat transfer) which may be time consuming and need many data, often known only with uncertainty.

3.4.4 CFD as a predictive tool for flash pyrolysis

In the previous section, CFD analysis was used as a diagnostic tool for evaluating the effective thermal histories of the particles in the DTR, in different operating conditions. Once high HR kinetic parameters are obtained, an attempt is also made to evaluate the capability of the CFD model in predicting particle conversion in fast pyrolysis runs.

Therefore, global biomass conversions are estimated from CFD simulations by introducing the different sets of kinetics obtained in the previous section. Summarizing, the obtained simulations are:

- CFD_1, assuming a mono-dimensional class of particles and kinetics KIN 1;
- CFD_2, assuming a distribution of diameters and kinetics KIN_2;
- CFD_3, assuming a distribution of diameters and separating the kinetics at low and high nominal temperature with the sets KIN_3lowT and KIN_3highT, respectively.

The conversions for all runs are reported in Tab. 3.4 and compared with the experimental values. The CFD_2 simulation predicted more reactive biomass particles with respect to CFD_1. However, the CFD_2 model predictions of biomass conversion showed more significant discrepancies with the experimental values than SFOR_2 predictions (see Tab. 3.3). In particular, large errors are observed for low nominal temperatures, as well as for the shortest reactor length (Z1). In the latter case, it is worth reminding that also the SFOR_2 model showed significant deviations from the experimental data.

Conversion values obtained from CFD_1 runs are also reported in Tab. 3.4, showing a bad description of low temperature runs. The high temperature conversions are better predicted (especially those for reactor length Z1) than with CFD_2, but this is logical as for these runs SFOR_1 outperforms SFOR_2.

In general, the CFD predictions suffer of many sources of errors which propagate from experimental to modelling steps. For instance, experimental errors are likely to take place in both conversion and gas thermal profiles measurements (and thus they can induce errors in the setting of boundary conditions at the DTR walls).

The CFD prediction of biomass conversion obtained adopting KIN_3lowT and KIN_3highT kinetics for the relevant runs are encouraging. The error is rather low for the high temperature runs, whereas some discrepancies still exist for some of the low temperature runs. Such behaviour needs to be further investigated. In most cases, poor predictions regard runs for which also the SFOR fitting was inadequate.

Conversion	Exp	CFD_1	CFD_2	CF	D_3
			global	Low T	High T
Size model		MD	DD	DD	DD
Kinetic parameters		KIN_1	KIN_2	KIN_3 lowT	KIN_3 highT
Run					
400Z2	61.6	32.5	41.4	42.5	-
400Z3	65.1	48.5	53.6	59.8	-
500Z3	72.2	77.5	69.8	80.3	-
600Z1	74.9	44.6	45.7	61.9	-
600Z3	75.9	80.7	78.6	80.8	80.7
700Z1	75.5	66.1	52.9	72.8	73.3
700Z3	78.4	80.8	80.5	-	80.8
800Z1	76.1	73.1	58.6	-	75.1
800Z2	79.3	80.3	80.2	-	80.8
MD: mono-dim	ensional	class (D _{32,}), DD: size	distributior	of diameter

Table 3.4 - Comparison of biomass conversion values (% wt dry) obtained from experimental tests and predicted by the CFD model.

As highlighted previously, the particle thermal histories predicted with different kinetics showed insignificant deviations. Nevertheless, changes in conversion due to different kinetics may have secondary effects on mass loss (size change during the devolatilization run) and, thus, on the particle equation of motion. A difference in the particle residence time implies a difference in the effective thermal history. Therefore, the CFD treatment of particle diameter change with mass loss deserves a brief discussion.

The CFD code describes by default the particle as a solid sphere whose density is determined by a weighed sum of the components' densities. As the particle loses its volatiles content the amount of biomass, char and ash are recomputed leading to a smaller particle diameter. Consequently, also the particle average density is modified. This hypothesis is assumed in the results reported and discussed in the previous sections. As a matter of fact this is an ideal behaviour, because a fuel particle can either swell or shrink in different ways [19, 24, 25]. A deep investigation of this topic is beyond the scope of this work, so the relevance of change in diameter treatment is simply addressed.

Fig. 3.11 compares the particle thermal histories with high HR kinetics (KIN_1), obtained with both the available model of diameter change based on mass loss and a constant diameter model. This latter case was numerically performed by changing the particle apparent density during the devolatilization. The constant diameter curve is close to the other especially in the upper part of the DTR, which is likely to affect mostly the biomass conversion. The deviation is significant in the lower part of the DTR, i.e. where the temperature is relatively lower. It can be concluded that even if available, the inclusion of swelling or shrinking phenomena would lead to a sophistication of the model, which is excessive in comparison to all hypotheses used in the present kinetic derivation procedure as well as intrinsic errors associated with experiments.



Figure 3.11 - Effect of diameter change on predicted particle thermal histories for: (a) Tn = 700°C, reactor length Z1; (b) Tn = 500°C, reactor length Z3 (KIN 1).

3.5 Summary

In this Paragraph a procedure which gives global biomass devolatilization kinetics was developed, applied to biomass devolatilization and validated in the temperature range 400-800°C. The obtained kinetic parameters are not the intrinsic devolatilization kinetics but global kinetics at high heating rates. These global kinetic parameters are useful to simulate practical systems (characterised by high heating rate) with comprehensive codes (CFD), since detailed particle kinetics require additional sub-models (e.g. of external and internal heat transfer) which may be time consuming and need many data, often known only with uncertainty.

A CFD model of a Drop Tube Reactor was developed in order to provide valuable global kinetic parameters for practical applications of biomass fuels. Many phenomena and lot of information can be addressed with Eulerian/Lagrangian approaches, so that the use of CFD for the characterization of advanced experimentation for biomass/coal pyrolysis is appealing. This approach is comprehensive as it considers reacting particles which exchange chemical species and heat (convective, radiative and associated with mass transfer) with the gaseous phase. The effective residence time and particle thermal history have been obtained for different conditions of reactor length and nominal temperature. These results were used for elaborating suitable global high heating rate kinetics. removing strong hypotheses (e.g. constant particle temperature in the DTR) commonly adopted in literature works. Biomass particles in fast pyrolysis runs were found to be more reactive than in low heating rate runs (in thermogravimetric balance). Furthermore, kinetics differed significantly from those obtained assuming the strong hypothesis of constant particle temperature. Therefore, a detailed and accurate characterization of the experimental apparatus and the development of a diagnostic model for elaborating the numerous data of advanced facilities are recommended. CFD is less expensive and time demanding than experimental multi-phase diagnostics, which usually requires also optical access to the experimental apparatus interior. In addition, once the CFD model is assessed, it can be applied to full-scale.

On the other hand, the development of the DTR model by using CFD has shown some difficulties, which are worthy of discussion. Firstly, the definition of the boundary conditions may be not straightforward, the real temperature of the DTR walls being usually unknown. Therefore a procedure based on preliminary measurements of the gaseous phase temperature along the DTR axis is suggested.

Secondly, the derivation of kinetics for biomass devolatilization obliges to make some modelling choices. The particle size representation (i.e. use of discrete distribution instead of a mono-dimensional size) was found to affect substantially the determination of global kinetics. The inclusion of swelling or shrinking phenomena was numerically evaluated by comparing predicted thermal histories under different hypotheses, but it led to minor variations in the investigated cases. In addition, in this manner the sophistication of the model would be excessive especially in comparison to experimental errors.

The predictive capability of the CFD model was also investigated. An improvement in the predictions could be achieved by using two different SFOR kinetics, for low and high temperature runs. However some poor predictions of low temperature runs were observed. This can be explained by considering that such runs are affected by errors in particle thermal history representation, because they lay within the biomass devolatilization range, so that small discrepancies in the temperature evaluation can give a strong deviation in the conversion. Conversely, high temperature runs are at conditions near the end or above the final devolatilization temperature, where errors in the simulated thermal histories are logically of less importance. Nevertheless, to the author knowledge data available in the literature concerning CFD prediction validation focused on near complete devolatilization or char oxidation [13, 26].

CHAPTER 4. QUALIFICATION OF A TAR SAMPLING SYSTEM AND A TAR CHARACTERIZATION METHODOLOGY

In Chapter 1 we have introduced tar as a technological barrier limiting the diffusion of biomass gasification. It is important to evaluate the tar content in the gas for several reasons:

- determining the tar production of a gasifier;
- evaluating the effect of primary abatement measure;
- evaluating the abatement performance of a tar removal system;
- determining the tar load to the end-user

Moreover the understanding of the gasification process involves a full characterization of the fuel devolatilization; this is remarkable for biomass fuel since, usually, more than 70% of their mass will be released in this step. Tar is one of the main macro-product of biomass devolatilization and investigating its formation and yield is a key aspect in the study of biomass thermo-chemical conversion processes.

All these aspects rely on the possibility to evaluate the tar content in a gas stream, thus involving sampling of the tar and further analyses for its characterization. This latter aspect is somewhat complex since, as mentioned in Chapter 1, tar represents a group of several organic compounds with different molecular structure and physical properties. The investigation of tar components is required for:

- modelling studies related to biomass devolatilization and gasification;
- evaluating of the performance of a clean-up system (such as catalytic tar cracking);
- evaluating toxicological properties of the tar or contaminated wastes (wastewater, filtering media etc.).

This Chapter deals with the development and qualification of a tar sampling system and the identification of tar characterization methodology. First of all sampling and characterization methods reported in the literature are reviewed, highlighting pro and cons and suitable applications. Subsequently the tar sampling system is described and the steps concerned in its qualification are reported. This involved the development of a pyrolysis reactor used as tar generator. The collected tar was analyzed with different techniques (TGA, TG-FTIR, CHN, GC-MS) and the results and capabilities of each technique are reported. This allows developing a methodology that integrates several experimental techniques to achieve a complete characterization of tar.

4.1 Literature survey of tar sampling systems

Tar sampling has long been a debated topic in the scientific community. During the past decades, several institutes have developed methods for the sampling and analysis of tars, on-line and off-line. The most common off-line method is based on trapping the tar by condensation on cold surfaces or filters, by absorption in a cold organic solvent or by adsorption on a suitable sorbent. The analysis of the tars is most often performed by gas chromatography (GC) or gravimetrically (by weighing the collected tars, after careful evaporation of the solvent and condensed

weighing the collected tars, after careful evaporation of the solvent and condensed water). The method proposed by the UNDP/ World Bank monitoring program [1] belongs to this group and it has been used worldwide for over a decade. However [2] at the end of 1998 highlighted the lack of a standard sampling method and the issues that the researchers involved in tar sampling were facing:

The biggest issue, which confuses the meanings people apply to "tar" and the intercomparability of results from various researchers, are:

the conditions and solvents used for "tar" collection; and the subsequent solvent separation. The variety of analytical characterizations of the collected material gives different views of the makeup of the organics, but if clearly documented, do not mislead the reader. As detailed earlier, the temperatures, trapping schemes, and solvents used to capture organics vary greatly. Capture temperatures from -78°C to +190°C, with many temperatures between, are reported. Single-to-multiple used. containina solvents such as acetone. methanol. vessels are dichloromethane, methylene chloride, and toluene. Solid sorbents such as cellulose, fiberglass, and amino-bonded silica are also used. Sometimes the collection of aerosols of "tar" is mentioned. The extraction of the organic fraction of ash, char, and soot is seldom considered. Losses of solvent during sampling are also a concern when "tar" is measured gravimetrically, especially for gases with low "tar." Some measurements of the organics in the condensate do not require separation of the solvent or water. In most cases however, a pre-separation or extraction is used, especially when weight is the measure. Solvent removal has been reported by distilling at from 75°C to 150°C: by evaporating at 25°C to 105°C under ambient to 10 mmHq pressure; by air-drying at room temperature or at 93°C overnight; and by organic partitioning; depending on the fraction of "tar" that is of interest to the end use being studied. As one example of the large difference in quantity of "tar" being reported, Aldén et al. (1996) note that the "total tar" can be six times the commonly measured "condensable tar." There are issues in the probe design that are not always explicitly discussed. Probe and lines must be at a high enough temperature to prevent condensation of the least volatile tar component of interest, but not so high as to cause additional cracking or interaction with particulates of whatever nature. Because some of the tar can be in aerosol form or reside on ash, char, or soot particulates, isokinetic sampling would seem to be a prudent practice.

In the same year of the aforementioned publication the members of the Gasification Task of the IEA Bioenergy Agreement, the US DoE and DGXVII of the European Commission called a joint meeting in Brussels to address the tar sampling issue.

The result of the meeting was the planning of two sampling and analysis Protocols (one for small scale, fixed bed, engine-based systems and the other for larger utility scale plants) that could be used as reference methods for further work. The two draft Protocols were discussed in a workshop at the 10th European Biomass Conference in Wurzburg and will further be referred to as 'Wurzburg Protocols'. In order to further develop the Wurzburg Protocols to widely accepted and standardized Protocols and to integrate them to one Protocol, the EU fifth framework project 'Tar Protocol' [2] has been submitted. It was accepted and has started per April 1, 2000.

Recently, on-line methods have been developed and are gaining much interest from the scientific community.

This Paragraph briefly reviews the tar sampling methods reported in the literature. First of all it is useful to keep in mind that tar sampling has basically two aims:

- evaluating the tar content in a gas (usually in mg m_n^{-3});
- characterizing the chemical constituents.

The sampling methods can be classified in four groups:

- absorption methods;
- condensation methods;
- adsorption method;
- on-line gas phase analysis.

The first three groups are off-line sampling methods, they collect the tar which has to be weighted or characterized in a laboratory. The last group involves techniques based on the direct analysis of tar in the gas phase, which can be performed online.

4.1.1 Absorption methods

The aforementioned tar protocol is a standardized practice for absorption method, thus it will be the sole focus of this Paragraph. The technique is based on four steps: gas pre-conditioning, particulates filtering, tar sampling and evaluation of the gas volume. The final experimental setup is based on six impinger bottles of which the first acts a water condenser. The volume of the impinger bottles should be chosen according to the gas flow rate (250 ml for gas flow-rate > 0.3 m_n³ h⁻¹). Impinger bottles 1,2,3,4 and 5 contain approximately 50 mL of solvent usually isopropanol), impinger bottle 6 is empty. With high moist gas, a large amount of condensate will be generated, thus the volume of condenser should be large enough.

Two setups for the six impinger bottles are possible depending on the allowable pressure drop in the sampling train.

The first is referred as the *standard setup* (reported in Fig. 4.1); in this case impinger bottles 2, 3, 5 and 6 contain glass frits. The standard procedure recommends G3 frits; nevertheless if the pressure drop is too high G2 frits can be used. The temperature of impinger bottles 1, 2 and 4 shall be between 35°C and 40°C, while 3,5 and 6 should be maintained between -15 and -20°C.

The second one is referred as the *alternative setup;* in this case impinger bottles 1, 5, and 6 contain glass beads with outside diameter of 6 mm. The temperature of impinger bottles 1, 2, 3 and 4 should be maintained between 35 and 40 °C, the temperature of impinger bottles 5 and 6 should be between -15 and -20°C. If this latter setup is used the operator should pay attention to the collection efficiency. Once the sample is collected two analysis methods are proposed in the tar protocol: gravimetrical determination and quantitative GC determination (either by GC-MS or GC-FID analysis). The assessment of the protocol was mainly carried out from two institutions: ECN (Energy research Centre of the Netherlands) and VTT (Technical Research Centre of Finland). It was pointed out that several parameters may affect the tar collection efficiency:

- solvent in impinger bottles;
- temperatures of the impinger bottles;
- flow-rate of the producer gas through the impinger bottles;
- actual design of the impinger bottles;
- presence of glass frits and glass beads in the impinger bottles;
- pressure drop over the sampling train as a consequence of the presence of the glass frits;

During the testing campaign the removal efficiency of ECN (100% not including benzene) was higher than VTT (82.4%-97.7%). This was attributed to the use of glass frits in the impinger bottles (ECN) instead of glass beads (VTT); glass frits provide higher contact surface, reduce the bubble size and may capture part of the aerosol. In addition ECN found that a second temperature drop helps increasing the removal efficiency. VTT found that 40°C is a limit temperature in order to avoid excessive solvent evaporation. The tested solvents were ethanol, isopropyl alcohol, dichloromethane, methoxy-propanol.



Figure 4.1 - Sampling train according to the standard setup of the tar protocol.

As reported from ECN and VTT the collection efficiency is not complete due to some aerosol that may form in the impinger train and slip out of the system. The tar protocol is very well accredited in the scientific community [3], however its use present two disadvantages:

- the experimental setup is rather complex;
- the high number of impinger bottles and the glass frits filler may lead to high pressure drops which could affect the sampling conditions.

[4] compared the results obtained with the tar protocol with other experimental techniques. It was found that despite the tar protocol is developed for tar concentration down to 1 mg m⁻³, it is not reliable for low tar concentration (< 30 1 mg m⁻³). Therefore the tar protocol is suitable to estimate the tar content and composition at the gasifier outlet, but it is not reliable to estimate the tar before a demanding end-user.

4.1.2 Condensation methods

The most common tar sampling off-line methods are based on trapping the tar by condensation on cold surfaces or filters. In these techniques the gas is continuously removed from the system and forced to a separation train of cooled glass bottles. The glass bottles are kept at low temperature (from room temperature to -20°C), in order to remove the condensable organic compounds from the gas. The separation efficiency is a major issue in these techniques; it can be enhanced by increasing the contact surface, thus filling the glass bottles with glass tubes, frits or beads, silica gel or glass wool. Notably these methods are very similar to the tar protocol except for the use of solvent in the bottles. It is worthy to note that these techniques are less reliable than the tar protocol (due to lower removal efficiency); therefore there is no standard reference for these methods. However these methods are still in use (for instance [5]) due to the simple setup and since they allow to easily determine the tar content by weighting the bottles. The main reference on this method is probably the work of [6] that compared a solvent-free method to the protocol of the International Energy Agency (namely IEA protocol) [7]. The aim of this research group was to develop a simple method for the estimation of the heavy tar (thus excluding light hydrocarbons), which could be easily applied in practical context (notably the IEA protocol is slightly different from the tar protocol). Fig. 4.2 reports a schematic representation of setup. It consists of a filter for particulate removal (1), a six meters long Santoprene tube (3) positioned in a bath of distilled water (2, 5) heated at 105°C to prevent water condensation in the Santoprene tube. At the exit of the Santoprene tube a glass-wool-packed canister is placed. Subsequently the gas enters a cooled impinger (6) bottle which is meant to condense water and, possibly, light hydrocarbons before the vacuum pump (7). The system is completed with a rotameter and a volumetric counter. The sampling flow-rate was 2 L min⁻¹. The comparison consisted in the tar sampling from a CFB gasifier operating with seed-corn. The authors determined the heavy tar content in the sampled gas only by weighting the Santoprene tube and glasswool-packed canister. Obviously this practice resulted simpler than the serial evaporation needed for the determination of the heavy tar in the IEA protocol.

The authors reported the precision of the method to be within 5%, which is as good as or better than the precision of the IEA tar protocol. Accuracy was within 5% of the IEA tar protocol. The authors believed the lower detection limit to be 0.01 g m⁻³. Both the dry condenser method and the IEA method reported poor precision in the valuation of the water vapour concentration, which varied by as much as 25% and discrepancy up to 50% was found between the two methods. This lack of precision was related to dissolution of light hydrocarbon in the water, which may alter the real water content.



Figure 4.2 - Sampling system based on a dry condenser as developed by [6].

4.1.3 Adsorption methods

The most common adsorption method is SPA (Solid Phase Adsorption). This technique is based on a solid matrix which allows to adsorb the tar from the gas. The gas is sampled by means of a probe maintained at room temperature where the tar is adsorbed; the sampled gas is continuously measured with a volumetric counter. At the end of the sampling the tar is removed from the solid phase by solvent extraction or by thermal-desorption and it is analyzed via GC-FID or GC-MS. The main advantage of SPA is its high sensitivity, tar amount as low as 10 nanograms can be detected thus requiring short sampling time. On the other hand it is necessary to accurately determine the sampled gas volume in order to provide reliable quantitative data. One of the first developers of SPA was [8], who studied the use of an amminic phase on silica support as adsorbing medium. SPA has been widely addressed in the last decade, for instance this method was used at ECN and VTT to quantify the removal efficiency of the tar protocol. [9] compared the Tar protocol with the SPA/TD (Solid Phase Adsorption/Thermal Desorption) in the sampling of tar produced from wood pyrolysis, the analysis was then carried out by GC-MS. The authors highlight the very short sampling time (few seconds vs. 1 hour for the Tar protocol) and the absence of solvent which facilitate the chromatographic separation. The results of the two methods were comparable for aromatic compounds such as phenantrene and phenols, but not for benzene. The SPA/TD evaluation of PAH was found to be more reproducible than the Tar protocol (18% vs. 4%) due to aerosol formation in the latter. [4] used a CFB plant to compare the SPA/TD technique both with micro-GC analysis (used as reference for benzene and toluene) and the Tar protocol (used as reference for naphthalene). They found that for a wide range of benzene concentrations the SPA analysis report a deviation of ±20% from the micro-GC analysis, while for toluene the disagreement was larger (±30%). Concerning the naphthalene evaluation the discrepancy was rather large (from -30% to + 50%). [4] concluded that SPA is a simple and rapid method convenient for biomass processes. Thermo desorption plus GC-MS analysis must be well adjusted to provide reliable and precise results (split ratio, desorption temperature and duration). For a real syngas containing high concentration of steam, sampling is a key point for the quality of measurements. Results are consistent for light hydrocarbons in a wide scale (mg to g mn⁻³). For heavier tars, values are over estimated and scattered. Despite the last results, the impression of the author of this Thesis at the 18th European Biomass Conference held in Lyon (2010) was that SPA is increasingly being used in laboratories and applications and considered as a reliable technique. The main advantages of this technique are very short sampling time and, most of all, the simplicity of the setup and connections. However well trained personnel with expertise in the field is required to use this technique since, despite the simplicity of the sampling, it is based on GC-MS to evaluate the tar content.

4.1.4 On-Line methods

The methods presented until now are off-line techniques. These involve some problems:

- non real-time evaluation of the tar content (very useful for control);
- delay from the sampling and the analysis which could affect the results;
- needs for an analytical instrument (for instance GC-MS) near to the plant.

To fix these issues some on-line methods have been proposed in the last years, this allow to evaluate the gas composition in a very short time and thus are suitable as a tool to monitor the process dynamic; with a proper calibration and calculation software these techniques can provide quantitative information.

The most common technique is micro-GC analysis. However, as reported by Ravel [4] this method is suitable only for light compounds such as benzene and toluene, but cannot provide information for heavier compounds which are usually the main focus of the tar evaluation. It may be considered complementary to a condensation method or the Tar protocol since they are likely to underestimate the light compounds.

Two interesting methods are Molecular Beam Mass Spectrometry (MBMS) and Laser Induced Fluorescence (LIF).

The first one has been addressed by [10] as quantitative technique "real-time" more accurate than the Tar protocol. In this technique the sample is continuously (down to 1 sampling per seconds) forced in a 300 microns orifice and enters into the first of three stages of increasing vacuum. This free-jet expansion results in an abrupt transition to collisionless flow that quenches chemical reactions and inhibits condensation by rapidly decreasing the internal energy of the sampled gases. The result is that the analyte is preserved in its original state, allowing light gases to be sampled simultaneously with heavier, condensable, and reactive species. The components of the molecular beam are then ionized with an electron ionizer (optimized to minimize fragmentation) and then passed in a quadrupole mass analyzer. The MBMS and the Tar protocol were used to measure gasifier tar concentrations in a model compound study and during actual biomass gasification. Both methods showed good reproducibility, but the MBMS method showed better

accuracy. On average, using model compounds, impinger measurements deviated from actual tar concentrations by 11-21%, depending upon the compound, whereas the MBMS measurements deviated on average by only 2-6%. Similar results were obtained during comparative sampling of corn-stover-derived syngas under actual gasification conditions, with the exception that the impinger measurements were even lower relative to the MBMS measurements (28% lower on actual syngas versus 18% lower using model compounds).

LIF has been presented at the 18th European Biomass Conference held in Lyon as viable technique for the on-line identification of PAH [11]. It is based on electronic excitation of gas molecules by means of a laser. As the gaseous species return to their initial state they release energy through light emission (fluorescence), in a wave length larger than the laser, which is measurable and used as an indicator of the gas concentrations. [12] reported the experimental setup of Fig. 4.3. The measuring cell has been specifically designed to allow an optical access. The whole system is kept at 300°C to prevent PAH condensation. The gas is subsequently delivered to a GC-MS. The authors tested the technique with a reference mixture of PAH compounds. The method exhibited a linear relationship between fluorescence intensity and concentration and an accuracy of $\pm 20\%$.

This technique is very interesting since it could be carried even by personnel with not large expertise; however a lot of investigations are required since nowadays the method has been tested only with reference mixtures.



Figure 4.3 - Experimental setup reported by [12] for PAH-LIF.

4.1.5 Tar analysis

Tar analysis is required for several purposes. For instance using SPA it is necessary to perform GC-MS analysis on the desorbed sample to estimate the tar content, and the use of the tar protocol can be coupled with this analysis as well. In addition it widely recognized that the sole tar content information it is not enough to evaluate the gasifier performance or the suitability of a syngas for a certain enduser. Several techniques are reported in the scientific literature, the most applied to tar characterization is Gas Chromatography; this technique allows to separate the tar compounds over a separation column and to identify and quantify them with a proper detector. The most used detectors are MS (Mass Spectrometer) and FID (Flame Ionization Detector), although other detectors have been used in the literature such PID (photo-ionization detector) or TCD (thermo-conductivity detector). GC-MS allows evaluating the composition of tar thus providing both gualitative and guantitative information. A major issue in tar sampling by means of the tar protocol or condensation methods is to determine the water, which is usually mixed to the organic compounds. In the case of the Tar protocol the water content can be estimated with the Karl-Fisher test. In the case of condensation method the overall organic content can be evaluated with a Total Organic Carbon analysis (TOC) or by mans of thermo-gravimetric analysis coupled with Fourier transform infrared analysis (TG-FTIR). This latter technique can be useful also to identify light components. Standard thermo-chemical analyses are usually carried out on tar such as Thermogravimetric analysis (TGA). Ultimate analysis (UA) and Calorimetry. Some others techniques have been applied to PAH such as High Performance Liquid Chromatography (HPLC) and Nuclear Magnetic Resonance (NMR).

4.2 Assessment of a tar sampling system

The main drivers associated to tar sampling in practical applications are the evaluation of the total tar content and the identification of its composition into classes. Tab. 4.1 reports a comparison of the sampling methods described in the previous Paragraph. Focusing on small-medium scale gasification applications MBSM and, in principle, LIF seems not suitable due to the complexity of the technique and the possible high cost of the setup. SPA is widely used in research labs and Universities but it is not likely to be used in small contexts the determination of the tar content in the gas require GC-MS analysis and, therefore, well personnel with expertise in the field. The Tar protocol and the dry condenser methods are more suitable since the tar content can be achieved by gravimetric determination; GC-MS is required in a second stage, if tar classes are required. The Tar protocol setup is far more complex than the dry condenser but it is likely to exhibit better tar collection efficiency. In this Thesis an attempt was made to develop a tar sampling system. The main purpose of this system is to allow reproducible and stable conditions, in order to perform a standardized procedure. The sampling system is based on a condensation method without any solvent or organic media. This method was chosen for two reasons for the simplicity of the setup and to allow fractional condensation of the sampled vapours.

Method	Pro	Cons	Reference
Tar protocol	 high collection efficiency; reproducible; 	 off-line; complex set-up; possible aerosol losses; possible high pressure drop. 	[2,4,6,9,10]
Dry condenser	 simple system; reproducible for heavy tar; no solvent; simple evaluation of the tar content by gravimetric determination 	 off-line; not reliable for water and light hydrocarbons contents. 	[6]
SPA	 short sampling time; believed reliable; no solvent. 	 off-line; may be affected by water content in the gas; GC-MS required even for tar content evaluation; Personnel expertise. 	[4,9]
MBMS	• On-line; • High accuracy;	 Rather complex spectrum interpretation; Personnel expertise; Believed expensive. 	[10]
LIF	 On-line; High accuracy on PAH; Believed simple to be run. 	 Still under development; Tested only for reference mixtures; Needs complementary techniques since it is suitable only for specific tar classes (e.g. PAH); Believed expensive. 	[11,12]

Table 4.1 - Comparison of tar sampling methods.

4.2.1 Sampling system description

The sampling system has been developed in cooperation with Gamba & Botteghi, snc. The system is composed of 3 cabinets maintained at different temperatures which allow to condensate the vapours in 4 glass bottles (30 mm diameter x 150 mm length). A pump at the end of the line operates the sampling, thus the bottles are maintained in vacuum conditions. Fig. 4.4 shows a schematic representation of the main components. The gas entering the system is filtered with syntherized steel filter heated at 200°C, to prevent particle contaminations. The first cabinet contains one glass bottle (1) and its temperature can be modulated with a temperature controller connected to a resistor. This bottle is designed to condense heavy tar and avoid water condensation, thus the temperature can be modulated from 100 to 200 °C. The second cabinet contains two bottles (2A and 2B). The temperature of this impinger can be modulated from 40°C to 0 °C by means of a Peltier cell system. These bottles are designed to condense water and light tar (the purpose of the second bottle is to double the available volume for condensation). The third cabinet contains one bottle (3) and can be chilled from 0 to -15°C by means of a Peltier cell; this impinger is designed to complete water or light organic components condensation. A glass trap in an ice bath and a glass-fibre filter are positioned at the end of the line to prevent any damage to the pump in case of malfunctioning.



Figure 4.4 - Schematic representation of the sampling system.

Fig. 4.5 shows the complete setup as well as some of its components. The filter and the cabinet 1 are seated in a mobile case, connected to a 5 m piping line, which can be heated from 100 to 200°C to prevent condensation in the piping. The piping connects the mobile case with the main frame of the instrument which is a mobile structure where the second cabinet and the third cabinet are positioned. The mobile structure and heated piping allow moving the sampling system in a plant with no limitation associated to the sampling point position. All the regulator of the resistors and Peltier cells are group into a control box positioned over the second case. The four bottles are positioned in a metallic tube with a calibrated spring fixed at its bottom; the metallic tube is supported onto a Teflon or plastic base. The lower part of the metallic tube is threaded thus it is possible to insert or remove it from the bottom of the cabinet. As the metallic tube is screwed up into the cabinet the bottle reach the top of the cabinet, further screwing compress the spring which allow to seal the top of the bottle. The tubing is made of stainless steel and glass in the first case and in the second case, respectively. Small connections are made of Teflon or silicon to avoid very fragile parts. The pump as well as the volumetric counter, rotameters (from 0.1 to 30 L_n min⁻¹) and vacuometer is included in a commercial sampling group.



Figure 4.5 - Pictures of the tar sampling system: (1) mobile case internal, (2) filter with resistor, (3) first cabinet with resistor, (4) second case, (5) control box, (6) heated piping, (7) sampling group, (8) second cabinet with Peltier cell, (9) third cabinet with Peltier cell, (10) glass bottle position in a metallic tube with spring.

4.2.2 Preliminary tests

First of all the sampling system was characterized in terms of collection efficiency, in order to identify the optimal sampling conditions. Two groups of tests were carried one with mineral oil and one with distilled water, in order to quantify the separation efficiency of the system with different components.

The test was made as follow: a known quantity of oil or distilled water was added in a flask; this was positioned in a heated bath and connected to the sampling system though a lateral tube, the top of the flask was left open to maintain the atmospheric pressure in the flask. As the test started the pump of the tar sampling system was activated and heat was provided to the bath. After 40 minutes the amount of sample collected in the bottles was weighted and compared to the mass loss occurred in the flask. The sampling conditions (temperature of the cabinets and gas flow-rate) were changed in order to identify the optimal collection efficiency.

The tests were carried out with flow-rates varying from 1 to $30 L_n min^{-1}$. With empty bottles the collection efficiency was poor (70%) even at $1 L_n min^{-1}$. Therefore it was decided to fill the bottles with packing material in order to increase the contact surface. Bottle 1 and 2A were filled with ceramic rings (1 cm diameter), while

bottles 2B and 3 were filled with glass beads (1 mm diameter); in addition the upper part of bottle 3 was filled with glass wool. With this setup the collection efficiency was increased up to 88%. It must be noted that the collection efficiency could have been affected by oil or water evaporation from the open top of the flask. It was recognized later that a condenser positioned over the flask would have provided a more reliable calculation of the efficiency.

The final temperature setup is reported in Tab. 4.2. The filter is maintained at 200°C to avoid condensation. Cabinet 1 induces a first cooling of the gas to condense the heavy compounds. The piping temperature is kept at to 200°C to prevent condensation. Cabinet 2 is maintained at 20°C to chill dramatically the gas and remove light tar and water. Cabinet 3 is kept at the minimum temperature (-15°C) for further light tar and water removal and to avoid evaporation losses from the bottles.

|--|

Filter	200 °C
Cabinet 1	120 °C
Piping	200 °C
Cabinet 2	20 °C
Cabinet 3	-15 °C

Since the collection efficiency of the system was not completely satisfactory a cooled glass traps with a volume of 2 L was positioned after cabinet 3; the glass trap was filled with glass beads and glass wool in order to ensure complete condensation and protect the sampling group.

4.2.3 Pyrolysis tests

The tar sampling system was further qualified by performing pyrolysis test of woodchips in a batch reactor, in order to perform sampling in conditions similar to the practical applications. The pyrolysis plant is located at CRIBE, a research centre on bioenergy. The aim of this testing was to evaluate the sampling performance of the system in terms of collection efficiency and tar fractionation.

4.2.3.1 Pyrolysis reactor

The pyrolysis reactor (see Fig. 4.6) is part of a system designed for the study of tarcracking processes; this small plant will be described in Chapter 5. The pyrolysis reactor is a stainless steel tube positioned in an electric heater. The upper part of the reactor can be opened screwing up the three screws that block a fitting. The biomass is loaded into the reactor with a perforated basket. The reactor is connected to a gas tank which provides nitrogen to the reactor to maintain an inert environment and remove the gases from the reactor. The nitrogen flow-rate can be regulated with rotameter and a valve. The gas released from the biomass devolatilization leaves the reactor from the top and enters the sampling line, here a certain amount of gas is sampled from the tar sampling system, in this point both pressure and temperature are monitored in order to estimate the sampling condition. The remaining gas moves to the other reactors which are filled with inert materials and maintained at room temperature to condensate tar and water, finally

the gas is sampled and analyzed with a micro-GC and totalized with a volumetric counter. The micro-GC system is described in detail in Chapter 5. Also this sampling point is equipped with temperature and pressure measurements. The tubing before the reactor and until the sampling line are insulated and heated by means of electric resistors above 200°C to prevent water and tar condensation. The reactor head is insulated. Three thermocouples (TC1, TC2, TC3) are positioned at different heights inside the reactor in order to evaluate the temperature profile. TC1 is positioned in the reactor head which is believed to be the coldest point of the reactor. TC2 and TC3 are inserted in the biomass bed formed in the basket at 400 mm and 550 mm from the bottom, respectively. All the thermocouples of the plant are connected to an Agilent Data Logger to convert the signals into data for a PC.



Figure 4.6 - Pyrolysis reactor: (a) schematic flow-sheet, (b) picture of the reactor without insulation and resistors.

4.2.3.2 Testing procedure

The pyrolysis tests were carried out with pre-dried poplar woodchips as biomass, the proximate and ultimate analysis are reported in Tab. 4.3.

Parameter	Sample	Unit	Woodchips
Moisture	bf	%	14.0
VM	dry	%	83.8
FC	dry	%	15.5
ASH	dry	%	0.7
С	dry	%	48.6
Н	dry	%	6.0
Ν	dry	%	0.2
Ο	dry	%	by diff.
Mean size	bf	mm	35x16x7

The pyrolysis conditions are reported in Tab. 4.4. A slow heating rate (10 °C min⁻¹) was chosen in order to let the conditions being as stable as possible despite the discontinuous nature of the system. The finale temperature of 600°C was found to be enough for the purpose of tar production.

Table 4.4 - Pyrol	ysis conditions.
Nitrogen flow	$1.5 \mathrm{m_n^3 h^{-1}}$
Heating rate	10 °C min⁻¹
Final temperature	600°C

The aim of the test was to evaluate mass balance closure of the plant and the tar fractionation of the sampling system.

The testing procedure was the following.

Preliminary operations:

- Weight the glass bottles of the tar sampling system;
- Connect the sampling devices with closed valves (tar sampling and micro-GC);
- Fill the bottom of the loading basket with olivine rocks in order to maintain the biomass in the heated zone of the reactor;
- Weight the biomass;
- Fill the basket with the biomass (nearly 300 g with woodchips);
- Position the thermocouples into the biomass bed;
- Load the basket into the reactor and close the head;

- Connect the thermocouples to the data-logger;
- Open the nitrogen tank and set the flow-rate to $1.5 \text{ m}_n^3 \text{ h}^{-1}$.
- Set the electric heater at 120 °C and keep this temperature for one hour in order to dry the biomass;
- Set the resistors of the tubing at 220 °C;
- Start the micro-GC analysis in order to evaluate the absence of oxygen in the system.

Test operation:

- Start the heating ramp in the electric heater and open the valve to the tar sampling system and start the sampling pump (record the initial volume report by the volumetric counters);
- Once the TC3 temperature has reached 600 °C wait for the carbon monoxide concentration to go below 0.1% this is considered as an indicator of pyrolysis ending;
- Close the valve of the tar sampling and set 100 °C in the electric heater.

Final operations:

- Disconnect the tar sampling system, weight the glass bottles and record the sampled gas volume;
- As the TC3 temperature goes below 100°C stop the nitrogen flow;
- Switch off the electric heater and resistors of the tubing;
- Remove the basket from the reactor and weight the produced char.
- Collect char and liquid samples for laboratory characterization.

Mass balance calculations:

- Evaluate the mass loss during the test as the difference between the initial weight of dry woodchips and the char weight;
- Calculate the total mass of gas produced considering nitrogen as inert tracer;
- Evaluate the sampled condensate weight as the difference between the final glass bottle weight and the initial weight;
- Calculate the total condensate production as a linear proportion between the sampled volume and the total gas volume produced;
- Evaluate the total mass balance closure.

4.2.3.3 Results

The test encountered several operating problems, mainly due to losses of gases from the plant fittings. The reason was the quick pressurization of the system as the devolatilization started. In the end three tests (namely Test 1, Test 2 and Test 3) were considered reliable for the qualification of the pyrolysis and the tar sampling systems.

4.2.3.3.1 Pyrolysis evolution

The pyrolysis process is monitored by means of the thermocouples and the Micro-GC. Fig. 4.7 reports the temperature evolution as well as the gas composition evolution (except nitrogen which is the complement to 100%) during Test 1. It can be noted that despite the heating rate ramp was set to 10 °C min⁻¹, this value is not constant during the test and its mean value is slightly lower than the one specified. The three thermocouples show very different temperature. TC1 which is placed in the reactor head exhibits the lowest temperature. TC3 is in the reactor heart and reveal the highest temperature and it is the only one who reaches the set point specified in the controller of the electric heater (600 °C), TC2 is somewhat intermediate but closer to TC1; it can be noted that the reactor is far from being isothermal and consequently the biomass experience different thermal history depending on the position in the basket. However TC3 can be considered the main reference to interpret the gas composition evolution. Up to 180°C the gas is almost 99.9% nitrogen, subsequently the pyrolysis gases start to be released slowly. Notably the micro-GC follows fairly well the process dynamic in this range with an analysis every three minutes. As TC3 reaches 280 °C a sudden change in the composition occurs: the nitrogen content goes down to 77% and the carbon monoxide content increase dramatically from 1% to 11%. Clearly, despite the very slow heating rate, a sort of critical point is reached and the reaction reaches its maximum rate. The compositions are somewhat stable for nearly five minutes, subsequently another dramatic change in the composition occurs and the CO content goes down to 5% and the nitrogen content increases to 88%. It is worthy to note that in this stage of the process the micro-GC cannot follow the process due to the sampling time which is to slow (3-4 minutes) compared to the devolatilization dynamic. From this point (TC3 400°C) the overall content of pyrolysis gases start to decrease and in twenty minutes the nitrogen content returns above 99% (99.3%) and the TC3 temperature is 613 °C. Therefore the devolatilization and the tar production can be considered complete and the electric heater is stopped and the reactor start to cool down, in twenty minutes the micro-GC reveals only nitrogen.

At time 45 min there is an increase in the gas generation even if the process is close to be complete, this is likely to occur due the different temperature achieved in different regions of the reactor.

It is worthy to note that as the devolatilization rate dramatically increases (time 25 min, TC3 280 °C), the TC2 temperature is 210°C thus a lower different devolatilization rate can be assumed in this region of the reactor.

Most importantly the TC1 value is 160°C, as a consequence when the tar generation is strong the head temperature is not hot enough to prevent tar condensation (in particular heavy tar); therefore it is likely that some heavy compounds may condense onto the reactor head.



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Figure 4.7 - Temperature evolution in the pyrolysis reactor and gas composition (nitrogen is the complement to 100%) as function of test duration.

Tab. 4.5 reports indication about the woodchips pyrolysis behaviour. The comparison of the woodchips and char proximate analysis indicate that the sample are not completely devolatilized, even if the volatile matter reduction is large (from 80 to 15-20%). This is likely to be due to the temperature distribution in the reactor. In addition the devolatilization condition are different in the pyrolysis reactor and TGA, in the first the particle size is that reported in Tab. 4.3, while in TGA the sample is milled to less than 1 mm, as a consequence the temperature distribution in the particle is different and the devolatilization more efficient. The char composition is very similar for Test 2 and Test 3, Test 1 exhibits higher ash content, however on dry ash free basis the carbon content of the material is similar for three chars (~87%), which is an indicator of the test reproducibility.

CHAR	Sample	Unit	Test 1	Test 2	Test 3
VM	dry	wt%	18.4	13.2	15.0
FC	dry	wt%	70.9	80.2	80.0
ASH	dry	wt%	10.7	6.6	5.0
С	dry	wt%	77.6	81.4	83.4
Н	dry	wt%	3.0	2.6	2.6
Ν	dry	wt%	0.6	0.6	0.4
0	dry	wt%	by diff.	by diff.	by diff.
GAS					
СО	dry N ₂ free	vol%	44.6	41.0	41.5
CO2	dry N ₂ free	vol%	24.8	25.7	22.5
H2	dry N ₂ free	vol%	9.8	13.9	16.8
CH4	dry N ₂ free	vol%	14.5	14.2	13.3
C2H2	dry N ₂ free	vol%	0.5	0.4	0.5
C2H4	dry N ₂ free	vol%	5.4	4.4	5.1
C2H6	dry N ₂ free	vol%	0.4	0.4	0.4

Table 4.5 - Mean pyrolysis gas composition, char proximate and utimate analysis

Concerning the gas composition, carbon monoxide is the most abundant compound followed by carbon dioxide; ethylene and methane are the most abundant hydrocarbons. The gas composition are rather stable in the three tests, except for hydrogen which varies from 9.8% (Test 1) to 16.8% (Test 2); however on a mass basis this variation is much less important.

4.2.3.3.2 Tar sampling

The tar sampling system was able to condensate the vapours and separate the produced liquid into four different fractions (namely F1, F2A, F2B, F3). However some issues were raised during the sampling.

As highlighted in the previous Paragraph the devolatilization evolution reaches a critical point when TC3 signals 280 °C and a quick release of gases occur, this phenomena immediately pressurizes the reactor and was the cause for some tests to fail due to lack of containment from the fittings. No condensate was visible in the glass tubing of the system in the second case up this point. Subsequently the glass tubing were immediately filled of a white fog and a black liquid flowing into F2A was visible; notably for one minute the gas outlet temperature was considerably higher (more than 20°C) than that set in cabinet 3. This quick pressurization affects negatively the removal efficiency of the system. As a matter of fact the condensation of the lighter compounds in cabinet 3 was not complete at this stage; therefore the cold trap was filled with some sallow condensate. This was the most important effect on the collection efficiency; however some others issues encountered during the tests are presented in the following list:

- As the pressurization started the vacuometer of the sampling group passed from -0.1 bar to -0.3 bar and the sampling rate passed from 15 to nearly $10 L_n min^{-1}$; this indicate a reduction of the pressure in the tar sampling system and was imputed to partial plugging of the filter due to heavy tar condensation.
- The sampling connection from the pyrolysis reactor is maintained at nearly 350°C and no tar condensation was observed here, however the clamp connections cannot be covered with the resistors because the Viton gasket would break-up at this temperature, consequently some heavy tar compounds condense here despite the temperature is above 200°C.
- One minute after the pressurization the gas outlet temperature becomes cool and after some minutes no additional condensation is visible in the glass tubing revealing a dramatic reduction of the vapours concentration; consequently an almost dry nitrogen stream flows in the bottles eventually producing aerosol (in particular the nitrogen gurgles in bottle 2B and drag the liquid to bottle 3) and evaporating some liquids, this was the reason for stopping sampling and pyrolysis at 600°C.

Some observations for enhancing the quality and the performance of both the sampling system and the qualification pyrolysis test can be drawn:

- The sampling flow-rate 10-15 L_n min⁻¹ seems to be too high compared to the volume of the glass bottles (the residence time is nearly 0.02 s), using a 1 L_n min⁻¹ would let to higher separation efficiency (as highlighted in the preliminary tests); however in order to collect a sufficient amount of tar samples a high sampling rate had to be used, due to the sudden and short release of vapours from the pyrolysis.
- The steel filter is a very efficient protection; however using a filter with higher porosity would reduce the chance of plugging.

- It is mandatory to maintain the sampling line before the first cabinet over 200°C and avoid cold spots where heavy tar is likely to condense; the Viton gaskets can be substituted with copper gaskets.
- The present pyrolysis test is not very reliable to test the separation efficiency of the tar sampling system. From residence time distribution curve point of view, the batch pyrolysis provide a sort of Dirac input to the sampling system, which is not very representative of the sampling conditions on a gasifier or pyrolysis reactor where steady sampling are achieved.
- In order to improve the reliability of the qualification pyrolysis tests it is mandatory to perform as much as possible steady conditions. This can be carried out providing the pyrolysis reactor of feeding system which allows to feed continuously the biomass. By this way it is possible to heat the reactor without the biomass and achieve a more uniform temperature distribution. As the nominal temperature is reached it is possible to start a stable feeding. The new feeding system has been designed and it is based on a star valve place over the reactor head.

Fig. 4.8 shows a picture of the condensate products collected in the four glass bottles after test 1. F1 is a dark brown very sticky and dense fluid; it must be removed from the glass bottles as soon as possible after the sampling stop with a spoon. As the temperature decrease F1 becomes very viscous and it is very difficult to remove it from the glass bottle and recover the ceramic rings. F2A is again a dark brown fluid but is far less viscous than F1, more or less like heavy oil. F2B and F3 are wine-like liquids far less viscous than F2A, their tonality changed from test to test. F2A, F2B and F3 can be easily removed from the glass bottles by pouring the ceramic rings soaked with liquids over a metallic or plastic net placed above a beaker. As an indication of the different viscosity it is necessary to wait ten minutes to collect most of the condensate from F2A, while in one minute the glass beads have lost almost all the F2B and F3 condensate (which are then likely to contain water). All the four fractions are strongly smelly and it is necessary to wear gloves and safety mask to manage them.

All the tubing and surface where tar may adhere were weighted, in order to evaluate the collection efficiency of the glass bottles. It was found that the condensate in the bottles ranges from 90 to 98% of the total condensate. This result is somewhat unsatisfactory since one of the main objectives of the sampling system is to attain an easy and quick procedure for determining the tar content.

Tab. 4.6 reports the relative proportion of condensate collected in each bottles, the trap content is added to F3 since the liquid in the trap is mainly due to dragging of the condensate in F3. It can be noted that the light fractions F3 is always the most abundant fraction and, in general, the lighter fraction (F2B+F3) are always more than 70% of the total. However, except from these observations, the three tests resulted to be quite dissimilar. This discrepancy is likely to be related to the aforementioned problems of the sampling system and not to the pyrolysis test which (see Tab. 4.4) was fairly reproducible.

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Table 4.6 - Fractionation of the sampled condensate in the four bottles.						
	Fraction	Unit	Test 1	Test 2	Test 3	
	F1	wt%	10	9.5	3.2	
	F2A	wt%	17	13.5	10.1	
	F2B	wt%	11	28	16.5	
_	F3	wt%	62	49	70.3	



Figure 4.8 - Picture of the four glass bottles after a pyrolysis test.

4.2.3.3.3 Mass balance

The evaluation of the condensate collection efficiency can be made on the basis of the mass balance of the plant. The procedure has been illustrated in the previous Paragraph and the results are reported in Tab. 4.7. It can be noted that it is not possible to close the mass balance for the woodchips pyrolysis and thus it is not possible to evaluate the collection efficiency of the sampling system. The closure of the balance is always below 100% (from 77 to 87%), thus indicating some underestimation of the produced macro-products. The estimations involved in the calculation of the mass balance are the following:

- woodchips weighting;
- char weighting;
- sampled condensate weighting;
- rotameter reading;
- micro-GC analysis;
- acquisition of the total sampled volume and the produced gas volume.
The weighting operations are not likely to introduce such errors in the balance, even if (as discussed before) some error may arise from the condensate sampling.

The rotameter reading is not likely to introduce errors, since is specifically calibrated for nitrogen. Finally the main source of errors can be attributed to the micro-GC analysis and the volumetric counters.

As observed in Paragraph 4.2.3.3.1 the micro-GC sampling frequency is slow compared to the devolatilization dynamic during the quick release of gases, this stage of the process is represented with two data and an average composition is calculated over this period. Notably this practice may lead to large underestimation of the released gases since in this stage most of biomass volatile matter is released.

Concerning the volumetric counters these may introduce large errors since the sampled gas is different from the calibration gas.

1 abie 4.						
Fraction	Unit	Test 1	Test 2	Test 3		
Dry woodchips	g	258.8	258.5	259.4		
Char	g	54.9	61.1	62.1		
Condensate	g	69.5	74.5	70.4		
Dry gas	g	75.4	88.3	86.9		
Balance closure	%	77	87	85		

Therefore the pyrolysis setup should take into account the following remarks in order to achieve a better closure of the mass balance:

- Integrate the evaluation of the gas composition with an FTIR system (at present under commissioning and described in Chapter 5), this instrument allows a real-time monitoring of the gas composition evolution leading to lower errors in the estimation of the produced gas; however the micro-GC has to be used in order to evaluate the nitrogen and hydrogen contents.
- Deliver all the gas exiting from the pyrolysis reactor to the sampling system in order to avoid the calculation of the total condensate production on the basis of two different volumetric counters, this imply using a lower nitrogen flow-rate (< 10 L_n min⁻¹).

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4.3 Assessment of a tar characterization methodology

The fractions collected were subjected to four different characterization techniques: TGA, UA, TG-FTIR, GC-MS.

4.3.1 TGA

In this Thesis TGA is manly employed to determine the proximate analysis of solid samples or their reactivity as in Chapter 3 and Chapter 5. Here it is presented as a first screen of the nature of the four collected fractions.

4.3.1.1 Instrument and methodology

The TGA used in this Thesis is a TA instruments-Q500 type. The analyzer is composed of central body, an external heat exchanger and a connection to a PC. The central body is formed of a furnace and micro-balance. The sample (10-15 mg) is usually placed in an alumina crucible which is positioned on a plate hanged to one branch of the micro-balance which is inside the furnace. The furnace is continuously fluxed with a gas stream to control the reaction atmosphere and remove the degradation products generated by the thermal treatment. The temperature control is based on a thermocouple positioned in the proximity of the crucible. The analyzer requires a periodic calibration of weight and temperature. The temperature of the system is 1000° C; the heating rate can be varied from 0 to $100 ^{\circ}$ C min⁻¹. The microbalance resolution is 0.1 micro-grams. It is possible to set different thermal history of the sample (by varying temperature, time and heating rate) and gas atmosphere.

The condensate samples are mixtures of water and organic compounds, therefore it is not possible to separate their moisture content and their volatile matter content, since heating up the samples would lead to the release of organic compounds even at very low temperature. Consequently the sample characterization was carried out with following procedure:

- heating ramp from 20°C to 800°C at 20°C min⁻¹ with nitrogen as gas in order to release all the volatile compounds (moisture + organics);
- switching the gas to air and maintain the temperature at 800°C in order to oxidize the eventual organic residue.

With this procedure it was possible to identify three fractions:

- volatiles (as moisture + organics);
- fixed carbon (organic residue);
- ash (final residue).

In addition the temperature ramp can provide a finger-printing of the composition of the four fractions.

4.3.1.2 TGA Results

The TGA analysis of the four fractions resulted as a useful tool for a preliminary characterization of the samples and to assess the reproducibility of the sampling.

Fig. 4.9 shows a comparison of the mass loss rate (dTG) of the sample as function of the temperature. The dTG curve can be considered as an indication of the boiling range of fractions or, at least, of their molecular weight. However it must be taken into account that a further heating of the fractions may also lead to thermal decomposition rather than evaporation.

The three tests exhibit similar trend. As expected the mass loss of F1 is at the highest temperature, the dTG peak is usually between 230 and 250 °C and the mass loss is appreciable up to 400°C. F2A exhibits a dTG curve at lower temperature, with an appreciable mass loss up to 300°C. F2B is concentrated toward lower temperature, the dTG peak is close to 100°C and the mass loss occurs until 250°C. Finally, F3 is the lightest fraction with a dTG peak at 100°C and mass appreciable up to 150°C. It is worthy to note that from F1 to F3 the mass loss range become narrower and the peak intensity is higher. This may indicate that F1 is composed of a broad range of different compounds with different boiling point and molecular weight, and that moving toward F3 the fractions become more concentrated in a smaller number of components. In particular given the position of the dTG peak of F2B and F3 (~100°C), it is likely that these fractions contain a large amount of water.

These observations are confirmed by the analysis of the TG profiles of the four fractions which allow dividing the mass loss in VM (moisture+volatile compounds), FC and ASH (Tab. 4.8). Moving from F1 to F3 the VM content increases and FC content reduces. The presence of the fixed carbon may indicate some degradation of the organic compounds occur due to the heating. The comparison of the proximate analysis and the dTG curves of the four fractions can be an indication of the test and sampling reproducibility. It can be noted that F2A, F2B and F3 are rather similar both in the composition and in the dTG curve shape. F3 is somewhat variable both in the relative VM and FC content.





Figure 4.9 - dTG curves of the four fractions obtained in the three tests.

Test 1	Unit	VM	FC	ASH
F1	wt%	85.5	13.7	0.8
F2A	wt%	93.5	6.1	0.4
F2B	wt%	95.4	4.1	0.5
F3	wt%	99.6	0.0	0.4
Test 2				
F1	wt%	88.6	11.0	0.3
F2A	wt%	93.2	6.5	0.3
F2B	wt%	95.6	3.9	0.5
F3	wt%	97.6	2.1	0.3
Test 3				
F1	wt%	82.7	16.1	1.2
F2A	wt%	92.1	7.5	0.5
F2B	wt%	95.4	4.2	0.4
F3	wt%	98.8	0.8	0.4

Table 4.8 - Proximate analysis of the four fractions collected in three tests.

4.3.2 TG-FTIR

TGA was able to give a first finger-printing of the tar fractions. However in order to evaluate the tar production it is fundamental to assess the water content in the four fractions, to this purpose TG-FITR was used.

4.3.2.1 Instrument and methodology

TG-FTIR analysis is based on the simultaneous measurements of the on-line analysis of volatile compounds formed during TG runs; this is carried out coupling an FTIR spectrometer and a TG balance [13]. Thermogravimetric data are obtained using a Netzsch STA 409/C thermoanalyzer. A constant heating rate of 10 °C min⁻¹ is used in all experimental runs, from 15 to 500 °C. The typical sample weight is 10-20 mg. Experimental runs are carried out using a purge gas flow (60 ml/min) of pure nitrogen. FTIR measurements are carried out using a Bruker Equinox 55 spectrometer, equipped with MCT detector and a specifically developed low volume gas cell (8.7 ml) with a 123mm path-length, heated at a constant temperature of 250°C. The transfer line and the head of the TG balance are heated at a constant temperature of 200 °C to limit the condensation of volatile decomposition products. During TG-FTIR runs, spectra were collected at 4cm⁻¹ resolution, co-adding 16 scans per spectrum. This resulted in a temporal resolution of 9.5s, more than sufficient to follow the gas evolution rates characteristic of TG runs at heating rates of 10°C min⁻¹. It is worthy to note that TG-FTIR may be used

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for a qualitative and quantitative analysis of the compounds released by the tar fractions. However, this requires the availability of a wave-number absorption interval of the compound of interest free of additional contributions from other substances. The contemporary formation of a wide number of volatile compounds complicates the selection of these intervals. TG-FTIR data were used for a quantitative determination of the water content in the tar fractions. The calibration was carried out with distilled water runs according to the vaporization-based pulse method [14].

4.3.2.2 TG-FTIR Results

Given the rather good reproducibility of the fraction thermal behaviour obtained from TGA, the TG-FTIR analysis was carried only on the fractions obtained from Test 2. Figure 4.10 reports an IR spectrum achieved in correspondence of the maximum mass loss rate of F3 due to the temperature ramp in nitrogen in the thermogravimetric analyzer. It can be noted the presence of water between 4000 cm⁻¹ and 3500 cm⁻¹. A specific wave number range (3792-4025 cm⁻¹) is used for the evaluation of the water content, integrating the integral absorbance signal over the analysis time [14]. As mentioned before the TG-FITR analysis can provide indications of the presence of organic compounds, for instance the absorption range between 3100 cm⁻¹ and 2750 cm⁻¹ indicates the presence of both saturated and unsaturated carbon-hydrogen bonds, while the absorption peak at 1700-1800 cm⁻¹ indicate the presence of carbonyl groups. The spectrum reveals also the presence of light organic compounds (which are more easy to be recognized) such as methanol and formic acid (not highlighted in Fig. 4.10). As aforementioned the large number of different compounds does not allow for the specific identification of heavier molecules, due to signal overlapping.



Figure 4.10 - IR spectrum obtained in correspondence of the maximum mass loss rate of a sample of F3 in the TG.

Tab. 4.9 reports the water content of the four fractions. The water content of the four fractions increase from F1 to F3. F1 is almost dry and this can expected since this fraction is collected at 120°C. In the other fractions the water content is more remarkable, in particular F2B and F3 contain large amount of water; this last result confirms the observation drawn from the analysis of the dTG curves. Given the water content of each fraction the total amount of water collected in Test 2 is 36.4% of the total condensate.

Test 2	Unit	Water
F1	wt%	1.0
F2A	wt%	11.8
F2B	wt%	26.3
F3	wt%	56.1

Table 4.9 - Water content of the four fractions collected from Test 2.

4.3.3 UA

In this Thesis UA is manly employed to determine the ultimate analysis of solid samples as in Chapter 3 and Chapter 5. Here an attempt is made to apply it to the characterization of the condensate fractions.

4.3.3.1 Instrument and methodology

The ultimate analysis is carried out with the instrument LECO TruSpec CHN. This instrument is designed for the analysis of organic compounds. It is composed of a furnace heated by a resistor up to nearly 1000°C and fluxed with pure oxygen and three detectors: TCD for nitrogen, IR for carbon and hydrogen. The operating principle is based on the quick and complete combustion of the sample (which is loaded in tin foil) in the furnace at 950°C in pure oxygen; the complete combustion is ensured by a second chamber maintained at 850°C and filled with catalysts. The combustion products (carbon dioxide, water and nitrogen oxides) are collected in a 4.5 L tank where the gas sample becomes homogeneous. A certain amount of gas is then delivered to the IR detectors, for the evaluation of the water and carbon dioxide content in the gas. Another portion of the gas is carried in helium flux to a copper based catalyst for nitrogen oxide reduction to pure nitrogen which is detected in the TCD. The instrument is connected to a PC for data acquisition and recording. After calibration of the instrument with standard compounds (usually EDTA) it is possible to determine the percentage of carbon, hydrogen and nitrogen in the sample. The analysis duration is rather short (~ 4 minutes) and it is possible to analyze sample quantity up to 1 g. Tab. 4.10 reports the measurement range and precision for the three elements on the basis of 500 g sample.

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	Range	Precision
С	0.005%-50%	0.5% RSD
Н	0.02%-50%	1% RSD
Ν	0.008%-100%	0.5% RSD

Table 4.10 - Measurement range and precision of the ultimate analyzer.

The solid samples are usually milled and dried overnight before being analyzed. The sample must be as much as dry as possible in order to perform a good analysis, since the moisture contained in the sample increase the water content in the gas thus leading to an overestimation of the hydrogen content. Another issue of the analysis is the combustion behaviour of the sample, since it fundamental to perform a complete combustion of the sample in order to perform a good analysis. Therefore according to the nature of sample (for instance the volatile matter content determined from the proximate analysis) it is possible to select the proper combustion method by regulating the oxygen flux to the furnace. Two methods were used in this Thesis. The method "Biomass" is generally applied to sample with high volatile matter (such as woodchips), since the quick release of combustible gases it is important to provide a large amount of oxygen in the initial stage. The method "Coal" is applied to sample with low volatile matter (such as char), in this case it is important to operate a complete combustion of the solid matrix, and therefore the total combustion time is more than the double of the "Biomass" method.

As far as F2B and F3 contain large amount of water (see Tab. 4.8), it is not possible to apply ultimate analysis to this fractions. Therefore the analysis was carried out for F1 and F2B, even if some errors are likely to arise in the latter. Due to the large amount of VM (see Tab. 4.8) the method "Biomass" was used in the analysis, in addition a double tin foil was used to avoid liquid escape.

4.3.3.2 UA Results

Tab. 4.11 reports the ultimate analysis of F1 and F2A collected from the three tests. The comparison of the values of the different tests highlights that the ultimate analysis of F1 is largely reproducible, more than observed with TGA. Concerning F2A the results are not reproducible, both the hydrogen and the carbon content vary widely among the three tests; this is likely to be related to the rather high content of water in these samples and no major observations can be drawn for this fraction. F1 is a highly oxygenated fraction (nearly 30%), as confirmed by the presence of methanol and the carbonyl groups in the FTIR analysis. Therefore this fraction is likely to contain not only hydrocarbons but also species like phenols, ethers, carboxylic acids etc.

Test 1	Unit	С	н	N	ASH	0
F1	wt%	62.4	6.5	0.4	0.8	by diff.
F2A	wt%	44.6	7.8	0.1	0.4	by diff.
Test 2						
F1	wt%	62.1	6.7	0.4	0.3	by diff.
F2A	wt%	62.1	7.3	0.2	0.3	by diff.
Test 3						
F1	wt%	61.6	6.4	0.3	1.2	by diff.
F2A	wt%	55.7	6.7	0.1	0.5	by diff.

4.3.4 GC-MS

GC-MS was used as a characterization tool in order to provide qualitative information on the composition of the four fractions.

4.3.4.1 Instrument and methodology

A Fisons MD 800 quadrupole mass spectrometer interfaced to a Fisons GC 8060 gas chromatograph was used for gas chromatography/mass spectrometry (GC/MS) analysis. A Mega SE30 fused silica capillary column (25m length, 0.32mm internal diameter, cross-bonded, 0.25 μ m film thickness) was employed for the chromatographic separation, with helium as carrier gas. The column temperature programme was the following: 5min isothermal at 40°C, heating to 250°C (6°C/min), then 20min isothermal. An injector temperature of 250°C and split-less mode were used. Mass spectrometric detection was performed in full scan conditions (scan range, m/z 10-819) in electron impact ionization mode. The condensed products were dissolved in acetone solution and then analyzed.

The mass spectra obtained for each degradation product were analyzed in order to obtain information about the molecular mass and the molecular structure. The structural identification of the products was achieved by comparison of their mass

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spectra with the best fits found in the NIST library or by analysis of the fragmentation patterns. In this Thesis GC-MS analysis was carried out only to get qualitative information, however quantitative analysis can be carried out with the use of standard mixture and calibration standards.

The GC-MS analysis was carried out only for Test 2.

4.3.4.2 GC-MS Results

Fig. 4.11 compares the total ionic current chromatogram obtained for the four fractions collected after Test 2. It is clear that the fractions are composed of complex mixtures of products. Many compounds can be identified in all the four fractions. Nevertheless F1 seems to contain the heaviest compounds. This fraction contains the compounds with the highest retention times and lacks some light compounds (compounds with low retention times which can be identified in the other fractions). F2A and F2B are almost identical from a qualitative point of view, so the main difference between the two fractions seems to be water content. Finally F3 contains only the lightest compounds. Tab. 4.12 shows the results of GC-MS qualitative analysis of the four fractions. It is worthy to note that the presented compounds must be considered as representative of a certain class, since it is not possible to identify isomers or the exact position of a group.



Figure 4.11 - Total Ionic Current Chromatogram obtained through the GC-MS analysis of the four fractions collected after Test 2.

It was not possible to indentify all the compounds present in the fractions due to the complexity of the fractions. The organic fraction are mainly composed of class 1 and class 2 tar (see Chapter 1), class 4 tar (anthracene and naphtol in F1 and naphthalene in F2A) seems to be less abundant. No class 5 (heavy PAH) are identified, this can be attributed both to the low maximum pyrolysis temperature $(600^{\circ}C)$, and to the relatively low temperatures of the pyrolysis system (< $400^{\circ}C$) where these compounds can easily condense before reaching the sampling system. Some low molecular weight compounds can be recognized in F2A and F2B such as furan, butyrolactone, aldhehydes, ketons, cyclic alkenes. Notably many oxygenated compounds with methoxy or hydroxy groups are identified. This confirms the result of the ultimate and TG-FTIR analysis where a certain extent of oxygen is observed. Compared to TGA, GC-MS indicates the lack of light compounds in F1 and the presence of very high boiling compounds (such as anthracene), this is in agreement with the TGA results. On the other hand, organic compounds more volatile than phenol can only be found in F2A, F2B and F3 fractions. Furthermore, these fractions may contain high-volatile compounds which are not detected by GC-MS analysis due to a retention time similar to the solvent (e.g., methanol which was identified by TG-FTIR analysis). It is worthy to note that many of the components of F1 can be found also in F2A and F2B and F3. An inspection of the results reported in Fig. 4.11 also reveals a different product distribution in F1, F2A, F2B and F3. In particular the presence of low volatile compounds decreases from F1 to F3. The different organic product distribution as well as the different water content may well explain the different physical appearance (very viscous fluid vs. oily liquid or almost water-like) of the four fractions.

Fraction: F1					
Compound	MW [g mol ⁻¹]	Тb [°С]			
phenol	94	181.7			
1,2-benzendiol	110	245.5			
2-methoxy-4-methyl-phenol	138	220			
3-methoxy-1,2-benzendiol	140	-			
1-hydroxy-2-acetyl-4-methyl-benzene	150	-			
4-ethyl-2-methoxy-phenol	152	-			
2,6-dimethoxy-phenol	154	261			
7-methyl-1-naphtohl	158	-			
2-methoxy-4-(1-propenyl)-phenol	164	-			
1,2,4-trimethoxy-benzene	168	-			
anthracene	178	340			
3,5-dimethoxy-acetophenone	180	-			
1,2,3-trimethoxy-5-methyl-benzene	182	-			
2,6-dimethoxy-4-(2-propenyl)-phenol	194	-			
4-hydroxy-3,5-dimethoxy-acetophenone	196	-			

Table 4.12 - Organic species identified by GC-MS analysis in the four fractions ofTest 2.

Fraction: F2A and F2B					
Compound	MW [g mol ⁻¹]	Тb [°С]			
2-methylfuran	82	65			
butyrolactone	86	204			
phenol	94	181.7			
2-methyl-2-cyclopenten-1-one	96	-			
3-furaldehyde	96	161.7			
3- methyl-2-cyclopenten-1-one	96	-			
2-furanmethanol	98	170			
2-methyl-phenol	108	191			
1,2-benzendiol	110	245.5			
2-hydroxy-3-methyl-2-cyclopenten-1-one	112	-			
3,5-dimethylphenol	122	222			
4-methoxy-phenol	124	-			
3-ethyl-2-hydroxy-2-cyclopenten-1-one	126	-			
naphthalene	128	218			
2-methoxy-4-methyl-phenol	138	220			
3-methoxy-1,2-benzendiol	140	-			
1-methyl-naphthalene	142	240			
4-hydroxy-2-methyl-acetophenone	150	-			
2,3-dimethoxy-toluene	152	-			
4-ethyl-2-methoxy-phenol	152	-			
2,6-dimethoxy-phenol	154	261			
2-methoxy-4-(1-propenyl)-phenol	164	-			
2-methoxy-6-(2-propenyl)-phenol	164	-			
2-methoxy-4-(2-porpenyl)-phenol	164	256			
1,2,4-trimethoxybenzene	168	-			
3-tert butyl-4-hydroxyanisole	180	265			
1,2,3-trimethoxy-5-methyl-benzene	182	-			
2,6-dimethoxy-4-(2-propenyl)-phenol	194	-			
4-hydroxy-3,5-dimethoxy-acetophenone	196	-			

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Fraction: F3				
Compound	MW [g mol ⁻¹]	Тb [°С]		
2-methylfuran	82	65		
phenol	94	181.7		
2-methyl-2-cyclopenten-1-one	96	-		
3-furaldehyde	96	161.7		
3- methyl-2-cyclopentan-1-one	98	-		
3-furanmethanol	98	170		
2-methyl-phenol	108	191		
1,2-benzendiol	110	245.5		
4-methoxy-phenol	124	-		
3-ethyl-2-hydroxy-2-ciclopenten-1-one	126	-		
2,5-dimethoxy-tetrahydrofuran	132	-		
2-methoxy-4-methyl-phenol	138	220		
3-methoxy-1,2-benzendiol	140	-		
1-hydroxy-2-acetyl-4-methylbenzene	150	-		
4-ethyl-2-methoxy-phenol	152	-		
2,6-dimethoxy-phenol	154	261		
2-methoxy-4-(1-propenyl)-phenol	164	-		
2-methoxy-6-(2-propenyl)-phenol	164	-		
2-methoxy-6-(1-propenyl)-phenol	164	-		
1,2,4-trimethoxybenzene	168	-		
3,5-dimethoxy-acetophenone	180	-		
4-hydroxy-3,5-dimethoxy-benzaldehyde	182	-		
1,2,3-trimethoxy-5-methyl-benzene	182	-		
2,6-dimethoxy-4-(2-propenyl)-phenol	194	-		
4-hydroxy-3,5-dimethoxy-acetophenone	196	-		

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4.4 Summary

This Chapter reported the qualification procedure of a tar sampling system as well as the experimental methodology used for the tar characterization. The qualification of the sampling system involved the development and testing of a pyrolysis reactor. Slow pyrolysis of poplar woodchips was carried to test the capabilities of the system. It was found that the current experimental setup does not allow a totally reliable evaluation of the sampling capabilities. In order to enhance the testing capabilities of the system the most remarkable improvements are:

- use a lower sampling flow-rate (1 L min⁻¹);
- maintain higher temperatures in the pyrolysis reactor tubing (350°C would be the best);
- provide a continuous biomass feeding in order to maintain stable pyrolysis conditions and avoid sudden increase of the pressure;
- integrate the micro-GC gas sampling with an FTIR system in order to achieve a real time monitoring of the gas composition evolution.

As far as the tar characterization methodology is concerned the following observations can be drawn:

- TGA is a helpful tool for a preliminary screening of the fractions and can provide an indication of the boiling point range;
- FTIR analysis is a very important tool to properly determine the tar content, since it allows to evaluate the water content in the fractions even in sample with a very high amount of water;
- UA is somewhat the less useful technique since the rather high water content of the fraction makes the sample unsuitable for this analysis;
- qualitative GC-MS is a very useful technique to estimate the tar classes and nature of tar components.

The results of the characterization of the four fractions lead to following conclusions:

- the four fractions exhibit a different water content, which increases from F1 to F3, as consequence the tar sampling system is capable to fractionate the condensate;
- the chemical composition of the four fractions is somewhat similar from a qualitative point of view and it is mainly composed of oxygenated compounds with one aromatic ring; however it is worthy to note that very light compounds cannot be detected by GC-MS due to a retention time similar to the solvent, in addition heavy compounds (if any are generated from the slow pyrolysis) are likely to condense before they can reach the sampling system.

5. DEVELOPMENT AND TESTING OF A PILOT SCALE BIOMASS GASIFICATION FACILITY

In this Chapter the development of a pilot scale biomass gasification facility is described. The facility is part of the research centre on energy biomass (CRIBE – Centro di Ricerca Inter-Universitario Biomasse da Energia), which is devoted to study several biomass valorisation and exploitation platforms. The core of the plant is a 200 kWth downdraft throated gasifier, which has been the main subject of work on the facility. First of all a brief review of the scientific literature related to downdraft gasifiers is reported for comparison. Subsequently the facility components and analytical instruments and methodology are described. Finally the tests carried out as well as the results achieved are presented.

5.1 Literature review on recent studies about downdraft biomass gasifiers

Chapter 1 has been devoted to highlight the status of biomass gasification and challenges that this technology is facing nowadays. This Paragraph is aimed to provide a brief survey of the recent literature involved in biomass gasification with downdraft gasifiers. Obviously, this survey does not reflect the real state of the art nor can be complete, since a lot of work in the field is carried out from private companies interested in technological development but not in academic publications. However it is believed that scientific publications can be a fair indicator of the main drivers of the interest in biomass gasification. As pointed out in Chapter 1, biomass gasification with air in a downdraft gasifier coupled to ICengine is maybe the most common application of biomass gasification. This is somewhat widespread in developing country with important rural areas, like India, where there is large need for electrification. As mentioned in Chapter 1 research on biomass gasification has been gaining importance in last fifteen years and much attention has been paid to downdraft gasification. The research in this field has been devoted to improve the performance, to test different fuels, to increase the user-friendliness and also to find other uses for the gas than in an IC-engine, for example liquid fuel production.

Most downdraft gasification studies include wood derived materials as feedstock. cut in different shapes such as chips or briguettes [1-6], and some attention has been paid to hazelnut shells [7-9]. Peculiar works have been carried by [10-12] who investigated the gasification of wood sawdust and pelletized residues, such as bagasse and empty palm oil fruits, and sewage sludge, respectively. It is worthy to note that these works have been carried with downdraft gasifiers with different configuration and capacity. Downdraft gasifiers have been used also tot tests cogasification of biomass and other fuels, such as coal [13] or high density polyethylene [14]. It is worthy to group these works according to the scale of the experimental setup. At the laboratory scale (mass sample ~200 mg) it is not possible to sustain the gasification reactions, therefore the gasifier have to kept running by means of external heating [13, 15, 16], however this studies are mainly concerned with the effect of operating conditions so indirect heating provide a careful control of the temperature and allows to change the equivalence ratio independently of it. These small scale reactors are usually tube inserted in electric heating system provided with a support for the sample and are therefore batch reactors. Some studies have been carried out with small capacity gasifiers (biomass feeding ranging from 1 to 5 kg h⁻¹) which are close to practical applications [4, 7, 8, 11]. These gasifiers are usually very flexible and allow the authors to carefully monitor the gasifier behaviour (for instance the temperature profile) and to vary the operating (especially the equivalence ratio) and feeding conditions (gas and solid flow-rate). The group of the Newcastle University [7,8], investigated in detail the gasification of hazelnut shells, carefully monitoring the gas composition, the condensate, tar and char production achieving mass closure balance above 90%. This allowed the author to evaluate the performance of the gasifier and find the optimal air to fuel ratio in terms of gas LHV and hydrogen content. [4] analyzed the effect of equivalence ratio on the gasification of Dalgerbia Sisoo, in order to find the optimal value in terms of cold gas efficiency. [11] carried out a very detailed work to assess the gasification of pelletized agricultural residues; the aim of the work was to assess the possibility to gasify agricultural residues which are not suitable for gasification as raw material, such as bagasse, after pelletizing. [11] have taken into account the effect of equivalence ratio and analyzed the evolution of the pelletized material and its influence on the gas pressure drop across the char bed. Notably, as underlined by [11], all these gasifiers have different designs. Some studies have been carried out also at larger gasifier capacities [1, 3, 5, 10], these studies are very interesting because they resemble real small scale applications. On the other hand as the size of the gasifier increases mass closure balance and measurements become difficult issues. Nevertheless these studies are similar to those carried out at smaller scale: the effect of mass and gas flow rate as well as the equivalence ratio are investigated by considering the impact on gas composition, gas LHV and gasifier temperatures. [5] performed a large series of experiments in a complete gasifier-IC engine plant and reported the performance of the system for different air-fuel ratios and different fuels (wood chips, furniture wood and charcoal). For their specific gasifier, the lower mass consumption resulted in an overall better system efficiency (15%). [3] performed tests with an open-top gasifiers using Acacia briguettes as feedstock. much attention was paid to the gasifier behaviour in terms of pressure drops and gas flow-rate as well as the pressure drops of the components of the clean-up system. Some works have explored the limitations of this technology. [10] tried to gasify wood sawdust, which is of course a tricky feedstock for fixed bed gasification; the author were able to gasify sawdust but reported operational problems due to the bed mechanics characteristics, it was possible to perform the gasification with gas recirculation and by supporting the oxidation with additional heat provided by a LPG flare. [1] investigated oxygen-steam gasification of pine wood blocks with the purpose of hydrogen production; they reported that it was not possible to achieve very high hydrogen content in the syngas without the use of downstream reactors (such as a catalytic water gas-shift reactor). Once again the authors employed different gasifier designs. Higher scale (\sim 50 kg h⁻¹) works can be found in the literature such as [6, 14]. The excellent study of [6] carried out by the Swiss department of Energy involved the full characterization of a gasification plant using several types of wood as feedstock; it was demonstrated that producing power by means of internal-combustion engine is feasible, on the other hand some issues related to the wastewater disposal [17] were rose to cope with the Swiss legislation. As pointed out in Chapter 1, [18] highlighted that downdraft gasification was suitable up to 1 MWth, which can be considered roughly equivalent to 200-250 kg h⁻¹ of biomass feedstock. As the plant capacity increases the available literature reduces, this is obviously due to the lack of personnel and funds to support such testing. The gasifier design has to be adapted to the plant capacity. [14] reported two different designs for a 25-50 kg h⁻¹ and a 200-300 kg h⁻¹ gasifier. [2] suggested a modification of the throat shape and discharge system to increase the plant capacity of a downdraft gasifier from 125 kg h⁻¹ to 375 kg h⁻¹. Notably test on fluid bed gasifier (for instance [19, 20]) are usually carried out in the same range of fixed bed gasifiers (50-100 kg h⁻¹), although these studies are very important for the technology development and evaluation of the tested apparatus and those of practical applications. Tests on practical size are required in order to achieve useful data about the reliability of the technology, in addition, as pointed out by [11] it is fundamental to expand the range of fuels which can be fed to gasifiers, since it is not very likely to imagine scenario where the same kind of biomass and same properties is always available.

5.2 Gasification facility description

The gasification facility located at CRIBE is based on a gasification plant; ancillary equipments are a drying system and a tar cracking system. Since it is in the focus of this Thesis, the gasification plant is described in detail; only a brief description of the drying and tar cracking systems is reported.

5.2.1 The gasification plant

The gasification plant (named Gastone) is specifically designed to operate with woodchips; it was commissioned in March 2010. Tab. 5.1 reports some nominal parameters of the gasifier provided by the vendor.

. i - <u>Norminal yasin</u>	er character	nsiic provided b
Thermal input	kWth	350
Biomass input	Kg h⁻¹	85
Syngas output	$m_{n}^{3}h^{-1}$	200
Syngas LHV	MJ m ^{3 -1}	5
Power Output	kWel	85

Table 5.1 - Nominal gasifier characteristic provided by the ven	ndor.
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The plant can be divided in three sections, according to the blocks represented in Fig. 5.1:

- 1. Feeding system and gasifier;
- 2. Clean-up system and gas management;
- 3. Water handling system.

The gasifier is the core of the plant, where reactions take place; the produced syngas leaves the gasifier and enters the clean-up system which is required to

remove tar, particulates and water from the syngas and make it suitable for combustion in an internal-combustion engine. The gasification plant operation is based on a water handling system. Water is used both for gasification residues removal from the gasifier and for gas cleaning in the scrubber, thus along with condensation water a lot of exhaust water carrying suspended solids is produced form the plant. This is delivered to a first tank (collection tank) where part of the solid residues are removed, and then to the equalization tank where water is further clarified by settling and cooled by means of a cooling tower. Fig. 5.2 shows the flow-sheet of the plant; the chipped biomass is charged to the gasifier via a screw conveyor controlled by a level sensor inside the gasifier. The plant is operated slightly below atmospheric conditions due to a fun-blower positioned at the end of the cleaning line, as consequence air enters the gasifier from the environment through four nozzles positioned in the oxidation zone which are just above the throat of the gasifier. The biomass is supported on a grate at the bottom of the gasifier. As the gasification reactions occur, the biomass becomes smaller in size and the biomass residue (vegetal charcoal) falls under the grate. The charcoal is washed away from the bottom plate through running water to a settling tank and recovered with a screw conveyor. The produced gas moves upward from the bottom of the gasifier in an external ring and enters the clean-up system. The clean-up system consists of a cyclone, a venturi scrubber, a chiller-condenser, two sawdust filters and a bag filter. After the cleaning the gas is destined to a flare.



Figure 5.1 - Representation of the gasification plant sections and streams.



Figure 5.2 - Flow-sheet of the gasification plant.

5.2.1.1 Feeding system and gasifier

The biomass is charged to the gasifier top by means of a feeding system represented in Fig. 5.3. The biomass is loaded into a storage tank (T-00) manually or aided by a mechanical arm. The primary conveyor (C-01) transports the biomass to the secondary conveyor (C-02), this feeds the biomass to the feeding shell (T-01) positioned at the top of the gasifier. The feeding shell has a capacity of 200 L and it is equipped with a level sensor (LV-00) and two sliding plates located at its top (SP-01) and bottom (SP-02), respectively. As biomass level in the gasifier is below a certain limit the lower sliding plate opens, the biomass in the feeding shell drops down in the gasifier by gravity. As LV-00 detect that T-01 is empty, SP-02 is closed, subsequently, so there is no communication with the atmosphere at the top of the gasifier, SP-01 is opened. C-02 starts to charge T-01 with the biomass until LV-01 reveals that the level is reached. SP-01 is closed and C-01 starts charging C-02.



Figure 5.3 - Biomass loading system: (a) Screw Conveyors (b) Feeding shell.

The biomass is discharged into the upper part of the gasifier from T-01 (Fig. 5.3). This is entirely built in steel and it is made up of two elements and kept together with a fitting. The upper element has a conical shape, at its bottom there are four diagonal tubes which allows the nozzles to be inserted in the gasifier throat. Fig. 5.4 reports a cross section of the gasifier. The biomass moves downward, aided by a mechanical vibrator; the biomass velocity in the gasifier progressively decreases due to the conical shape of the upper element so that drying and devolatilization have enough time to take place. The lower element starts with a reverse conical shape where the four nozzles are positioned; this zone is called the throat and is meant to speed up the combustion reaction thus increasing the temperature and gas turbulence. The throat ends into a constant diameter zone, which is the reduction bed, the bed is supported on a grid where a mechanical device scrapes the charcoal and ash from the bottom grid. These residues fall into a tank below the grid where a water stream washes them away to the collection tank through a vertical pipe. The syngas moves upward into an annular jacket which is meant to reduce the heat dispersion from the gasifiers and then enters the clean-up system. The gasifier is equipped with two level sensors (LV-01 and LV-02), two manometers (P_a and P_n). LV-01 indicates the upper level of the biomass and LV-02 the lower. As LV-02 detects that the biomass is below that level SP-02 is opened to feed the gasifier, this keeps going until LV-01 detect biomass. Usually a charge is enough to restore the proper level of the biomass. P_g is a differential manometer which indicates the depression inside the annular jacket of the gasifier, P_n is another differential manometer which indicates the depression inside the gasifier at nozzle outlet. The difference of the two readings indicates the pressure drop across the gasifier bed.



Figure 5.4 - Front view of the gasifier: (a) Picture (b) CAD Sketch.

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Figure 5.5 - Gasifier cross-section and gasification zones.



Figure 5.6 - Gasifer cross section with some components highlighted.

5.2.1.2 Clean-Up section

As reported in Fig. 5.2 the clean-up section is based on the following devices.

A cyclone for particles bigger than 100 micron, the particles are collected into a tank below the cyclone. The gas subsequently enters the scrubber where it is mixed with nebulized water so to remove particles and tar droplets as well as dramatically reducing the temperature. The washing water is collected at the bottom of the scrubber and delivered to the collection tank, while the gas moves toward the condenser. The condenser is a shell and tube heat exchanger equipped with a chiller cycle based on the expansion of a mixture 70% water-30% glycole. The purpose of this component is to quench the gas as much as possible so to remove steam and condensable organic compounds from the gas. The condensate is delivered to the collection tank. A differential manometer is positioned on the condenser to monitor the pressure drop, which indicates the presence of deposit on the tubes. Subsequently the gas enters a battery of three filters. The first one is defined as raw-filter and removes particles below 50 microns, the second one (fine filter) and the third one (safety filter) are meant to remove any residual solids or droplets that may have by-passed the other equipments. The raw-filter and the fine-filter are steel tank filled with wood-sawdust, the safety filter is a bag filter; all of them are provided with differential manometer to monitor the pressure drop as indicator of plugging. The blower is positioned at the end of the clean-up section, to maintain the gasifier and the clean-up under vacuum and prevent the release of syngas; a pressure sensor is placed just before the blower in order to identify excessive vacuum or over-pressure. Finally, the syngas is delivered to a flare which is activated through an electric igniter and controlled by a thermocouple; as the temperature goes below 200°C the igniter starts to spark.

5.2.1.3 Water handling section

The water used as char removal from the bottom of the gasifier and in the scrubber for gas washing as well as the water deriving from the condenser are delivered to the collection tank. Both the movable piping from the clean-up and the fixed tube of the char removal are partially submerged in the water of the collection tank, this solution prevents air flowing into the plant trough these pipelines as well as syngas to ignite in case of over pressure into the plant. The solids discharged from the fixed piping are recovered with a screw conveyor. A probe monitors the level in the tank and activates a drainage pump that conveys water to the equalization tank. As the level goes below the limit the pump is stopped and activated as the level reach the upper limit.

The equalization tank is divided into four sections, with the purpose to enhance the water clarification before re-introduction into the plant. The water of the last section is continuously re-circulated to a cooling tower to keep the water temperature below 30-40°C. Two pumps deliver the water from the fourth section to the scrubber and gasifier bottom, respectively.

5.2.1.4 Plant control and operation

The gasification plant is partially automated and controlled by means of a programmable logic controller (PLC). The operator can activate the plant in automatic (PLC activated) or manual (PLC not activated) mode. The automatic mode is based on two cycles. Cycle 1 activates the water pumps, the cooling tower

and monitors the level of the two water tanks. Cycle 2 activates the biomass loading system, opens the nozzles, starts the blower and the flare as well as the level control in the gasifier and the pressure control in the clean-up line. An operator is required to carry out some activities. Before activating Cycle 2, a safety valve positioned between the scrubber and the condenser has to be opened. If the blower is activated when the valve is not open then the safety procedure is activated, since the pressure sensor detects a too low pressure in the clean-up line. The safety procedure stops Cycle 2, thus preventing any propagation of the reaction which is immediately suffocated by the lack of oxygen. Once Cycle 2 is active the operator has to ignite the gasifier, this is carried out by means of a propane flare which is positioned for fifteen seconds at the top of each nozzle. As the blower is driving air through the nozzles the flames can reach the throat of the gasifier and start the biomass combustion. The control of the gasifier includes two basic operations:

- 1) Regulating the discharge frequency of the gasifier bottom grid;
- 2) Modulating the syngas flow-rate by means of a by-pass valve in front of the blower.

The basic data that monitor the gasifier behaviour, as provided by the manufacturer, is the ratio between the reading of the manometer P_n and P_n . It is recommended by the vendor that P_n reading should be equal to 5-20% of the P_n reading. When operated in this range the gasifier operates at its optimum. As P_n reading starts to equalize P_{α} no pressure drop across the bed is achieved, this could represent by-pass of the bed through preferential channels as well as a reduction of the bed depth. On the other hand as P_n reading gets below 5% of the P_{a} reading, a thickening of the bed or a loss of permeability is taking place. Both conditions should be avoided because, according to the vendor recommendations, may lead to poor syngas quality, high tar content and low biomass conversion. The operator can try to fit this ratio between the two readings by regulating the frequency discharge from the bottom grid. This is done by selecting different frequency of activation of the scraper positioned over the bottom grid. Five frequencies are possible numbered from 0 to 4 and reported in Tab. 5.2. As the pressure drop across the bed increases, the discharge ratio has to be increased in order to avoid bed thickening, on the other hand if the pressure drop starts to reduce the frequency has to be reduced to allow for bed build up.

Another parameter which can be controlled by the operator is the by-pass valve, the start up and warming up of the plant are carried out with this valve open, so to keep the plant at its minimal capacity. As the pressure readings become stable it is possible to progressively close the by-pass valve so to increase the air adduction to the plant and thus the syngas flow-rate. This usually destabilizes the pressure readings ratio, as consequence the discharge frequency has to be adapted in order to recover stable conditions. The plant shut down is pretty simple, it is enough to stop Cycle 2 and after a 30 seconds Cycle 1 and immediately close the safety valve to prevent syngas being released outside of the plant.

Position	Time ON [s]	Time OFF [s]
0	0	-
1	15	150
2	15	100
3	15	60
4	15	40

Table 5.2 - Discharge frequency of the mechanica
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Running the gasifier for syngas production requires one operator who has to be properly trained to the gasifier operation. After three tests with the gasifier vendor, the operator can be confident enough and properly instructed. However, the operator expertise certainly affects the gasifier performance; in particular the management of the discharge frequency is strictly related to the bed behaviour which can be different from test to test, especially with different biomass feedstock. In order to carry out tests involving data acquisition and sampling it is necessary to support the gasifier operator with other two experimenters. This is a limitation of the plant, due to personnel shortage. In addition the two experimenters must be trained people and confident with their operations.

5.2.1.5 Gasifier feedstock specifications

The gasification plant is specifically designed to operate with woodchips, the vendor provided the fuel specifications reported in Tab. 5.3 and Tab. 5.4; outside of these specifications the vendor does not guarantee the proper operation of plant. From Tab. 5.3 it can be noted that many lignocellulosic biomass can meet such specifications, aside of the moisture content and the particle size distributions, which imply a conditioning step of the lignocellulosic biomass (as already highlighted in Chapter 1). Other biomass feedstock may not be suitable for the gasifier, in particular herbaceous crops or agricultural residues can reach ash content much higher than 3% or exhibit LHV lower than 4200 kcal kg⁻¹. The feedstock size distributions is a remarkable limitation for industrial and agricultural residues, since many of these by-products or residues (for instance bagasse, olive cake, sawdust) have small size or even dusty appearance.

Parameter	Norm	Units	Sample	Limit
Moisture content at 105°C	CEN/TS 14774	%	As received	<20%
HHV	CEN/TS 14918	MJ Kg⁻¹	Dry	≥ 18.84
LHV	CEN/TS 14918	MJ Kg⁻¹	Dry	≥ 17.58
Volatile compounds at 600°C	CEN/TS 15402	%	Dry	≥ 78
Ash at 950°C		%	Dry	≤ 3
TOC	CEN/TS 15104	%	Dry	≥ 48
Oxygen		%	Dry	≥ 38
Hydrogen		%	Dry	≥ 5
Nitrogen		%	Dry	< 1

Table 5.3 - Vendor specifications related to some chemical and physical properties of the biomass feedstock.

Table 5.4 - Vendor size specifications of the biomass feedstock.

Size range	Limit
>100 mm	0%
63-100 mm	<2%
8-63 mm	88-100%
3.15-8 mm	0-10%
<3.15 mm	0-2%

5.2.2 Plant measurements

As mentioned before the gasification plant is a commercial one. When delivered to the CRIBE site it was equipped only with differential monometers, which are required to control the gasifier operation and possible clogging of the condenser and filters. The plant was equipped with further measuring and sampling device in order to properly monitor the process variables.

5.2.2.1 Temperature

Four thermocouples have been installed along the clean-up line (see Fig. 5.2):

- TC0 syngas temperature at the gasifier outlet;
- TC1 syngas temperature before the scrubber;
- TC2 syngas temperature after the scrubber;
- TC3 syngas temperature after the blower (see Fig. 5.7a).

The four thermocouples are J-type, 6 mm in diameter and 150 mm long. The thermocouples are connected to signal concentrator National Instruments WLS/ENET 9163 (see Fig. 5.7b) which transmits a wireless signals to a personal computer in a range of 150 m. A Labview software configured on the personal computer allows to receive the wireless signal and to display the temperature values on a flow-sheet representation (Fig. 5.8). This allows to continuously monitor the gas temperatures in the four positions as well as recording the thermal history of the plant, which is saved as txt-file. In addition it is possible to insert comments or register events occurred during the plant operation; these can be inserted in the txt-file beside the temperature values recorded. K-thermocouples connected to a portable data-logger are used to evaluate the temperature into the gasifier. The only option to measure the temperature in the gasifier bed is through the four nozzles positioned radially on the gasifier body and used for air adduction to the gasifier throat. The thermocouples during the measure are inserted in a steel tube so to prevent damage and reduce the effect of the incoming radiating heat. The portable thermocouples are 1000 mm long, while the nozzles are nearly 830 mm long, as consequence it is possible to reach nearly the end of the throat (see Fig. 5.6).



Figure 5.7 - (a) TC-3 position after the blower (b) wireless transmitter.



Figure 5.8 - Labview interface for thermocouples signals displaying and recording.

5.2.2.2 Pressure

As aforementioned some differential manometers are available in the plant. For sake of clarity their positions and use is reported here.

The manometers provide the following readings (see flow-sheet):

- P_g is the vacuum compared to the atmospheric pressure in the annular jacket of the gasifier;
- P_n is the vacuum compared to the atmospheric pressure at the nozzle outlet;
- ΔP_{cond} is the pressure drop across the condenser;
- ΔP_{f1} is the pressure drop across the raw-filter;
- ΔP_{f2} is the pressure drop across the fine-filter;
- ΔP_{f3} is the pressure drop across the safety-filter.

The reading of P_g and P_g is reported in Fig. 5.9a, their use has already been discussed in Paragraph 5.2. Fig. 5.9b shows the manometer placed on the fine-filter which is equivalent to others measuring the pressure drop. The pressure drop of the clean-up is a very important parameter since affect the maximum flow-rate of the plant and indicates clogging or plugging due to particles or tar deposition. The vendor provided the following limits for each pressure drop:

- $\Delta P_{cond} < 30 \text{ mmH}_20;$
- ΔP_{f1} <70 mmH₂0;
- ΔP_{f_2} <70 mmH₂0;
- ΔP_{f3} <30 mmH₂0.

Above these values deposition is occurring and it is necessary to perform maintenance operations such as condenser cleaning and sawdust substitution.



Figure 5.9 - (a) P_n and P_g manometers reading (b) fine-filter manometer.

5.2.2.3 Gas flow-rate

The syngas flow-rate is evaluated by means of a flow-meter positioned after the blower and included in a by-pass of the pipeline to allow for start up and maintenance of the device. The flow-meter (reported in Fig. 5.10) is a rotameter based on a stainless steel body floating in the variable section tube. The glass surface allows reading the gas flow-rate in $m_n^3 h^{-1}$. The rotameter scale is calibrated for nitrogen, however the syngas properties, in terms of density and viscosity are meant to be similar to those a pure nitrogen.



Figure 5.10 - Flow-meter installed in a by-pass after the blower.

5.2.3 Gas sampling and analysis

Gas sampling is not an easy matter on a gasification plant, especially when the amount of gas to be sampled is relevant. The main issue is due to the fact that syngas is a flammable gas, therefore it must not enter in contact with possible source of ignition, such as spark from electric engine. In addition gas analyzer are usually employed on very clean gas, however on the gasification plant there is the chance that some particles or droplets may reach the instruments, with a consequent damage. Therefore a careful planning of the sampling system is required. The CRIBE gasification plant is equipped with two gas sampling analysis systems: a micro-GC and a Fourier Transformed Infra-Red Spectrometer (FTIR). The first one has been used during the testing so it is described more in detail, only a brief description of the FTIR system is reported.

5.2.3.1 micro-CG

The micro-GC is a portable instrument which samples a very small amount of a gas (1 micro-Liter), thus there are no problems related to syngas flammability.

5.2.3.1.1 Technique

Gas-chromatography is based on the different affinity of several gaseous compounds toward a gaseous mobile phase (which carries the samples) and a fixed substance called stationary phase which is usually supported in a column. The mobile phase and stationary phase are not mixable. The different affinity leads to the separation of the gaseous species in the sample, in particular the higher the affinity toward the stationary phase, the higher the residence time of the compound in the column. Since the sample and the mobile phase have to be kept in the gaseous phase both the injection system and the column are provided with a heating system. Four elements can be recognized in a gas-chromatograph:

- the mobile phase feeding system;
- the sample injector;
- the column;
- the detector.

The column can only separate the compounds of the sample in terms of the residence time in the column, in order to detect their presence and concentration a detector is required. This technique can be used to gain qualitative data as well as quantitative; in the latter case the response signal generated by the detector is proportional to the concentration of a certain compound. In order to perform quantitative analysis it is necessary that the sample to be analyzed contains almost the same compounds and to calibrate the instrument. The calibration can be carried out by injecting pre-determined quantity of a certain compound and thus measuring the area of the signals reported by the detector. By repeating this operation with different concentration and achieving the signal areas, it possible to draw a calibration curve for each compound. As a consequence when the analysis is performed the signals area will mirror in the calibration curve a certain concentration.

5.2.3.1.2 Instrument

The instrument used during the testing is a micro-GC Agilent 3000 (see Fig. 5.11). This instrument allows analyzing hydrogen, saturated and un-saturated hydrocarbons from C1 to C5 and permanent gases in less than 240 seconds. The micro-CG has to be provided with two gas tanks containing the mobile phases and has to be interfaced with a PC for data acquisition and instrument control. The micro-GC is equipped with two independent channels based on an injector, a column and a thermal-conductivity detector (TCD). The first channel is based on a Molsieve 5A column, using Argon as mobile phase and suitable for the separation of Hydrogen, Oxygen, Nitrogen, Methane and Carbon monoxide. The second channel is based on a PLOT U column using Helium as mobile phase and suitable

for the separation of Carbon dioxide, Ethane, Acetylene and Ethene. The micro-GC is equipped with a pump for gas sampling, membrane filter and allows performing several separation techniques by modulating the column pressure and the column and injector temperatures. Vendor data report the sensibility of the instrument in the range 1-10 ppm. The calibration of the instrument has been performed with the following gas mixture provided by SOL spa:

- H₂ 15.00% N₂ 85.00%
- CH₄ 2.997% N₂ 97.003%
- C₂H₄ 0.500% N₂ 99.500%
- CO 0.995% N_2 99.005% and CO 25.00% N_2 75.00%
- CO₂ 1.5% N₂ 98.05% and CO₂ 19.98% N₂ 80.02%

and the Agilent Universal Calibration Standard.



Figure 5.11 - micro-GC and sampling line.

5.2.3.1.3 Sampling point and procedure

The micro-GC (see Fig. 5.11) is connected to the plant right after the blower, near thermocouple TC-3 in order to monitor the temperature in the sampling point. The sampling line includes a ball valve, a 1/8" copper tube, a 1/8"-1/16" junction, a 1/16" steel tube, a five microns membrane filter, a sampling pump. It is worthy to note that membrane protected the micro-GC fairly well, this imply that the clean-up system operated properly since this device is very sensible to moisture and particulates. The sampling lasts nearly 15 seconds while the separation and analysis is carried out in 3-5 minutes. It is worthy to note that while the analyzing is taking place the gas still flows inside the membrane, since the pressure is slightly

above the atmospheric pressure, but is purged from another pipe. This provision avoids any delay in the gas composition detected by the micro-GC compared to that in the plant. Before starting the analysis, it is necessary to perform a preliminary conditioning step to purify the columns from any trace compounds still adsorbed.

5.2.3.1.4 Data acquisition and elaboration

The micro-GC is interfaced by means of a LAN connection with a PC and controlled by the software SRA *Soprane Networked Data System*. The software allows setting and controlling all the parameters involved in the system, such as temperature and pressure, and allows displaying the detector signals (chromatograms) as reported in Fig. 5.12. The signals data can be processed to identify the gaseous compounds, on the basis of the residence time, and their concentration, on the basis of the calibration curves.



Figure 5.12 - Chromatogram reporting the detector signals for the column supporting Molsieve.

5.2.3.2 FTIR

The FTIR system has encountered was commissioned on February 2011 so it was not used during the tests. Its development involved several issues. The FTIR samples a larger amount of gas than the micro-GC (0.5-1 $m_n^3 h^{-1}$), this implies that the sampling system should not contact the syngas with possible ignition sources. As consequence an air ejector was chosen since it avoids using electric device. Other issues are:

- the possible presence of condensable species in the syngas, which may damage the FTIR;
- the FTIR cannot be used outside of the building, since it is very likely to contaminated and damaged by dust and other gases.

As a consequence the sampling line was provided with a heating system, in order to keep the vapours in gas phase. In addition a steel cabinet (Fig. 5.13) was developed and equipped with flushing system and conditioning system in order to avoid contact with the environment and variation of the operating conditions (temperature and pressure) that may negatively affect the analysis of the FTIR which is located into the cabinet. The FTIR is a Bruker Tensor 37 with a spectral range 8000-350 cm⁻¹. The IR source is a medium infra-red (MIR) air cooled, the detector is a high sensibility DTGS (Doped Triglycine Sulfate) so to avoid the use of liquid nitrogen. The FTIR is equipped with a heated gas cell realized in stainless steel, 10 cm optical path, volume 25 cm³ and zinc selenide windows.



Figure 5.13 - Pressurized cabinet for FTIR.

5.2.4 Liquid sampling and analysis

The sampling system and characterization of the liquid fractions has been discussed in detail in Chapter 4. Only some considerations on the sampling on the gasification plant are reported. Two sampling ports are available in the plant and reported in the flow-sheet of Fig. 5.2. The first port is located before the scrubber near thermocouple TC-1, so to have a reference temperature of the gas. Here the gas is expect to have a reduced particles content (due to cyclone) but still retaining the condensable species (tar and water) due to the high temperature. Thus this sampling port is meant to provide the condensable fraction concentration exiting the gasifier. The second sampling port is located right after the blower near the thermocouple TC-3 and the micro-GC sampling line. This sampling port positioned after the clean-up line is meant to provide the condensable fraction concentration at the clean-up outlet. The sampling ports are the same of the pyrolysis plant described in Chapter 4, the box containing the first impinger is interfaced with the port by means of a silicon gasket and a clamp.

5.2.5 Solid sampling and analysis

The solid samples which can be collected from the plant are:

- the feedstock from the loading system;
- the gasifier bed from the nozzles;
- the bottom residues from the collection tank;
- the cyclone particles from the cyclone discharge tank.

5.2.5.1 Sampling points and procedure

The biomass feedstock can be easily collected from T-00 or T-01; it is worthy to note that in T-01 the material is more homogeneous due to the mixing effect of the screw conveyor; in addition the material may have lost its physical appearance due to mechanical strains.

The gasifier bed is somewhat difficult to be sampled, as pointed out in Paragraph 5.2.2.1 the only access to the gasifier bed is through the four nozzles, no other sampling port are available since it is believed that producing holes in the gasifier shell may severely damage its operation or lead to syngas release. However the nozzles are a suitable access, since they lead to the throat: the heart of the gasifier. Sampling at throat condition is a tricky matter since the particles are burning in a low oxygen environment and at high temperature (~1000°C). If some particles would be collected and exposed to air they will start to burn more violently than in the gasifier bed. This would cause safety risks and a not representative sampling. A simple way to obtain representative samples without health risks is to sample the gasifier bed after it has cooled down; this is done with a wood stick properly shaped at one end so to collect the particles. The wood stick is inserted though a nozzle and turned on its axis three times and then removed from the gasifier. However during the cooling some bed modifications may occur, even if the temperature and the oxygen start to drop immediately after the shut down. This is why another nitrogen quenched probe has been designed during this Thesis; a 3-D sketch of the probe is reported in Fig. 5.14.



Figure 5.14 - Sketch 3D of the probe for solid sampling in the gasifier bed.

The probe is based on an Inconel cabinet equipped with a sliding plate, the head of the probe is fixed on a steel pipe with nitrogen injection at its end and sliding control handles. It can be inserted down from the nozzles and allows sampling the bed particles during the gasifier operation. The conical head allows penetrating in the bed, when the probe is inside the bed nitrogen is fluxed and the slider is opened, after some seconds the slider is closed and the probe is extracted upward from the nozzle and kept under nitrogen flux (so to quench the particles and to prevent oxygen contacting the particles) until environment temperature is reached. The bottom residues are another tricky matter. As aforementioned the solid residues (char and ash) are discharged by the bottom grid by a mechanical scraper and washed away with water jet. They are delivered to the collection tank through a fixed pipe which is partially submerged. There are two options for sampling. The first one, adopted in this Thesis, is to collect the residues in the collection tank at the fixed pipe exit. The second one is to extract a certain amount of running water from the fixed pipe before it releases the solids in the collection tank. Notably, it is not possible to sample these residues without water. In addition, sampling from the collection tank implies that the solids contact a slurry of water, suspended particles, tar which derive from the scrubber and the condenser; moreover if the screw conveyor is not able to extract the solid residues form the bottom of the tank, these residues start to settle and accumulate. Sampling from the rigid pipe involves a careful planning, since producing holes in this pipe may lead both to air seepings, with consequent risk of fire in hot zone of the clean-up, or syngas release, in case of gasifier pressurization.

Finally, sampling the cyclone particles is pretty simple, it is enough to close the sliding plate at the cyclone bottom and remove the collection tank. It is necessary to carry out this sampling with protection devices (gloves and breathing mask), because the particulates release may vapours and strong smell.
5.2.5.2 Solids analysis

A standard procedure for solids characterization has been developed. This includes the following analysis:

- Moisture content;
- Proximate Analysis;
- Ultimate Analysis;
- Heating value.

The methodology and instruments related to Proximate Analysis and Ultimate Analysis have been discussed in Chapter 3 and 4. Here some details about the moisture content evaluation and lower heating value are reported.

5.2.5.2.1 Moisture content

The moisture content is evaluated as the weight loss of a sample after drying it in stove for ten hours at 105 °C. The sample (5-50 g) is weighted as received with an analytical balance (ACCULAB, Sartorius Group) and then inserted in ventilated stove (Binder) for ten hours at 105 °C (this period is usually enough to reach a constant weight of the sample), after this period the sample is cooled down in a glass desiccator filled with silica sand, and subsequently weighted. Notably this method assumes that the weight loss due to trying can only be related to moisture. However it is common to refer to this mass loss as moisture and volatiles at 105°C, since the samples (for instance, liquids or impregnated solids) can contain other compounds which can be released as vapours at 105°C.

5.2.5.2.2 Heating value

The heating values (MJ kg⁻¹) of the solid samples are determined by means of complete combustion in pure oxygen in a calorimeter. The measure is based on the method of Berthelot-Mahler: the heat released by the sample combustion is evaluated as temperature increase of a known amount of water. The calorimeter is based on an external tank containing water and a bomb. The bomb is a stainless steel tank where 0.5-1 g of the sample (dried at 105°C) is inserted in a crucible; an ignition wire is place in the sample and combustion is started applying voltage to the wire. The bomb is filled with pure oxygen up to 25-30 atm. The bomb is placed into the tank filled with 2 litres of distilled water. When the temperature of the water is stable the voltage is applied and the combustion starts, consequently the bomb release heat to the water, increasing its temperature. Once the combustion is completed the temperature increase is recorded. In order to achieve the higher heating value it is necessary to determine the heat absorbed by the calorimeter itself. This is evaluated performing combustion test on compounds with a known heating value, such as benzoic acid. The higher heating value (HHV) is calculated as the ratio between the heat released and mass of the sample. The lower heating value (LHV) can be calculated on the basis of the hydrogen content of the sample, it is assumed that all water generated by the hydrogen combustion remains in the gaseous phase, so that the latent heat is subtracted to the HHV. The instrument used in this Thesis is LECO AC-500 calorimeter with a temperature resolution equal to 0.0001°C. The method is isoperibolic in agreement with ASTM, ISO, DIN and BSI standards. Prior to analysis samples are milled and then pressed to form a

tablet, and finally dried in a stove at 105°C. When the experimental evaluation of the LHV is missing the DuLong formula was used.

5.2.6 Ancillary equipments

5.2.6.1 Drying system

The drying system (a frontal view is reported in Fig. 5.15) is based on a container where ten closed basket are positioned. The container is open on the right and the left sides. On the left side the gas is blown my means of a fan, the gases exiting the container are driven in cyclone positioned before the blower. On the right side there is a shell-finned tubes heat exchanger connected to a steam generator on the tube side, the steam is provided by a woodchips boiler, the steam flow rate and pressure can be regulated by means of an automatic and a manual valve, respectively. The shell side of the heat exchanger is open to air which is aspired due to the depression created by the blower. The biomass is inserted in the closed basket and positioned in the container. When the frontal door is closed it is possible to start the test by activating the blower and opening the steam adduction valves. Once the air inlet temperature is selected in the temperature control, the pneumatic valve modulates the steam flow-rate to achieve the desired drying temperature. The dryer can contain up to 80 kg of wet biomass and can completely dry woodchips with a moisture content of 55% in one hour.



Figure 5.15 - Front view of the drying system.

5.2.6.2 Tar cracking system

As mentioned in Chapter 1, one of the main problems associated with biomass gasification is the tar production. A possible downstream solution is the catalytic cracking of tar, in this case the syngas exiting the gasifier enters fixed beds filled with catalyst at high temperature where tar are decomposed to smaller compounds. To this purpose a lab-scale tar cracking-line named Tarek (Fig. 5.16) has been developed. It is based on two fixed bed catalytic reactors (reactors diameter DN65, bed length 400 mm) and can be connected to the gasification plant just before the scrubber, to sample a small amount (5 $m_n^3 h^{-1}$) of the gas from the clean-up line. Tarek can also be operated stand-alone to allow carrying out tests independently of Gastone. In this case a small cylindrical reactor positioned in an electric heater can be used both for biomass pyrolysis tests as well as for organic liquids evaporation. The guard bed is designed to be loaded with mineral material such as dolomite or olivine. The main bed is designed to support a metal catalyst (i.e. nickel). Both the guard bed and the main bed are positioned into cylindrical electric heaters to guarantee an accurate temperature control. Tarek is equipped with thermocouples and pressure indicators to monitor the temperature before and after every step of the treatment and the pressure drops through the beds. In addition three gas and tar sampling connections are available to evaluate the gas composition via micro-GC and FTIR and the tar content.



Figure 5.16 - Tar cracking line "Tarek" in stand-alone configuration.

5.3 Gasification tests of pelletized biomass

The development and commissioning of the gasifier required more than one year, the gasifier has been commissioned in March 2010. Subsequently two experimental campaigns have been carried out. The campaigns purposes were:

- understanding the gasifier behaviour;
- acquisition of plant parameters;
- evaluation of the sampling and testing capabilities;
- evaluation of the gasifier performance according to the feedstock.

The details of the tests are presented in the following paragraphs.

5.3.1 Biomass feedstock selection

As highlighted in Paragraph 5.1, it is fundamental to expand the range of fuels which can be fed to gasifiers, since it is not very likely to imagine scenario where the same type of biomass and same properties is always available.

During the Thesis a methodology for the design of suitable feedstock for biomass gasification has been developed. Fig. 5.17 schematizes the methodology. The grey area represents the fuel specifications required by the gasifier (ideal biomass). The red line represents the properties of a fuel which cannot be used in the gasifier. There are two options to fit the real biomass with the ideal envelop:

- pre-treatment/ conditioning steps;
- biomass-residues mixing.

After the identification of the suitable conditioning steps or the integrative biomass and its sharing (i.e. the amount of woodchips that have to be added to chicken manure) a new feedstock (yellow line) which meets the gasifier specifications is obtained. Both options were considered in this study. The selected pre-treatment is biomass pelletizing and pelletized wood sawdust was selected as the test feedstock; noteworthy the gasifier is specifically designed for woodchips

Pelletizing allows producing a fuel with homogeneous properties and high energy density; however the use of this type of biomass leads to some advantages and disadvantages which are reported in Tab. 5.5.



Figure 5.17 - Design methodology of suitable feedstock for a gasification process.

The use of loose material as fuel has to face some difficulties. These materials are not easy to be transported and managed and may be characterized by low heating values due to the poor density. Many industrial and agricultural residues are loose materials (sawdust, bagasse, olive cake, wheat straw, rice hull etc.). These materials are not suitable for biomass gasification in fixed beds, but, in principle, pelletizing can upgrade them in order to achieve a uniform particle size, high LHV and low moisture contents. The main disadvantages of pelletizing are the high economic and energy cost of the feedstock as well as the production of a biomass with a low mechanical resistance that, in case of heavy mechanical or thermal stress, may break up into its original form.

Biomass mixing was applied in order to enhance the range of possible gasification feedstock. In this case pelletized residues obtained from sunflower seeds pressing for oil production was used and mixed with wood sawdust pellets.

Table 5.5 - Advantages	and disadvantages	related to	pelletized fuels.

Advantages	Disadvantages
High LHV	Energy cost
Storage stability	Economic cost
Low moisture	Low mechanical resistance
Easy handling	
Homogeneous	

5.3.2 Biomass feedstock properties and characterization

Two biomass feedstocks were fed to the gasifier:

- wood sawdust pellet;
- mixture 50%wt wood sawdust pellet 50%wt sunflower residues pellet.

Hereafter it will be referred to the wood sawdust pellet as WSP, to the sunflower residues pellets as SRP, and to the mixture as MIX. Notably two biomass have been involved in the test and a mixture. The characterization and properties of the three samples is reported in Tab. 5.6.

WSP is provided by a local producer, the pellet is formed out of wood sawdust derived from wood processing. SRP is a by-product of sunflower seeds pressing for vegetable oil production. SRP is obtained from an experimental activity carried out at CRIBE related to sunflower cultivation, processing and trans-esterification for Biodiesel production. The use of SRP in the gasifier is an example of integration within different biomass exploitation platforms. The moisture content of WSP and MIX as received is 9% and 12.8%, respectively. The moisture content reported in Tab. 5.6 (defined as bf) is evaluated before feeding the biomass to the gasifier. Evaluating the moisture content before feeding it is very important for biomass, since the values reported from the producer may vary according to the storage period and location as well as climatic conditions.

WSP respects the limits specified in Tab. 5.3 and Tab. 5.4; therefore it is a very suitable fuel according to the vendor specifications. SRP shows some properties which make it not suitable for gasification. The ash content and the nitrogen contents are too high, which could cause clinker formation at the bottom grid and lead to high generation of nitrogen compounds (for instance NH₃) in the syngas. In addition this type of residues contain a relatively high amount of residual oil (18.8%), this could be harmful for the gasifier due to the generation of heavy volatiles in the gasifier leading to high tar production. As consequence this fuel cannot be used directly in the gasifier. To overcome this problem the MIX is designed, which is composed of 50% WSP and 50% SRP. Mixing is carried out manually in an external tank and some plastic bags are filled with it. The properties of the MIX are achieved by analyzing several samples of milled mixture. The resulting properties of the MIX are closer to SRP properties, maybe due to not completely homogeneous sample. The driving MIX properties (ash and nitrogen contents) are in agreement with 50% mixing. Notably other parameters such as the volatile matter and the carbon content cannot be related to the mixing, this is likely to be related to low homogeneity in the samples. The resulting MIX is closer to the vendor specifications; however the ash and nitrogen contents are still slightly beyond the limits. As far as concern LHV, pelletized materials are very suitable fuels, especially SRP exhibit a very high energy content, which makes it a very attractive fuel. The LHV of the MIX was not evaluated with the calorimeter but calculated according to the DuLong formula, resulting 19.54 MJ kg⁻¹. The oil content test was not performed on MIX, but this is likely to be half of the SRP value. The size distribution of WSP and SRP is very homogeneous. WSP and SRP are both cylinder with a constant diameter of 6 mm and 10 mm, respectively. The length range is 10-30 mm for WSP and 30-60 mm for SRP. The mean length. mean volume, mean ESD, mean sphericity values reported in Tab. 5.6 are calculated on the basis of 100 pellets of each biomass. Pellet materials have very high densities compared to normal biomass (for instance woodchips 200-300 kg m ³). The pellet density and bulk density are similar for WSP and SRP. The MIX size and density are obtained as an average of WSP and SRP.

Parameter	Sample	Unit	WSP	SRP	MIX
Moisture	bf	%	12.00	-	12.00
VM	dry	%	80.63	78.11	76.54
FC	dry	%	17.27	14.43	18.57
ASH	dry	%	2.10	7.45	4.99
С	dry	%	48.91	46.55	50.51
Н	dry	%	5.80	6.15	6.22
Ν	dry	%	0.18	3.83	1.98
0	dry	%	by diff.	by diff.	by diff.
LHV	dry	MJ kg⁻¹	18.43	20.66	n.d.
Oil content	dry	kg kg⁻¹	n.d.	0.188	n.d.
Length	ar	mm	17	49	-
Diameter	ar	mm	6	10	-
Volume	ar	cm ³	0.49	3.87	2.21
ESD	ar	mm	9.81	19.48	14.74
Sphericity	ar	-	0.783	0.699	0.74
Pellet Density	ar	kg m⁻³	1120	1090	1105
Bulk Density	ar	kg m⁻³	650	632.2	640.9

5.3.3 Test resume

The two experimental campaigns were carried out in five tests. The resume of the test is reported in Tab. 5.7. The two campaigns are identified with the names of the feedstock, WSP and MIX. The campaign WPS took three tests. At the beginning the reduction zone of the gasifier was fed with vegetal charcoal, in order to provide an initial char bed. Test 1 allowed substituting the initial charcoal bed with WSP char. Subsequently Test 2 and 3 were performed with WSP as feedstock and bed.

At the end of Test 3 MIX was fed, so that after some hours of Test 4 the char bed was substituted with the char produced from MIX. Finally Test 5 was entirely carried out with MIX as feedstock and char bed. Tests lasted from three to six hours; longer tests could not be performed due to personnel shortage, ice formation during the night in the winter tests (3, 4, and 5). During all the tests the pressure drop across the bed (readings of manometer P_n and P_g) and in the clean-

up, the syngas flow-rate, the syngas composition and the feedstock sampling and analysis were carried out. It was planned to record the temperatures of the cleanup in each tests, however in Test 5 it was not possible to configure the wireless connection to the PC. The char residue was sampled and analyzed during Test 1, 2 and 3, in order to be sure about the composition of the gasifier bed. K-thermocouples for bed temperature and the tar sampling system were available in November 2010, so it was possible to carry them out only in Test 3-5. Some "in deep" investigation were carried out only after Test 5 (bed sampling and analysis, cold flow characterization, cyclone particulates sampling), to clarify some aspects that emerged from the data analysis.

Test	1	2	3	4	5
Campaign	WSP	WSP	WSP/MIX	MIX	MIX
Duration [h]	6	3	3	5.30	3.30
Bed material	Char coal	WSP	WSP	WSP/MIX	MIX
Pressure drop	Х	Х	Х	Х	Х
Clean-Up Temperature	х	Х	Х	Х	
Clean-Up Pressure drop	х	Х	Х	Х	х
Bed Temperature			Х	Х	Х
Gas flow-rate	Х	Х	Х	Х	Х
Feed analysis	Х	Х	Х	Х	Х
Bed analysis					Х
Char analysis	Х		Х		Х
Gas analysis	Х	Х	Х	Х	Х
Condensate sampling			Х	Х	х
Particulate sampling					х
Cold flow					Х

5.3.4 Test procedure

The test procedure involved the following steps:

- preliminary checks: manometer level, pump pressure, biomass levels;
- Cycle 1 start;
- Cycle 2 start;
- gasifier ignition with the flare;
- starting gas analysis, clean-up temperature, bed and clean-pressure, gas flow-rate monitoring and recording;
- gasifier running with aim to reach a stable production of 100-120 m³_n h⁻¹ of syngas (varying the discharge frequency and the blower by-pass ratio);
- sampling during the test;
- shut-down procedure;
- final sampling and characterization when required.

5.4 Tests results

This Paragraph reports the results of the tests. The first part involves data on the gasifier behaviour such as temperature, gas composition, pressure drop and samples analysis. The second part is still based on some of these data which can be used to calculate the performance indicators presented in Chapter 1.

5.4.1 Gasifier behaviour

5.4.1.1 Temperature

5.4.1.1.1 Clean-up Temperature

The test history is continuously recorded according to the clean-up temperatures and gas composition. Fig. 5.18 reports the temperature evolution of the four thermocouples of the clean-up systems in Test 1, Test 3 and Test 4. As aforementioned the wireless system was out of order in Test 5, Test 2 is not included since there is some delay after the gasifier ignition. TC-0 in particular (measuring the gasifier outlet temperature) can be considered as an indicator of the gasifier dynamic. Despite the four monitored tests exhibited different behaviour (as it will be shown in following Paragraphs) in terms of pressure drops and, especially, gas flow-rate history, the temperature evolution at the gasifier outlet was quite similar. In all the tests this temperature reaches 50-60°C in roughly 40 minutes, this temperature is stable for 15-20 minutes and then starts to increase more quickly than before. During the next ramp the temperature increases up to 260-280 °C more or less 1 h (~ 3°C min⁻¹). After this the temperature gradient reduces to roughly 1 °C min⁻¹, until the temperature reaches a plateau at 330-350°C. This behaviour seems to be somewhat independent of process parameters (e.g. gas flow-rate) or feedstock composition. As far as the other temperatures are concerned, it can be seen that after the cyclone the temperature is reduced of 80-100°C in all the tests, this is a consequence of large thermal dispersion in the non insulted pipe. In the scrubber gas is guenched dramatically to 20-40°C due to contact with cool water, allowing for partial tar and water condensation. The condensation is completed in the chiller-condenser where the temperature (evaluated with portable thermocouple) reaches 5-10°C. After the blower the syngas temperature increases due to the engine thermal dispersions, leading to a temperature 30-50°C. of



Figure 5.18 - Temperature evolution of the four clean-up thermocouples.

5.4.1.1.2 Gasifier Temperature

As mentioned in Paragraph 5.2.2.1 it has been possible to evaluate the gasifier internal temperature only trough the four nozzles that allow air entering the gasifier. The temperatures are evaluated moving a portable K thermocouple down through a nozzle and measuring the temperature at fixed distances from the nozzle internal outlet for 210 seconds. This procedure is repeated once every two hours and is devoted to evaluate the throat temperature; this is an important parameter for the gasifier operation indicating the tar abatement and the combustion efficiency. However, it was found that it is difficult to define a throat temperature, since the local temperature varies along the throat and exhibits a rather large timefluctuations (as reported by [11]). Fig. 5.19 reports the evolution of the throat temperature during Test 5, the temperature has been recorded in four positions (nozzle outlet and 4, 7, 10 cm from the nozzle outlet, respectively). The temperature at the nozzle outlet is stable at 431 °C, in the other tests and evaluations this temperature was variable from 300 to 500°C. The temperature quickly increases as the thermocouple is moved down in the throat. At 4 cm from nozzle outlet the temperature varies from 928 to 1086 °C. As the thermocouple is moved deeper in the throat the temperature varies from 667 to 1109 °C and from 740 and 907 °C at 7 cm and 10 cm from the nozzle outlet, respectively. As can be seen there is a thermal profile along the throat which a large instantaneous fluctuation. This reveals a quick dynamic in this zone probably due to continuous ignition of fresh biomass coming from the top. Considering the average values for each position in Fig. 5.19, it seems that temperature reaches its maximum near the nozzle outlet and subsequently decreases moving down. However, in other evaluations the maximum temperature is achieved up to 15 cm from the nozzle outlet.



Figure 5.19 - Temperature acquisitions along the gasifier throat moving a thermocouple down from a nozzle.

Since the duration of each observation is short it can be concluded that the maximum temperature is surely achieved in the throat but its value can vary in space and time. The maximum temperatures achieved in Tests 3, 4, and 5 are 1060, 1104, 1086 °C, respectively. Data provided from the gasifier vendor reports temperatures up to 1200 °C. These high temperatures confirm that combustion occurs in the throat. This is supported also from the visual observation: from the nozzle upper opening a flame can be observed, this is likely to be a reverse flame due to the air downward motion, and indicates that volatile species, generated in the devolatilization step, are burning. No conclusions related to the biomass feedstock can be drawn, due to the large fluctuations and the limited number of observations.

5.4.1.2 Syngas composition

Fig. 5.20 reports the evolution of the syngas composition during three tests and Tab. 5.8 the average composition (along with the standard deviation) obtained from each test. After a little time (4-8 minutes depending on micro-GC sampling time) from the ignition the gas composition changes rapidly from air to syngas. The first sampling is somewhat poor compared to the other (for instance hydrogen near 10%) but the composition changes very quickly and in roughly 15 minutes the nitrogen content reaches a steady value close to the average reported in Tab. 5.8. At this stage the carbon monoxide content is higher than the steady state value, while the hydrogen and carbon monoxide contents are lower. It takes from 45 min to 1 hour to reach a stable syngas composition.

During this time the hydrogen and carbon monoxide contents increase, while the carbon monoxide decreases. This is likely to be related to the water-gas shift reaction and thermal equilibrium in the reactor. This reaction can be written as:

$CO + H_2O \leftrightarrow H_2 + CO_2$

(1)

When thermal equilibrium is reached in the reduction zone of the gasifier, this reaction affects significantly the final syngas composition as achieved both from numerical [21] and experimental [11] studies.

As a consequence after 1 hour the syngas composition is rather stable. The syngas is mainly composed of hydrogen, carbon monoxide, carbon dioxide, nitrogen and methane with a small amount of ethylene; other hydrocarbons such as ethane and acetylene are not relevant. The average syngas composition is quite similar for the five tests. Test 1,2,3,4 exhibit very close compositions, irrespectively of feedstock and char bed composition; a mean syngas composition of the four tests could be hydrogen (17.2%), nitrogen (46%), methane (2.5%), carbon monoxide (21.2%), carbon dioxide (12.6%) and ethylene (0.4%). The standard deviation is low (always below 2.5) indicating very stable values. The syngas composition is similar to those reported in the literature (for instance [22]). Test 5 exhibits carbon monoxide, carbon dioxide and hydrogen contents lower than the other tests. Fig. 5.19 shows some large instantaneous fluctuations in the gas composition of Tests 5, with high nitrogen and low carbon monoxide contents, which affects the average composition; without these fluctuations the average composition would be closer to Test 3. However, the lower hydrogen, carbon

dioxide as well as carbon monoxide contents may indicate a lower conversion of the fuel into syngas which could be both due to a bad fluid-dynamic in the gasifier (as confirmed by the large fluctuations) or to the higher ash content of MIX compared to WSP. The syngas LHV of Test 1 is higher than the other tests. A possible explanation is that, in this case, the gasifier reduction zone is filled with vegetal charcoal which provides an excellent reduction media with no moisture and high calorific value; in addition the methane content is the highest of the five tests. The syngas LHV is stable in the other tests ranging from 5.52 to 5.75 MJ m⁻³_n. These values are in agreement with literature values (for instance [22]), but very closet o the upper limit, indicating that the use of pelletized biomass leads to high syngas LHV, probably due to the high energy density of these fuels. Test 5 exhibits a LHV close to Test 2, 3, 4 despite the lower hydrogen and carbon monoxide content, this is due to the higher Ethylene content. The high Ethylene content can be a consequence of the residual oil in SPR, which is likely to generate hydrocarbons.

Gas	Test 1	Test 2	Test 3	Test 4	Test 5
H_2	17.46±0.80	17.56±0.73	16.35±1.56	17.55±1.76	15.81±1.84
N_2	44.24±1.06	46.05±1.11	47.25±2.39	45.91±2.02	49.53±3.70
CH_4	3.10±0.54	2.28±0.25	2.28±0.33	2.50±0.41	2.32±0.64
CO	21.31±1.68	21.63±0.67	21.29±2.35	20.65±2.23	19.69±4.27
CO ₂	13.31±1.79	12.03±0.65	12.39±1.77	12.80±1.89	11.57±2.11
C_2H_4	0.47±0.09	0.38±0.13	0.37±0.10	0.52±0.19	0.79±0.26
C_2H_6	0.07±0.02	0.04±0.04	0.03±0.01	0.04±0.01	0.05±0.01
C_2H_2	0.03±0.01	0.03±0.02	0.03±0.01	0.03±0.01	0.06±0.02
LHV MJ m ⁻³ n	6.02	5.71	5.52	5.75	5.55

Table 5.8 - Syngas compositions achieved in the five tests.





5.4.1.2 Pressure

As pointed out in Paragraph 5.2.1.4 the pressure drop across the gasifier bed is the main parameter for evaluating the correct operation of the gasifier. In addition the pressure drop across the gasifier is a basic information for preventing plugging as well as choosing the correct blower and engine to be coupled with the clean-up line.

5.4.1.2.1 Pressure drop in the clean-up system

The pressure drop of the clean-up system is plotted against the gas flow-rate during a cold test in Fig. 5.21. These values are representative of the gasifier operation, since after the scrubber the gas temperature is close to the environmental conditions. The filters are the components with the highest pressure drop varying from 30 to 60 mm_{H2O} and from 25 to 55 mm_{H2O} for the raw-filter and the fine-filter respectively. However, since during the gasification runs it was not possible to overcome 150 m³_n h⁻¹ the maximum pressure drops achievable are 50 and 45 mm_{H2O}. The pressure drop of the safety-filter was very low (3-5 mm_{H2O}) and was minimally affected by the gas flow-rate. No pressure drop was reported in the condenser during the gasification runs as well as in the cold test.

The pressure drops in the cyclone (50 mm_{H2O}) and in the scrubber (75 mm_{H2O}) are provided by the vendor. Therefore the average pressure drop of the whole clean-up system is 200 mm_{H2O}; this is not very affected by the gas flow-rate.



Figure 5.21 - Pressure drop in some components of the clean-up system.

5.4.1.2.2 Pressure drop across the gasifier bed

The pressure drop across the gasifier bed is evaluated as the difference between the reading of manometer P_g and manometer P_n . P_g is always higher than P_n , this means that the vacuum is higher in the annular jacket of the gasifier than at the nozzle outlet and that the pressure at the nozzle outlet is closer to the atmospheric. Fig. 5.22 reports the pressure drop evolution during the five tests, while Fig. 5.23 reports the evolution of the ratio between the P_n and P_g readings as well as the discharge frequency of the bottom scraper selected in the control panel of the gasifier. As aforementioned all the tests were carried out with the aim to reach and keep a constant syngas flow-rate of 100 m³_n h⁻¹ and then evaluate the maximum output of the gasifier.

The pressure drop evolution in Test 1 is somewhat different from the other tests. In particular the early stage of the test is characterized by values below 100 mm_{H2O} with a correspondent gas flow rate of 85-90 $m_n^3 h^{-1}$. In the second half of the test an attempt was made to evaluate the maximum output of the plant, thus the by-pass valve of the blower was gradually closed leading to a progressive increase in the gas flow-rate (up to 120 $m_n^3 h^{-1}$) and pressure drop (up to 208 mm_{H2O}) until 2.40 hours from the initial recording. At this stage the by-pass valve was completely closed, as a consequence the gas flow-rate quickly increased to 140-150 $m_n^3 h^{-1}$ and pressure drop reached values close to 350 mm_{H2O}. This test was rather easy to be operated as reported in Fig. 5.23. The ratio P_n to P_g is always in the optimal range specified by the vendor (5-20%) and it was necessary to increase the discharge frequency only when the gas flow rate was increased.

Notably in this test the reduction zone was based on the pre-loaded charcoal, but at the end of the test this was substituted with WSP char. Consequently Test 2 was carried out with WSP char in the reduction zone. The pressure drop evolution in Test 2 is very different from Test 1. In the first hour the pressure drop was immediately higher than 300 mm_{H2O} with a gas flow rate equal or lower than 100 $m_n^3 h^{-1}$ and the by-pass valve had very poor effect in increasing the gas flow rate due to the very high resistance to flow of the gasifier. After 1.30 hours there was a dramatic reduction of the pressure drop (close to 100 mm_{H2O}) and, since the by-pass was completely closed, a consequent increase of the gas flow rate (140 $m_n^3 h^{-1}$). Therefore there was a dramatic change in the gasifier resistance to flow.

In Test 3 the reduction zone was still based on WSP char. The pressure drop was immediately higher than 200 mm_{H2O} with a gas flow-rate of 100 m_n^3 h⁻¹ and increased during the first 30 minutes up to 350-400 mm_{H2O} with a correspondent reduction in the gas flow-rate to 85 m_n^3 h⁻¹. As for Test 2 there was a sudden reduction in the pressure drop (down to 200 mm_{H2O}), this time after 2 hours, with further progressive reduction in the following 30 minutes to 90 mm_{H2O}. This led to an increase of the gas flow-rate up to 110 m_n^3 h⁻¹. Due to this dramatic reduction in the bed resistance it was possible to progressively close the by-pass and reach a gas flow-rate of 150 m_n^3 h⁻¹ with a correspondent increase of the pressure drop up to 350 mm_{H2O}. This test was pretty hard to be operated, as reported in Fig. 5.23 the first part of the test was out of the optimal gasification range; in addition the discharge frequency had to be modulated briskly in order to guarantee the minimal gasifier performance. The discharge frequency was changed quickly from 0 to 4. In the first part in was not possible to vary the gas flow-rate by means of the by-pass, indicating very high resistance to flow. In the second part it was possible to use the

by-pass valve and operate in the optimal range, indicating a more controllable condition.

In Test 4 the very early stage of the test is characterized by a steep increase in the pressure drop, from 100 to 500 mm_{H2O}. The gas flow-rate reduced from 80 to 50 m³_n h⁻¹. Again a sudden reduction in the bed resistance occurred after 80 minutes. The pressure drop reduced dramatically to 130 mm_{H2O} with a correspondent increase in the gas flow-rate up to 110 m³_n h⁻¹. This time it was not possible to completely close the by-pass valve, since after a slight increase in the gas flow-rate to 120 m³_n h⁻¹ the pressure drop started to increase independently of the gas flow-rate. During this ramp the pressure drop increased from 237 to 400 mm_{H2O} in two hours, and the gas flow-rate progressively decreased from 110 to 95 m³_n h⁻¹. As reported in Fig. 5.23 it was difficult to keep the pressure ratio in the optimal range and the discharge frequency was often varied in order to follow the gasifier behaviour. In addition it was not possible to reach gas flow-rate above 117 m³_n h⁻¹. At the end of Test 4 the reduction zone was filled with MIX char.

Test 5 was the hardest to be operated. The pressure drop in the first hour was higher than 400 mm_{H2O} with a correspondent very low gas flow-rate (50 $m_n^3 h^{-1}$). After one hour the pressure drop began to decrease down to 250-300 mm_{H2O} with a correspondent increase in the gas flow-rate to 120 $m_n^3 h^{-1}$, which is the maximum flow-rate achieved in this test. The very low pressure ratio indicates a very high resistance to flow of the bed and the optimal range was achieved only in the very final stage of the test.

The comparison of Test 1 with the other tests highlights some issues involved in the gasification of pelletized material. Test 1 was easy to be controlled, it was possible to modulate the gas flow-rate by means of the by-pass valve and easily achieve a gas flow rate of 155 $m_n^3 h^{-1}$. During the operation at 100 $m_n^3 h^{-1}$ the pressure drop was below 100 mm_{H2O} and stable.

During the other tests the reduction zone was formed of pelletized material char. The average pressure drop was higher than in Test 1 and the gasifier bed less controllable. In particular periods with high resistance to flow followed by a dramatic reduction can be identified in tests 2, 3 and 4. During the high resistance period the effect of the by-pass valve is negligible. The comparison of WSP tests (2 and 3) and MIX tests (4 and 5) indicates that with WSP it is still possible to have some control of the bed and reach gas flow-rate up to 150 $m_n^3 h^{-1}$. However, this maximum flow-rate cannot be guaranteed. The situation is even worse during the MIX gasification. In this latter case the pressure drop is higher (up to 500 mm_{H2O}), it is not possible to use the by-pass valve to control the gas flow-rate, and there is a de-rating of the gasifier output (maximum gas flow-rate 120 $m_n^3 h^{-1}$).

This behaviour may be explained on the basis of the fuel morphology. The vegetal charcoal in Test 1 is a solid material with high mechanical strength compared to pellet (especially SRP) and mean size ranging from 30 to 50 mm. Notably the charcoal was loaded directly into the gasifier. On the other hand biomass pellets are likely to break up due to mechanical (i.e. in the screw conveyor) and thermal stress, thus generating dust into the gasifier. The formation of dust may explain the high resistance to flow, since the original size and shape of the biomass pellets are not very different from the charcoal, except for the cylindrical geometry. The dramatic reduction in the pressure drop may explained with the discharge of dust from the bottom of the gasifier and substitution with fresh material which retains (at

least partially) the original morphology. The higher pressure drop values observed in Test 4 and 5 may be related to the lower mechanical resistance of SRP.

As a matter of facts the main characteristic of the pelletized biomass gasification is the variable resistance to flow during the test that generates instabilities and difficult control. Fig. 5.24 plots the gas flow-rate against the correspondent pressure drop across the gasifier bed. Again the stability of Test 1 is highlighted, the higher the gas flow-rate, the higher the pressure drop across the bed. As mentioned in Paragraph 5.4.2.1.1 the pressure drop in the clean-up system is very slightly affected by the gas flow-rate, consequently the resistance to flow of the gasifier is constant. Closing the by-pass allows the flow-rate to increase and higher pressure drops are achieved.

In the other tests there is no linear relation between the gas flow-rate and the pressure drop and multiple regimes can be identified, this is due to the variable resistance to flow during the tests. The variation of the resistance to flow of the gasifier bed modifies the pressure curve of the system; therefore even if the pump curve is constant different operating point can be identified. The higher the resistance to flow in the gasifier, the higher the pressure drop and the lower the gas flow-rate. This takes place for Test 2, 3, 4 and 5. In Test 2 and especially Test 3 and Test 4 two regimes can be identified, according to the resistance to flow, which appear as parallel lines in Fig. 5.24. In the regime with high resistance to flow (hereafter HFR), opening or closing the by-pass valve has no effect, the flow is completely controlled by the resistance of the gasifier which is double (or more) the pressure drop of the clean-up. When the resistance reduces dramatically a regime with low resistance to flow (hereafter LFR) occurs; in LFR the modulation of the bypass valve affects the pump curve and operating points with lower pressure drop and higher flow rate are achieved. However, independently of the regime, the resistance to flow is variable throughout the test.

A cold test was carried out three days after Test 5 to assess the impact of the reactions and temperature on the gasifier behaviour. Fig. 5.25 reports the gas flow-rate plotted against the pressure drop across the gasifier bed in cold condition.

The effect of temperature and reactions is immediately evident, in cold condition the pressure drop across the bed is very low (below 50 mm_{H2O}) even at very high gas flow-rates. Two effects influence the bed resistance: gas viscosity and biomass break-up. When the gasifier is running the mean temperature can be taken as 800°C, in this condition the gas viscosity doubles that of air at 15 °C. In addition during the tests the high temperature and the biomass consumption reduce the particle mechanical strength possibly breaking the particles into dust; this may lead to higher resistance to flow of the bed.



Figure 5.22 - Evolution of the pressure drop across the gasifier bed during the tests.



Figure 5.23 - P_n to P_g ratio and discharge frequency modulation in four tests.



Figure 5.24 - Gas flow-rate/Pressure drop relationship in the five tests.



Figure 5.25 - Relationship between gas flow-rate and pressure drop in cold condition after Test 5.

5.4.1.4 Bed permeability

In Paragraph 5.4.1.4 we have been using the term resistance to flow to indicate the relation between the gas flow-rate and the pressure drop across the gasifier bed. Here an attempt is made to describe the gasifier bed according to the most common relationship describing packed beds: the Darcy and the Karman-Kozeny laws.

The Darcy law expresses the relationship between the total discharge rate from a packed bed as a function of the pressure drop and viscosity of the fluid over a given distance:

$$Q = \frac{b \cdot A_b \cdot \Delta P}{\mu_g \cdot L_b} \tag{2}$$

Where Q is the volumetric flow-rate $[m^3 s^{-1}]$ b is the permeability $[m^2]$ of the packed bed, A_b the cross-sectional area $[m^2]$, ΔP the pressure drop across the bed [Pa], μg the gas viscosity [Pa s] and L_b the bed length [m].

Assuming a constant gas viscosity, cross-sectional area and bed length, each operating point of Fig. 5.24 can be represented with a permeability value. Tab. 5.9 reports the mean, permeability values for each test; when multiple regimes can be identified a value for each regime is reported. The assumptions involved in the calculation are the following:

- the pressure drop is concentrated in the cylindrical zone under the throat (reduction zone) with A_b equal to 0.785 m² and L_b equal to 0.8 m²;
- constant gas viscosity evaluated as the air viscosity at 800 °C (3 10⁻⁵ Pa s);
- gas low-rate evaluated as correcting the rotameter reading at 800°C.

The cold flow test is reported for comparison. It is worthy to note that the Darcy law is valid within the laminar regime of the gas in the packed bed (Re < 10), this is verified for most of the operating points. However assuming that the pressure drop

is concentrated only in the cylindrical part and deviation from the Darcy law due to irregularities in the packed bed may affect the calculation. As expected, Tab. 5.9 shows that during Test 1 the permeability was higher than the other tests. The permeability of Test 1 is nearly two times those of tests 2 and 3, three times that of Test 4 and four times that of Test 5. It can be noted also that, except for Test 3, the mean permeability has been decreasing from Test 1 to 5, thus the use of pellets seems to reduce the permeability of the bed; MIX seems to lead to lower permeability than WSP. Comparing the two regimes very large variations are observed, the permeability in LFR is from 2.5 to 5 times higher than in HFR. The comparison of Test 5 with the cold test highlights that temperature and chemical reactions affect the properties of the packed bed, as mentioned in Paragraph 5.4.1.3.

Table 5.9 - Mean permeability values [10 ⁻¹⁰ m ²].						
	Test 1	Test 2	Test 3	Test 4	Test 5	Cold
Mean	36.8	17.0	19.9	11.6	9.51	28.1
HFR	-	8.68	11.7	6.08	-	-
LFR	-	42.1	36.8	15.2	-	-

Further investigation on this aspect can be carried out according to the Karman-Kozeny equation:

$$\frac{\Delta P}{L_b} = \frac{150 \cdot Q \cdot \mu_g}{A_b \cdot ESD \cdot \Phi_p} \cdot \frac{(1-e)^2}{e^3}$$
(3)

Where ESD is the equivalent spherical diameter [m], Φ_p is the particle sphericity and e the void fraction of the packed bed. On the basis of the initial ESD and sphericity of the particle it is possible to evaluate the void fraction of the gasifier bed. Tab. 5.10 reports the results, results are not included for Test 1 since the properties of the pre-loaded charcoal are unknown. The void fraction results variable from 0.1 to 0.2. This value is somewhat unrealistic since assuming that the particles retain the same size and shape in the gasifier would be equal to retain the initial void fraction, which is instead close to 0.4.

	Test 1	Test 2	Test 3	Test 4	Test 5	Cold
Mean	-	0.147	0.154	0.105	0.1	0.138
HFR	-	0.120	0.131	0.086	-	-
LFR	-	0.192	0.184	0.115	-	-

Table 5.10 - Void fraction according to the initial size and shape of the particles.

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Another attempt to calculate the void fraction is to assume the gasifier bed formed of particles with ESD equal to 4mm and sphericity equal to the initial condition. The results are reported in Tab. 5.11. According to these assumptions the void fraction ranges from 0.2 to 0.3, these values seem to be more realistic than those of Tab. 5.10. Both Tab. 5.10 and Tab. 5.11 report void fraction in the cold test higher than in Test 5, highlighting that in the reacting system some other phenomena are involved in reducing the permeability.

	Test 1	Test 2	Test 3	Test 4	Test 5	Cold
Mean	-	0.245	0.255	0.230	0.215	0.29
HFR	-	0.203	0.222	0.190	-	-
LFR	-	0.312	0.302	0.245	-	-

Table 5.11 - Void fraction assuming ESD equal to 4 mm in the gasifier bed.

5.4.1.5 Sampling

5.4.1.5.1 Condensate

The condensate sampling was carried out in Test 3, 4 and 5. It was decided to start sampling 1 hour after the gasifier ignition. The sampling procedure encountered some difficulties. It was expected that the particle content would be reduced after the cyclone, however in Test 3 and 4 the filter of the tar sampling system got plugged very briskly with sticky particles; consequently the sampling was stopped for safety reasons. In Test 5 the filter was removed and the system was allowed to sample gas and particles. Bottle 1 acted as filter collecting the particles, but no condensate was found in it as well as for bottle 2A. 2B and 3 were able to collect some sallow (see Fig. 5.26) condensate, 26% in bottle 2B and 74% in impinger 3. The condensate content of the gas was found to be 35 grams per m_n^3 of gas. The TG-FTIR analysis of the two fractions reported a water content of 89.4% in F2B and 98.6% in F3. On the whole the water content would be of 34 grams per m_n^3 of gas. The remaining fraction can be attributed to condensed organic compounds which would be equal to 1 gram per m_n^3 of gas, a common value reported for downdraft biomass gasifiers (for instance [23]).

It must be noted that this sampling is not very representative, since it was carried out only one time and solid particles may have contaminated the samples. In addition the TG-FTIR analysis may introduce some other errors in the evaluation of the organic condensate due to the very high water content of the sample. For future investigations some improvement can be proposed:

- use a filter with very large mesh to prevent plugging, impinger 1 will act as filter; this is not a problem since it is likely that if the gasifier is properly operated no fractions will condense at 120°C;
- start the sampling when the temperature in the sampling point is above 200°C, this is somewhat difficult to be achieved since rather long runs are required; conversely insulating the line from the gasifier outlet to the scrubber inlet could be a useful solution.

F2B and F3 were subjected to GC-MS analysis in order to identify the organic compounds mixed in the water. Only few species could be detected:

Acetic acid, propanoic acid, phenol, cresol and phenol and cresol in F2B and F3, respectively. The fact that phenol and cresol are identified in F3, while the organic acids (even if more volatile) are in F2B can be attributed to their higher concentration. Noteworthy all these compounds are secondary tar (see Chapter 1) and all of them have boiling points below 200°C and are water soluble; consequently it is likely that these compounds can contaminate the water used for gas scrubbing.

No condensate sampling was carried out after the blower due to the problems encountered with first sampling point. Some comments can be pointed out concerning this sampling. The tar content is already low in the first sampling point; however the condensation method can fix this issue if the run is long enough (at least 5 hours). In the second sampling point (after the lower) the tar content is expected to be a least one order of magnitude lower than after the cyclone, as a consequence a longer run would be required to get a representative amount of sample, in addition the separation efficiency of the tar sampling system in these conditions has still to be proved. However sampling after the blower has also two main advantages: the absence of particle and water.



Figure 5.26 - Condensate collected in impinger 3 after Test 5.

5.4.1.5.2 Gasifier residues from the collection tank

The gasifier residues discharged from the gasifier bottom in the collection tank were sampled during Test 1, 3, 5 (namely C1, C3, C5). Notably the collection tank is equipped with a screw conveyor to remove the gasification residues coming from the bottom grid. This provision allows convoying the solid residues into an external tank, minimizing the residence time of the residues in the collection tank and allowing collecting the residues from the external tank. This was possible for C1, these residues are relatively big (average size 1 cm, see Fig. 5.27), so they settle at the bottom of the screw conveyor and can be recovered. Conversely C3 and C5 (see Fig. 5.27) are in the range 1-2 mm. Therefore the charcoal bed produced bigger residues than pelletized biomass; this is a consequence of pellets break-up and fragmentation in the gasifier. The causes of this fragmentation are several; biomass particles partially break-up due to mechanical stress in the loading screwconveyor and in addition thermal stresses and consumption are likely further fragment the particles (as pointed out in Paragraph 5.4.1.4.2), however before reaching the collection tank the particles are removed from the bottom grid with the mechanical scraper and then washed away with a water stream, this last phases may have a great impact in disaggregating the original pellets. The screw conveyor was not able to convoy dust (as a matter of fact it is not designed for this particle size). Consequently the heavy fraction of the pellet residues settled on the bottom of the collection tank (forming a thick layer), while the light fraction was suspended in to the water. This latter fraction is harmful for the water handling system of the plant, since after short time the water of the collection tank is filled with suspended solids which can damages pumps and form (in a short time) thick deposit in the equalization tank. Tab. 5.12 reports the composition of the three samples. C1 is somewhat different from C3 and C5, in particular it seems that a lower conversion

of the organic material has occurred (lower ash content). However it is not very representative to compare C1 with C3 and C5 since the original composition of the charcoal is unknown. C1 and C5 are very similar, especially the ultimate analysis. Noteworthy these compounds are almost completely devolatilized (compare with Tab. 5.6). It is possible to calculate the conversion of the organic material (see Chapter 1) on the basis of the ash content of original biomass (WSP and MIX) and the charry residues (C3 and C5). The conversion values result 75.7% for WSP and 36.8% for MIX. These values are not realistic. In particular the MIX conversion is too low and is in disagreement with composition of C5. A conversion value of 36.8% indicates a charry residue (comparing to MIX) still containing half of the original volatile matter, with hydrogen content probably close to 2-3%. Conversely the hydrogen content is 0.2% indicating an almost complete loss of volatile matter and some degree of char oxidation. The same comment can be valid for C3 even if less remarkable. The uncertainties related to this sampling have been pointed out in Paragraph 5.2.5.1.

Parameter	Sample	Unit	C1	C3	C5
VM	dry	%	7.79	7.65	5.96
FC	dry	%	87.63	83.69	86.64
ASH	dry	%	4.58	8.65	7.90
С	dry	%	81.63	84.79	84.60
н	dry	%	1.28	0.44	0.20
Ν	Dry	%	0.78	0.64	0.65
0	Dry	%	by diff.	by diff.	by diff.

Table 5.12 - Charry residues proximate and ultimate analysis.



Figure 5.27 - Charry residues recovered from the collection tank during Test 1 and Test 5.

5.4.1.5.3 Gasifier bed from the nozzle

After Test 5 an attempt was made to sample the gasifier bed from the air nozzles (namely BED), the sample was compared with the original biomass and the charry residues, in terms of morphology, size and composition. Fig. 5.28 shows a comparison of the original feedstock (WSP) and BED. Tab. 5.13 reports the proximate and ultimate composition of BED. The MIX and BED compositions are not directly comparable since it is not the same sample. This explains the lower ash content in BED than in MIX. However the black colour as well as the volatile matter content below 70% and the hydrogen content below 5% indicate that BED is a partially devolatilized biomass. Hence the devolatilization step is far to be completed at the nozzle outlet, conversely devolatilization is still occurring. This result may suggest that flaming pyrolysis is taking place at the nozzle outlet; this observation is supported from three reasons:

- oxygen is available at the nozzle outlet;
- high temperature are achieved close to the nozzle outlet (Paragraph 5.4.1.1.2);
- a reverse flame is visible from the nozzle top opening.

In flaming pyrolysis the volatiles generated from the fuel are immediately ignited generating a flame attached to the solid and providing heat for further devolatilization.

In BED the original WSP particles can be easily recognized, except for the black colour, these particles are similar in size and shape to the original ones. Their mechanical resistance seems still high even if some cracks appear on their surfaces. On the other hand SRP cannot be recognized thus they are likely to generate the dust visible in Fig. 5.28; their presence is verified by the relevant nitrogen content in the BED sample (see Tab. 5.13). Consequently it seems that SRP are easier to break up and form dust than WSP, at least it may be suggested that SRP break up before WSP during gasification. This result is in agreement with the observations of Paragraph 5.4.1.4.



Figure 5.28 - Comparison of WSP and BED.

Parameter	Sample	Unit	BED
VM	Dry	%	55.32
FC	Dry	%	41.42
ASH	Dry	%	3.26
С	Dry	%	62.24
Н	Dry	%	4.51
Ν	Dry	%	1.31
0	Dry	%	by diff.

Table 5.13 - BED proximate and ultimate analysis.

5.4.1.5.4 Gasifier particulates

After Test 5 some particulates samples were collected from the plant. The samples are:

- PA, collected at the bottom of the tank positioned under the cyclone for particulates removal;
- PB, collected on the wall of same tank of PA;
- PC, collected at the gasifier outlet in the proximity of TC0 by removing the pipe in this position.

Fig. 5.29 shows pictures of the sampling points and appearance of the collected samples. The bottom of the tank below the cyclone contains a muddy residue (PA). The residue is wet with water and releases a strong smell of organic compounds. A thick layer of particles is adhered to wall of the tank (PB). These particles are smelly as PA but its appearance is powder-like, formed of several light and soft particles.

Sample PC was collected during an inspection of the pipeline immediately after the gasifier outlet. The inspection was carried out to verify the level of dirt deposited onto the pipe walls, as an indicator of possible plugging. Fig. 5.29 reports a frontal view of the pipe section. A layer of particles is adhered to the pipe wall; the layer is 2 mm thick in the upper section and 4 mm thick in the lower section. This layer has been formed in nearly 25 hours of gasifier operation, however this is not a reference for a continuously operated plant, since the very frequent start-up and shut-down in our testing are likely to increase the level of dirty in the pipelines. Sample PC can be removed in compact slices from the pipe wall. The three samples were dried overnight and analyzed. After drying the physical appearance of PA was similar to PB. Tab. 5.14 reports the proximate and ultimate analysis of the three samples. Samples PA and PB are similar; they are charry material but not completely devolatilized. The composition of PC is not easy to be interpreted; this residue is likely to be a mixture of different deposits (organic particulates, alkaline vapours, tar) which are condensed or adhered in the first cold spot.

Parameter	Sample	Unit	ΡΑ	PB	PC
VM	Dry	%	19.63	16.65	27.85
FC	Dry	%	60.53	64.16	24.66
ASH	Dry	%	19.84	18.88	47.49
С	Dry	%	68.41	73.36	n.d
Н	Dry	%	1.30	1.19	n.d
Ν	Dry	%	0.90	1.23	n.d
0	Dry	%	by diff.	by diff.	n.d



Figure 5.29 - Sampling point and appearance of gasification particulates.

Subsequently an attempt was made to verify the presence of condensed organic species in particulates, suggested by the strong smell of PA and PC as well as the lack of heavy tar (especially PAH) in the sampled condensate. PA and PC were dissolved in acetone in order to extract eventual organic compounds contained in the particulates. The filtered solvent was then analyzed with GC-MS analysis. Figure 5.30 reports the total ionic current chromatogram obtained for PA and PC. It can be noted that the spectrum of PC is shifted toward higher retention time than PA. This can indicate the presence of heavier compounds in PC than in PA. The results of the compounds identification is reported in Tab. 5.15. PC contains a broad distribution of aromatic compounds, in particular PAH. Except for phenols (the lightest compounds) and benzofurans, all the extracted components are polycyclic aromatic hydrocarbons ranging from naphthalene to coronene. According to Table 1.12 these compounds belong to tar class 4 and 5 and, as confirmed by the boiling temperatures, and are likely to condense immediately at the gasifier outlet (maximum temperature 350°C). The composition of the extract of PA is somewhat similar to that of PC, containing many PAH such as naphthalene and anthracene. However, the presence of light compounds such as acetic and propanoic acid, and the absence of coronene, indicate that the composition of this extract is slightly shifted toward lighter compounds compared to PC (as reported by Fig. 5.30). According to Table 1.12 these compounds belong to tar class 2, 4, and 5. Given these results and the lack of heavy tar in the sampled condensate it can be stated that heavy tar can condense in the plant before reaching the scrubber

and the tar sampling point. It is likely that in the early stage of process heavy tar condense immediately at the gasifier outlet due to the low temperature. As the temperature increases the condensation point is shifted toward the cyclone where the temperate is always below 250°C. Here almost all the fractions condense and a broad range of compounds can be identified in PA. Therefore the tar content at the sampling is much lower than at the gasifier outlet and its composition is qualitatively shifted toward very light compounds. On the basis of this result the composition of PC can be explained as a mixture of charry particles with a high conversion (which explains the high ash content) and some condensed PAH (which explains the volatile matter content in this charry material).

FIACUUM. FA		
Compound	MW [g mol ⁻¹]	Tb [°C]
acetic acid	60	118
propanoic acid	74	141
butyrolactone	86	204
phenol	94	181.7
3-methyl-2-cyclopenten-1-one	96	-
2-methyl-phenol	108	191
indene	116	-
3,5-dimethyl-phenol	122	-
naphthalene	128	218
1-methyl-1H-indene	130	-
4-(1-methylethyl)-phenol	136	-
1-ethyl-4-methoxy-benzene	136	-
2-methoxy-cresol	138	-
1-methyl-naphthalene	142	240
2-isopropyl-5-methylphenol	150	232
biphenyl	154	256
acenaphtene	154	-
1,2-dimethyl-naphtalene	156	-
fluorene	166	295
phenalene	166	-
dibenzofuran	168	285
4-methyl-biphenil	168	-
1,4,5-trimethyl-naphtalene	170	-
anthracene	178	340
1-methyl-fluorene	180	-
9H-fluoren-9-one	180	-
4-methyl-dibenzofuran	182	-
3-methylphenanthrene	192	-
2,3,5-thrimethyl-phenanthrene	220	-
benzo[ghi]fluoroanthene	226	-
benzo[a]antracene	228	438
benzo[j]fluoroanthene	252	-
benzo[ghi]perylene	276	500

Table 5.15 - Organic compounds identified in the acetone extracted of PA and PC.

Fraction: PC				
Compound	MW [g mol ⁻¹]	Tb [°C]		
phenol	94	181.7		
2-methyl-phenol	108	191		
indene	116	-		
naphthalene	128	218		
1-methyl-naphthalene	142	240		
Cyclopent(de)naphtalene	152	-		
biphenyl	154 256			
1,2-dimethyl-naphtalene	156	-		
1-ethyl-naphtalene	156	-		
fluorene	166	295		
dibenzofuran	168	285		
4-methyl-biphenil	168	-		
2-isopropyl-naphtalene	170	-		
anthracene	178	340		
1-methyl-fluorene	180	-		
3-methylphenanthrene	192	-		
2-methylanthracene	192	-		
fluoroanthene	202	375		
pyrene	202	404		
1-indene-1-(phenylmethylene)	204	-		
2-phenylnaphtalene	204	-		
9-ethyl-phenantrene	206	375		
2,5-dimethyl-phenantrene	206	-		
1-methyl-pyrene	216	-		
benzo[b]naphto[2,3-d]furan	218	-		
2,3,5-thrimethyl-phenanthrene	220	-		
benzo[ghi]fluoroanthene	226	-		
benzo[a]antracene	228	438		
5,6-dihydrochrisene	230	-		
7H-benz(de)anthracen-7-one	230	-		
1,2,3,5-tetrahydro-thriphenylene	232	-		
3,4,5,6-tetramethyl-phenanthrene	234	-		
6-methyl-chrisene	242	448		
benzo[j]fluoroanthene	252	-		
3-methyl-benzo[j]aceanthrylene	266	-		
benzo[ghi]perylene	276	500		
dibenzo[j]anthracene	278	-		
benzo[a]naphtacene	278	-		
coronene	300	525		
dibenzo[fg,op]naphtacene	302	-		



Figure 5.30 - Total Ionic Current Chromatogram obtained from GC-MS analysis of the compounds extracted in acetone from PA (a) and PC (b).

5.4.2 Gasification performance

The gasification performance for the two feedstocks can be evaluated according to the indicators presented in Chapter 1. In order to calculate such indicators it is necessary to characterize the material, elemental and energy balance of the plant.

5.4.2.1 Balances approach

The calculation of the material, elemental and energy balance relies on much information. Fig. 5.31 highlights the data required for the calculation. The particulates and tar productions are assumed to be negligible compared to the total output (according to [23], the particulates and tar content can be assumed to 3000 mg m_{n}^{3} , which is negligible compared to 120 kg h^{-1} of gas) Tab. 5.16 reports the possible measures and analysis to fully characterize the material and elemental balances. The biomass loading rate is calculated as the total mass of feedstock charged in the time elapsed from the gasifier ignition; consequently this is an average loading rate. The syngas volumetric flow-rate is achieved averaging the rotameter readings on the total elapsed time. Therefore it is possible to calculate the syngas mass-flow on the basis of the average gas composition achieved with the micro-GC. The air flow-rate can be calculated assuming that all the nitrogen in the syngas is equal to nitrogen entering the system with air. This hypothesis is verified for biomass with very low nitrogen content (such as WSP), but may introduce uncertainties as the nitrogen content increase. The water production can be calculated on the basis of the condensate content reported in Paragraph 5.4.1.5.1. Finally the charry residue production can be calculated on the basis of the biomass loading rate and assuming that the ash in the biomass are completely retained in the charry residue, thus acting as a tracer. According to these data and calculations the material balance of the plant is fully characterized, consequently the elemental balance can be easily drawn on the basis of the biomass, charry residue ultimate analysis and syngas compositions.



Xc Xh Xo Xash

Figure 5.31 - Representation of the material and elemental balances.

	Measured Variables	Data from analysis & sampling	Calculated variables
	Biomass loading rate	Biomass ultimate analysis	
		Charry residues ultimate analysis	Charry residue production
	Syngas flow-rate	Gas composition	Air flow-rate
		Syngas water content	Water production

Table 5.16 - Material and elemental balance calculation.

The simplified energy balance of the plant is represented in Fig. 5.31. The simplifications are:

- both the sensible and latent heat as well as the chemical energy of particulates and tar are neglected;
- kinetic, potential and pressure terms are neglected;
- electric and mechanical works entering the system is neglected;
- thermal dispersion from the gasifier and clean-up pipe-line is neglected.

The main parameters of the calculation are the energy streams associated to the chemical energy of biomass, charry residue and syngas as well as the water latent heat; these terms can be calculated on the basis of the material balance and the LHV of biomass, charry residue and syngas as well as the water latent heat. The sensible heats associated to all the material fluxes are less important; once a reference temperature is fixed these terms can be calculated on the basis of the material balance, the specific heat and inlet or outlet temperature. The main assumption that has to be made is the outlet temperature of the charry residue, which is not monitored.



Figure 5.32 - Representation of the energy balance.
5.4.2.2 Balances calculation

The balances were carried out for two groups of tests. The first group is related to WSP gasification and include Test 1, 2 and 3 and it is named B1, while the second group (namely B2) including Test 4 and 5 is related to MIX. As highlighted in the previous Paragraph the system can be fully characterized in terms of material and elemental balances. However, as pointed out in Paragraphs 5.4.1.5.1 and 5.4.1.5.2, the liquid sampling and the charry residue sampling encountered some problems and, consequently, cannot be considered as completely reliable. In particular the char sampling leads to non valid biomass conversions on the basis of the char proximate analysis. As a consequence some assumptions related to these sampling were made in order to draw the balances. For both B1 and B2 the water content in the gas was taken as 90 grams per m_n^3 of dry syngas. This value is higher than the only data achieved during Test 5 but similar to literature values (for instance [8]). For MIX another little assumption was made, the nitrogen content of the original biomass and residue is considered as oxygen. However, these hypotheses are believed to affect very slightly the results. On the other hand, formulating a hypothesis for the composition of the charry residue would affect too much the results, therefore an optimization approach was chosen. The ultimate analysis of the charry residue is assumed to be composed of carbon and ash, and the relative proportion of the two fractions is varied in order to minimize the closure of the material, elemental and energy balance. This procedure is believed to be quite reliable since five constraints (material, carbon, oxygen, hydrogen and energy balance) are involved in its calculation. The results of the optimization are reported in Tab. 5.17. The material balance is scarcely affected by the variation of the composition since both the water production and the residue production are less important than the syngas flow-rate in the closure of this balance (considering only the syngas as output leads to a closure of 111% for B1 and 110% for B2).

	inai anu elementai D	
Balance	B1	B2
Material	99%	98.5%
Carbon	88.3%	89.5%
Oxygen	105.1%	99.5%
Hydrogen	109.8%	102.5%
Nitrogen	100%	100%
Energy	104.3%	102%
Ash content in the sampled residue	8.65%	7.90%
Ash content in the fictitious residue	16%	35%

Table 5.17 - Material and elemental balance closures.

More important is the impact of the optimization on the elemental balance, especially the carbon balance, which is difficult to fix. The hydrogen balance is affected by large errors due to the small quantities, even the slightest change in the variables values leads to large variation in the balance closure. The nitrogen balance is obviously closed a 100% due to assumption used in the calculation. The high LHV of the charry residue compared to the syngas (indicatively 27 MJ kg⁻¹ VS 4.5 MJ kg⁻¹) leads to a worse closure of the balance compared to the mass balance. Tab. 5.17 reports also the comparison of the ash content of the sampled and fictitious residues. The ash content of the fictitious residue is higher than the sample leading to a higher conversion of the organic material, 87% vs. 75.7% and 86% vs. 36.8% for B1 and B2, respectively. This is a further proof of the unreliability of sampling of the charry residue, as discussed in Paragraphs 5.2.5.1 and 5.4.1.5.2. Tab. 5.18 reports the results of the mass balance, notably these data are related to average conditions during the group of tests, actually these values are variable during the test (for instance the syngas flow-rate as reported in Paragraph 5.4.1.2.2). The two tests were similar; however the biomass loading rate was slightly higher in B1 than B2, generating higher syngas flow-rate and requiring a higher air flow-rate. This seems to be in agreement with the observations reported in Paragraph 5.4.1.4. The average permeability of B1 is higher than B2 $(18.45 \cdot 10^{-10} \text{ m}^2 \text{ vs. } 10.55 \cdot 10^{-10} \text{ m}^2)$. The higher the permeability the higher the gas flow through the packed bed, as a consequence the higher the air flow-rate leading to an higher biomass consumption and syngas production. It is worthy to note that the gasification of pelletized biomass led to a de-rating of the nominal gasifier capacity (see Tab. 5.1). The de-rating is close to be 50% for both B1 and B2. On the other hand the gasification of pelletized biomass produced a syngas with a higher LHV than Tab. 5.1. This is likely to be related to the higher LHV of the pelletized biomass compared to woodchips. On the basis of the biomass load and air flow-rate it is possible to evaluate the equivalence ratio (ER) of the two groups. ER is very similar for the two groups (0.29 vs. 0.3) despite the different biomass load and syngas production. Noteworthy the ER is an average data: the gasification process on the whole is a continuous process formed of several semibatch steps, determined by the biomass load frequency.

Table 5.18 - Mass balance results.			
Parameter	Unit	B1	B2
Biomass load	kg h⁻¹	54.2	44.7
Air flow-rate	m ^³ nh⁻¹	63.1	60.45
Syngas flow-rate	m ^³ nh⁻¹	106.3	97.5
Water production	kg h⁻¹	9.57	8.77
Residue production	kg h⁻¹	6.30	5.68
ER	-	0.29	0.3

Consequently during a batch of biomass load the equivalence ratio is variable since the organic content in the gasifier keeps reducing in time; in addition the air flow-rate is variable during a single batch due to the permeability fluctuations, affecting the instantaneous ER. In this regard an important parameter is the discharge frequency of the charry residue. This parameter regulates the residence time of the biomass particles in the gasifier and thus their residence time and ER range. Unfortunately, the quick modulation of this parameter due to the instability of biomass pellets gasification makes it difficult to evaluate its effect.

5.4.2.3 Gasification performance

The data achieved from the mass and energy balance can be used to calculate some of the performance indicators presented in Chapter 1. The results are reported in Tab. 5.19. B2 exhibits slightly higher values of specific gas production (2.4 vs. 2.2) and CGE (70% vs. 67.7%), but if the error associated to the balance calculation is taken into account the performance of the two sets of tests can be considered almost equal. A straight comparison of the gasification performance of the two feedstocks is not possible since it was not possible to operate the tests in the same operating conditions (biomass loading rate and air flow-rate).

It is worthy to note that these values are comparable to those reported in the literature for biomass gasification with air in downdraft gasifiers [2, 5, 8].

Table 5.15 Operating parameters and performance indicators.				
B1	B2			
2.2	2.4			
87%	86%			
67.7%	70%			
	B1 2.2 87% 67.7%			

 Table 5.19 - Operating parameters and performance indicators.

5.5 Summary

In this Chapter the development and testing of a pilot scale gasification facility based on a downdraft gasifier has been presented.

Tests have been carried out with pelletized biomass as feedstock. Two biomass feedstocks were used: wood sawdust and a mixture of wood sawdust and sunflower seeds residues. The gasification runs allowed to study the gasification behaviour of pelletized fuels in terms of gas composition, temperature, pressure drop across the gasifier bed and gas flow-rate.

The following conclusions about the gasification behaviour of pelletized fuels can be drawn.

- The clean-up system reaches a steady state condition in three hours, at the gasifier outlet the temperature increases up to 350°C.
- The temperature profile in the gasifier throat is variable in space and time, indicating a dynamic process; temperatures up to 1100°C are reported.
- The gas composition is rather stable during the five runs, irrespectively of the feedstock; a steady gas composition is achieved after one hour and it seems to be related to the equilibrium of the water gas shift reaction.
- The average lower calorific value of the syngas was close to 5.6 MJ m_n⁻³, except for Test 1 where the reduction bed was filled with charcoal;
- Pelletized biomass produce a rather high pressure drop across the gasifier bed; in particular the resistance to flow was variable during the tests, as a consequence the bed was very unstable. This led to a de-rating of the syngas flow-rate and difficult plant operation due to the variable pressure drop.
- The variable gas flow-rate and the general de-rating of the gasifier output are likely to be critical limitations for the use of pelletized biomass in a downdraft gasifier; on the other hand the gas composition and the lower calorific values were satisfactory and stable during the runs.
- An attempt was made to determine the void fraction in the gasifier basis on the basis of the Karman-Kozeny equation: values ranging from 0.1 to 0.2 were calculated.

Concerning the sampling and analysis of the liquid and solid residues produced from the plant the following conclusion can be drawn.

- Sampling of condensate fraction has still to be enhanced and adapted to the gasifier, however it seems that at the sampling point (after the cyclone) the tar content is very low and only primary tar are identified.
- Sampling of the charry residues from the collection tank has to be improved. Biomass pellets generated very fine charry residues which were almost impossible to be recovered by the screw conveyor and quickly produced water with large content of suspended solids. It cannot be stated if the final size distribution of the residues is representative of the end gasifier bed due to the presence of the mechanical scraper.
- Sampling of the gasifier bed from the air nozzles revealed partially devolatilized particles supporting the flaming pyrolysis hypothesis. The particle size and shape were very similar to WSP, while it is likely that SRP fragments into dust before reaching this point.

• Sampling of the gasifier particulates was carried out in three points. The analysis showed that these residues are charry material but not completely devolatilized. The GC-MS analysis of the acetone extracted revealed that these samples contain a broad distribution of condensed tar from class 1 to class 5. Therefore most of the tar can condense within the plant before reaching the tar sampling point and scrubber.

The calculation of material balances suffers of the lack of some information (the syngas water content and the charry residue composition are considered not reliable). Consequently some assumptions were made in order to calculate the material and energy balance. In particular the composition of the charry residue has been assumed on the basis of a procedure which minimizes the closure of the material, elemental and energy balances.

The balance calculation pointed out the following operating parameters for pelletized biomass:

- Average biomass loading rate ~50 kg h⁻¹
- ER ~0.3
- Specific gas production ~2.3
- CGE ~70%

Finally some comments about future developments of the plant and improvement to the system can be made.

- The test run should have a duration of at least 6 hours in order to be considered completely reliable. This value is based on the observation that 1 hour is required to stabilize the gas composition and 3 hours are required to reach steady conditions in the clean-up system.
- The gasifier internal temperature profile needs to be determined as much as possible. Three fixed thermocouples can be inserted in the gasifier wall above the air nozzle in order to evaluate the temperature before the nozzles. Evaluation of the temperature down from the nozzle in the gasifier throat should be performed continuously with computerized data recording in order to shed more light on the temperature range and fluctuations in the bed. This may require a proper design of the thermocouples in order to avoid unrealistic values due to continuous exposure to radiation. Evaluating the temperature of the reduction zone could be a very precious information; unfortunately it is really complex to install thermocouples in this zone since the gasifier wall is completely insulated with refractory material.
- The condensate sampling system presented in Chapter 4 was not very effective. This is ascribed to quick plugging of the iron filter and low temperatures of the sampling point. The temperature of the sampling point can be increased both with longer test runs (starting the sampling when the temperature has reached steady conditions) and insulating the clean-up piping from the gasifier outlet to the cyclone. This latter practise could also reduce the build-up of charry deposit and tar onto the pipe walls. It seems that the actual sapling system can be used for the evaluation of the tar content at the gasifier outlet, especially when the sampling point is

moved at the gasifier outlet instead of the cyclone outlet; conversely it may not be effective for the evaluation of the tar content before the end-user due to very low content of condensable species.

- The evaluation of the production of charry residues and their sampling is a major issue for the complete characterization of the gasification plant. In the most favourable case the total fragmentation of the particles should be avoided (for instance using different biomass feedstock); this would allow collecting the charry residue in an external tank which could be weighed and easily sampled and analyzed. When this is not possible an on-line sampling of the charry residues from the water jet exiting the gasifier bottom should be installed in order to perform, at least, a representative sampling and analysis.
- The sampling and analysis of the gasifier could be improved with use of the Inconel sampling probe which has been designed during the PhD work. This device will allow to perform sampling during the gasifier operation, which will shot a sort of picture of the particle gasification.

6. MODELLING A PILOT SCALE DOWNDRAFT BIOMASS GASIFIER

The experimental activity on the pilot scale gasifier presented in Chapter 5 has been integrated with a modelling activity. The aim of this modelling activity is to provide an interpretative tool which allows understanding the phenomena occurring in the gasifier and giving indication about the effect of the operating parameters. In order to provide an interpretative tool it is necessary to describe the phenomena occurring in the gasifier and their coupling. As a consequence it is mandatory to use a dynamic and distributed representation of the system.

First of all a brief review of the main references is presented. Subsequently the phenomena and reactions taking place in a gasifier are analyzed and the choice of the sub-models as well as the kinetic parameters is discussed. On these basis the model development and approach is presented along with the simulation software and numerical solution methodology. Finally the results of the model are compared with the experimental results presented in Chapter 5 and the capabilities of the model are assessed.

6.1 Literature review of fixed bed biomass gasifiers and combustors models

This brief review focus on distributed model, although several different modelling approach are reported in the literature such as equilibrium models, composite model based on flow-sheeting codes, nodal description etc.

Most of the works carried out in the past on fixed bed gasifiers and combustors is related to coal gasification and combustion. In 1993 [1] reviewed the state of art of fixed bed coal gasifiers and combustors models. It was pointed out the all the models had in common five main features: (1) single initial particle size, (2) no momentum transport for the gas and solid phase, (3) radially uniform gas and solid phase flow, (4) axially and radially uniform bed void fraction, (5) char or carbon combustion with kinetic analysis. At the beginning of 1990 a group of the Provo University carried out comprehensive and detailed modelling studies. In particular, [2] took into account the full description of coal gasification in a fixed bed downdraft gasifier. The model is based on a plug flow description of the solid and gas motion. The solid and gas phase are described with the continuity, energy and species balances. No momentum balance is considered for the solid, while the Ergun equation is used to calculate the gas pressure drop across the bed. The solid reactions (drying, devolatilization, char reaction) are taken into account with dedicated sub-models and extensive parametric analysis of the kinetic parameters. The particles are assumed thermally thin, spherical and all identical in size. The gas phase reactions are described with an equilibrium approach. All the heat transfer phenomena are considered and described with effective coefficients. Radiation and conduction are grouped together into an effective conductivity. Similar approaches have been applied to biomass combustors. The authors presented a procedure to take into account the axial variation of the void fraction. The work of [3] focuses on the description of a sort of updraft biomass combustor with over-firing. The model does not take into account heat transfer by radiation or conduction, but includes a kinetic description of the gas phase chemistry. A further advancement in biomass combustor modelling can be found in the work of [4], who simulated a fixed bed combustor of solid wastes and compared the results with the experimental data achieved from a lab scale apparatus. The main advancement of their model is the description of the radiative heat flux across the packed bed based on the Schuster and Schwarzschild equation [5]: this allowed the authors to verify that in the packed bed conductive heat transfer is rather negligible compared to radiating heat transfer and the heat generated by combustion. Extensive work on waste combustors models have been carried out by [6, 7]. This author carried out comparisons of the result obtained from a lab-scale combustor and simulations, the works were focused on parametric analysis of the devolatilization kinetic parameters, fuel moisture and air flow-rate. Concerning biomass gasifiers, Di Blasi developed two excellent dynamic models related to an open-core downdraft gasifier [8] and an updraft gasifier [9]. The author included a detailed description of the drying process, gas phase chemistry and represented the conductive and radiating heat transfer as a cubic function of the temperature. It is worthy to note that in biomass combustor model the volatiles representation is not a critical issue. as a consequence the chemical species (tar, methane etc.) are grouped in fictitious compound which undergoes gas phase combustion. Conversely this is a major issue in biomass gasification, since the final syngas composition and gasifier behaviour depends very much on the fuel devolatilization. [8] represented the fuel devolatilization with a single global kinetic and related the macro-products (char, tar and gas) as well as the permanent gases distributions to the biomass with experimental mass yield coefficients. The model predicted gas composition in agreement with some published articles as well as a plausible temperature profile. Tinaut et al. [10] carried out an experimental and modelling study to develop and validate a steady state model of a lab-scale open-core downdraft gasifier. In order to use a steady state model the authors adopted a recursive procedure based on an initial guess of the solid temperature profile. The authors implemented a more advanced devolatilization sub-model based on three parallel reactions for the production of char, tar and gas. The composition of the devolatilization gas was described according to the approach proposed by Thunmann et al. [11]. The model represented fairly well the solid temperature profile but overestimated the gas temperature; in addition no validation of the gas composition was reported. Some authors [12, 13] focused their study on the oxidation zone of a downdraft gasifier. Both authors highlighted the necessity to include a char reactivity factor in the char reaction rates in order to take into account the increase in reactivity associate to char burn-off. In a recent work Sharma (2011) [14] developed a model of an opentop downdraft gasifier with a second air injection close to the gasifier bottom. The model introduce some innovative hypothesis such as a hierarchical approach to the gas phase oxidation and decouples the gasifier physics in three stages (fluid flow, heat transfer and physical and chemical phenomena) which are solved separately and then recomputed. To the author knowledge no attempts have been made to apply such description to throated downdraft gasifiers, which has been the subject of the present Chapter.

6.2 Gasifier modelling

The model developed in this Thesis is based on the information and results related to the downdraft gasifier installed at CRIBE and tests carried out during this Thesis and reported in Chapter 5. In particular Test 2 (WSP as feedstock) is taken as reference. Noteworthy the representation of a gasifier is a very complex task. As highlighted in Chapter 1, a gasifier is a complex system involving several chemical and physical phenomena with different time and spatial-scale. Each phenomena can be represented with different sub-models or parameters reported in the literature or developed during this Thesis. The choice of each sub-model is based on three main drivers: validity of the sub-models, numerical cost and implementation, availability of the required parameters. Often, some complex sub-models are not valid and may require parameters which are not experimentally verifiable. On the other hand too strong assumptions may lead to a critical loss of information. Therefore it was tried to perform a critical choice of the sub-models and parameters, and all of them are discussed in the following parameters.

6.2.1 Modelling approach

6.2.1.1 Domain

The gasifier is represented with a 1-D domain. This is clearly a quite important restriction of the model, since the variables distribution are likely to be at least 2-D (for instance the temperature at the gasifier wall is different from the gasifier centre) with radial profiles. However a 2-D model of the gasifier would require a very high computational cost and the main direction of gas and solid flow rate is surely more important in the axial direction than in the radial direction.

The model takes into account only a portion of the gasifier which is highlighted in Figure 6.1. During the experimental tests it was recognized that the reactive zone is concentrated after the air inlet trough the four nozzles, as a consequence it was decided to model only the gasifier throat and the reduction zone below it.



Figure 6.1 - Modelled portion of the gasifier.

6.2.1.2 Gasifier description

The modelling approach is similar to other authors ([4, 8, 10]) and it is based on the separated treatment of the gas phase and the solid phase in terms of balance equations. The two phases are then coupled by means of mass and energy fluxes as represented in Fig. 6.2. Both the solid and the gas phase are treated as continuous media. The motion of both phases is described with a sequence of plug flow-reactors. This hypothesis is further explained in the following Paragraph. The first couple of PRFs describe the portion of gasifier before the nozzles. The biomass entering from the top of this zone is represented as a boundary condition in the solid phase PFR. No gas enters from the top of this region thus the PFR of the gas phase is complementary to the solid phase, to take into account the gas generation in this region due to eventual drying and devolatilization of the biomass. The first gas phase PFR is connected to a completely stirred tank reactor, which takes into account the air (or other gasifying agent) inlet through the four nozzles. The resulting stream from the CSTR provides the inputs for the second gas phase PFR, which represents the lower portion of the gasifier. Concerning the solid phase, the second PFR is directly connected to the first to maintain the continuity of the medium. In agreement with the plug flow representation there is no possibility for back-flux from the lower portion of the gasifier to the upper portion. The heat transfer within the two phases occurs due to convection, radiation and conduction in the solid phase and only convection in the gas phase (as it will be discussed in the following Paragraph). Consequently heat can be transferred both downward and upward (thus moving in the opposite direction to the mass flow) in the solid phase, while only co-current to the mass flow in the gas phase. The two phases are fully



Figure 6.2 - Representation of the modelling approach and fluxes.

coupled in terms of mass and heat fluxes. The two phases exchange heat both through convection and mass transfer. Both phases are allowed to exchange heat with the gasifier walls convection. The PFRs are treated as distributed domains; therefore the gasifier axis is meshed with several small cells (see Fig. 6.3) of thickness *dz*. The mass and energy conservation equations are applied and solved over each cell. In each cell all the phenomena presented in Chapter 1 are included with source terms or additional equations. This allows evaluating the temperature, concentration and velocity distributions along the gasifier axis.



Figure 6.3 - Representation of the distributed domain.

6.2.1.3 Assumption and hypothesis

The representation of the gasifier cannot be carried out without some assumptions which allow simplifying the model equations and reducing the number of parameters (often not experimentally verified). The assumptions involved in the present model are here presented and discussed.

1. The gas pressure is considered equal to 1 atm and constant along the gasifier.

In Chapter 5 it is reported that the gasifier operates under slight vacuum conditions, and that the pressure changes along the gasifier axis. However, for the purpose of calculating the gas density and properties it is acceptable to assume a constant pressure of 1 atm. Once a constant pressure is assumed, it is not possible to describe the gas velocity as function of the pressure drop across the bed. Consequently no momentum equation can be written and the gas velocity has to be calculated from the continuity equation. This is surely a loss of accuracy of the model, since it misses one of the main features of the gasification process highlighted in Chapter 5. On the other hand the present model does not represent the variation of bed permeability and it is based on a very basic treatment of the particles, therefore an accurate evaluation of the pressure drop would not be satisfactory and valid. However, it is always possible to evaluate a mean pressure drop as post processing of the simulation data (temperature profile and size distribution along the gasifier axis).

2. The mass transfer by diffusion along the gasifier is neglected compared with the mass transfer by convection.

This hypothesis is not realistic since in Chapter 5 it was demonstrated that flow regime in laminar. On the other hand the introduction of a diffusive term require the use of a second order derivative of the gas species concentrations which increase the computational cost and may reduce the stability of the calculation.

3. The properties of the gaseous phase follow the ideal gas laws.

The assumption of the ideal gas law is valid for temperature higher than the critical temperature of the gas and pressure lower than the critical pressure of the gas. All the gaseous species involved in the gasification process exhibit critical pressures ranging from 12.8atm (hydrogen) to 217atm (water), therefore this condition is always respected. Except for water and tar, the critical temperatures range from -240°C (hydrogen) to 31°C (carbon dioxide). The critical temperature of water is 374°C, however a large portion of the gasifier is expected to operate above this temperature and once water is in the vapour state the temperature is likely to be close to this value. Therefore on the whole this hypothesis is not likely to introduce major sources of errors.

4. The gaseous phase is transparent to radiation, due to its negligible absorption coefficient compared to the solid phase. Conductive heat transfer in the gas is neglected as well.

This hypothesis is rather realistic since both the absorption coefficient (for instance and the thermal conductivity of the gaseous phase are much lower than the solid phase.

5. There is no particle size distribution; the particles are represented as spheres with a mean diameter. No shape evolution is considered, and the only term for size reduction is due to the reaction of the solid particle.

The representation of the particles in the gasifier is a difficult task. The real biomass feedstock is usually characterized by a certain initial size distribution and shape which in most of the cases is irregular (for instance woodchips). In addition as the particles enter the gasifier their chemical and morphological properties start to evolve. Temperature gradients, mechanical strains as well as reactions modify the particles size distribution and shape. It is very difficult to take into account all these phenomena and parameters, as a consequence some assumptions are usually made in order to simplify the calculation. It is worthy to note that from the point of view of a comprehensive model an accurate representation of the particle size distribution or shape cannot be experimentally verified and may lead to wrong conclusions. Concerning the present reference case (WSP) the initial particle shape would be adequately represented as cylinders, however due to particle break and consumption this initial shape is lost during the gasification process and for sake of simplicity the particle is considered as a sphere of equivalent diameter.

6. The void fraction is assumed constant and equal to 0.4 along the gasifier.

This hypothesis is very far from the reality and, as underlined by [2], the change of the void fraction can affect the results of the simulation. The initial void fraction of WSP (0.42) is derived as the ratio of the bulk and particle density is, but after the calculations reported in Chapter 5 the void fraction seems to vary between 0.1 and 0.2. For sake of simplicity in the calculation the void fraction is assumed constant and congruent with the hypothesis of spherical particles (almost equal to the initial value for WSP).

7. No momentum equation is included; consequently the solid velocity is calculated from a continuity equation.

Constitutive relations for solid flow have been proposed by some authors (for instance [15]). However their application leads to very difficult mathematical problems and require many parameters which are not verifiable; in addition these equations are often difficult to be solved. Therefore it is common to describe the solid motion only according to the continuity equation.

8. The solid particles are assumed to be thermally thin.

This assumption is rather common in comprehensive models of fixed beds combustors and gasifier and allows considering the particle as isothermal. This assumption depends on the relative importance of the external heat transfer due to convection, inter-particle conduction and radiation to the particles compared to the internal heat transfer due to intra-particle conduction. This validity of this assumption can be checked according to the thermal Biot number as reported by [16] and it is mostly important for the devolatilization stage which is a temperature controlled process.

9. The absorption coefficient used in the radiating flux calculation neglects the scattering term and assumes a regular distribution of the particles.

This hypothesis has become quite common in studies related to fixed bed combustors and gasifiers, starting from the work of [4]. The hypothesis is somewhat far from reality since implies that the particles are arranged in a regular grid and that the fraction of radiation transmitted through the layer of particles is proportional to void fraction of the bed.

6.2.1.4 Variables and Governing Equations

The model is based on dynamic equations that describe the conservation of mass, energy and chemical species within the gasifier.

Concerning the gas phase the following species are included in the model: oxygen, nitrogen, hydrogen, carbon monoxide, carbon dioxide, water, methane and tar. Compared to the chemical species reported in Chapter 5 light hydrocarbons such as ethane are ignored and represented as methane. Tar is considered as an additional gaseous species. The reactions considered in the equations are reported in Table 1.1, except for tar and methane reforming which are not included in the model. The variable *m* indicates the mass flux due to moisture evaporation from the solid phase to the gaseous phase. Following hyp.1, it is possible to express the partial pressure of the gaseous species as concentrations. Conservation equations are used to evaluate the species concentration and gas velocity, except for nitrogen which can be evaluated as a complementary compound after the calculation of the total gas concentration with the ideal gas law (hyp.3). The time derivative term in the conservation equations of the gaseous phase is multiplied by the void fraction to represent that this phase is included in the voids between the particles; consequently the velocity of the gas phase is superficial velocity. After hyp.4, the energy equation takes into account convective heat transfer with the solid phase (q_{os}) and reactor walls (q_{ow}) , heat of reaction in the gas phase and heat transfer associated to mass transfer from the solid phase to the gaseous phase (q_{ma}) due to heterogeneous reactions.

The equations describing the gas phase evolution are the following. Note that the conservation equations are reported for a cylindrical geometry for sake of clarity.

Ideal gas law:

$$C_{g} = \frac{P}{R \cdot T_{g}} \tag{1}$$

Species:

$$\varepsilon \frac{dC_i}{dt} + \frac{d(U_g \cdot C_i)}{dz} = \left(\sum_{j=1}^n V_{ij} R_j\right)$$
(2)

i = CO, CO2, H2, CH4, O2, TAR. *j* = C, G1, G2, G3, WS, TC, C1, C2, C3, C4.

Water vapour:

$$\varepsilon \frac{dC_{moi}}{dt} + \frac{d(U_g \cdot C_{moi})}{dz} = m + \left(\sum_{j=1}^n v_{moij} R_j\right)$$
(3)

Total gas continuity:

$$\varepsilon \frac{dC_g}{dt} + \frac{d(U_g \cdot C_g)}{dz} = m + \left(\sum_{i=1}^m \sum_{j=1}^n R_j\right)$$
(4)

i = CO, CO2, H2, CH4, O2, TAR, H2O. *j* = C, G1, G2, G3, WS, TC, C1, C2, C3, C4.

Nitrogen:

$$C_{n2} = C_g - \sum_{i=1}^{m} C_i$$
 (5)

Gas phase energy:

$$\varepsilon \frac{d\left(\sum_{i=1}^{m} C_{i} \cdot h_{i}\right)}{dt} + \frac{d\left(U_{g} \cdot \sum_{i=1}^{m} C_{i} \cdot h_{i}\right)}{dz} = \sum_{j=1}^{n} R_{j} \Delta h_{j} + q_{gs} + q_{gw} + q_{mg}$$
(6)

where:

$$h_{i} = c_{pi} \cdot (T_{g} - T_{0})$$
(7)

$$i = CO, CO2, H2, CH4, O2, TAR, H2O, N2.$$

$$j = WS, TC, C1, C2, C3, C4.$$

$$q_{gs} = h_{gs} \cdot a_s \cdot (T_g - T_s) \tag{8}$$

$$q_{gw} = \frac{h_{gw}}{D_{reat}} \cdot (T_g - T_w)$$
⁽⁹⁾

$$q_{mg} = (T_s - T_o) \sum_{i=1}^m c_{pi} \sum_{j=1}^n R_j$$
(10)

i = CO, CO2, H2, CH4, O2, H2O. *j* = Rp1, C, G1, G2, G3.

The solid phase is schematized with three main constituents: moisture, biomass and char. The reactions considered in the equations are reported in Table 1.1. The variable *m* indicates the mass flux due to moisture evaporation from the solid phase to the gaseous phase. Following hyp.6 the density of the solid phase constituents are expressed as bulk densities. Conservation equations are used to evaluate the constituents' densities. Due to hyp.7 there is necessity to identify an additional equation to evaluate the gas velocity; this will be discussed in the following Paragraphs. Following hyp.8 only one global temperature is identified and no intra-particle heat transfer is considered. The energy equation takes into account convective heat transfer with the gaseous phase (q_{sa}) and reactor walls (q_{sw}) , heat of reaction in the solid phase, radiative (q_{rad}) and conductive (q_{cond}) heat transfer within the solid phase as well as heat transfer associated to mass transfer from the solid phase to the gaseous phase (q_{ms}) due to heterogeneous reactions. After hyp.7, the equations describing the solid phase evolution are the following. Note that the conservation equations are reported for a cylindrical geometry for sake of clarity.

Moisture:

$$\frac{d\rho_{moi}}{dt} + \frac{d(U_s \cdot \rho_{moi})}{dz} = -m \tag{11}$$

Biomass:

$$\frac{d\rho_{bio}}{dt} + \frac{d(U_s \cdot \rho_{bio})}{dz} = -R_{p1}$$
(12)

Char:

$$\frac{d\rho_{char}}{dt} + \frac{d(U_s \cdot \rho_{char})}{dz} = n_c \cdot R_{p1} - R_c - R_{g1} - R_{g2} - R_{g3}$$
(13)

Solid phase energy:

$$\frac{d\left(\sum_{i=1}^{m} \rho_i \cdot h_i\right)}{dt} + \frac{d\left(U_s \cdot \sum_{i=1}^{m} \rho_i \cdot h_i\right)}{dz} =$$
(14)

$$m \cdot \Delta h_{ev} + \sum_{j=1} R_j \Delta h_j + q_{sg} + q_{sw} + q_{ms} + q_{cond} + q_{rad}$$

where:

$$h_{i} = c_{pi} \cdot (T_{s} - T_{0}) \tag{15}$$

i = BIO, CHAR, MOI.j = C, G1, G2, G3.

$$q_{sg} = h_{gs} \cdot a_s \cdot (T_s - T_g) \tag{16}$$

$$q_{sw} = \frac{h_{sw}}{D_{reat}} \cdot (T_s - T_w)$$
⁽¹⁷⁾

$$q_{ms} = (T_s - T_o) \sum_{i=1}^{m} c_{pi} \sum_{j=1}^{n} R_j$$
(18)

i = CO, CO2, H2, CH4, O2, H2O. *j* = Rp1, C, G1, G2, G3.

6.2.2 Phenomena and reactions

As highlighted in Chapter 1 (see Figure 1.1 and Table 1.1) the gasification process involves several phenomena (in particular heat exchange) and reactions. Both reactions and mass/heat transfers represent source terms in the aforementioned governing equations which have to be described with sub-models, kinetic expressions etc. From biomass drying to carbon monoxide combustion several different relations or kinetic parameters are reported in the literature. Here a brief discussion about the representation of the source terms in the model is provided.

6.2.2.1 Biomass drying

Moisture has a significant impact on the overall biomass gasification process, including changing the pyrolysis products and increasing the overall conversion time. There are three basic representations of biomass drying under gasification conditions. The simplest of these is an energy balance in which the drying front is assumed to be infinitely thin and an energy sink at 100 °C accounts for the heat of vaporization [16]. A second method [10,16] models drying of wood as an additional chemical reaction using an Arrhenius expression. A third method [8] describes the evaporation process as a function of the saturation pressure of the liquid water in the biomass and partial pressure of the water vapour, with steam leaving the biomass particle according to a diffusive flux. The energy sink approach is the

simplest one. Albeit in this case the drying zone is reduced to an infinitely thin moving surface and may not model drying and pyrolysis of small particles where the thickness of the drying zone is not negligible compared to the thickness of the material. The second approach allows describing drying as an Arrhenius-type relationship, which is a primary advantage for implementation in numerical codes. Conversely it may not be adequate when it is important to consider the effect of the water content in the gas phase. Finally the diffusion model is the one which takes into account most of the physical parameters, however, it has not been verified for gasification conditions and its implementation in numerical codes is more difficult. Concerning the Arrhenius-type relationship the most used kinetic parameters are reported in the work of [17] (Table 6.1), these parameters were later corrected by [16] to take into account to reach a drying plateau between 100 and 120°C.

Reference	A [s ⁻¹]	E[K]
[17]	10 ⁶	10600
[16]	10 ¹⁰	10600

Table 6.1 - Kinetic parameters for Arrhenius-type biomass drying.

Figure 6.4 exhibits a comparison of the diffusion and Arrhenius-type models (with [16] parameters) on the basis of case study model. The case study is a steady plug flow of both moist biomass and dry gas. The solid is exposed to a linear temperature ramp of 20000 k min⁻¹ (assumed from [8]); the reactor length is 0.01 m. It can be noted that in the adopted conditions the time and spatial scale (8 mm) of the drying rate is similar and represent a very fast drying rate; this is in agreement with the assumption of infinitely fast drying rate. Given this result of the Arrhenius-type relationship is used in this study.



Figure 6.4 - Comparison of the drying rate represented with an Arrhenius-type relationship and a diffusion limited mass transfer.

6.2.2.2 Biomass devolatilization

The description of the biomass devolatilization step is of remarkable importance for the validity of the model. This is obvious since for most biomass fuels more than 70% of the total dry mass is released in this stage.

The description of the biomass devolatilization involves three main tasks:

- macro-products (char, tar, gas) representation;
- devolatilization kinetic scheme and kinetic parameters;
- evaluation of the gas compositions.

In the past decades a lot of studies concerning these three features have been carried out and are carefully reviewed by [18]. As pointed out in Chapter 1 and Chapter 3 biomass devolatilization is greatly affected by the operating conditions, especially the heating rate; in addition the representation of the vapour and gas chemical species require detailed phenomelogical models in order to describe the chemistry of these phases. However it is recognized that when dealing with comprehensive gasification model it is not possible to use too complex devolatilization sub-models for sake of computational cost and simplicity.

In addition biomass devolatilization is highly affected by intra-particle heat transfer (as pointed out by [8, 16, 19]); this feature is usually simplified in comprehensive model with hyp.8.

Therefore hereafter biomass devolatilization is treated as a global reaction under the hypothesis of thermally thin particle.

6.2.2.2.1 Representation of the macro-products

The three macro-products generated from biomass devolatilization can be identified as gas (permanent gases), tar (organic components which are in the gas phase at the process temperature but start to condense as the gas is cooled down) and char (the solid residue). Gas is a fictitious compound which is actually divided in the chemical species presented in the previous Paragraphs. This fictitious compound is used to avoid the use of multiple kinetic reactions for each gaseous species. Tar (as reported in Chapters 1, 4 and 5) is a complex mixture of organic compounds, whose composition is highly dependent on the operating conditions. Therefore describing the tar formation and cracking require very complex kinetic scheme and mathematical treatment which are beyond the capability of a comprehensive model. Consequently tar is usually represented with a model compound [8, 10] or with multiple classes ([20, 21]). The model compound can be either a real chemical compound (for instance Levoglucosan) or a fictitious compound with raw formula derived from average compositions obtained in experimental studies. Some options are reported in see Table 6.2). The composition used by [8] is used in this study.

Table 0.2 - Naw composition of tar model compounds.			
Reference	Formula	PM [gm mol ⁻¹]	_
[8]	$C_{6.84}H_{10.41}O_{0.16}$	95	-
[11]	$C_6H_{6.2}O_{0.2}$	81.4	
[10,11]	$C_6H_8O_1$	96	
Levoglucosan	$C_6H_{10}O_5$	162	

Table 6.2 - Raw composition of tar model compounds.

Finally char is usually assumed to be composed of pure carbon; this is not completely true since depending on the pyrolysis condition char can still contain hydrogen and oxygen. This assumption in retained in this study.

6.2.2.2.2 Kinetic scheme and kinetic parameters

Two main kinetic schemes are usually adopted in comprehensive models of biomass gasifier.

1) First order global devolatilization reaction with constant coefficient for the macro-products distribution (reference [8]):

$$BIO \xrightarrow{kp1} n_g GAS + n_t TAR + n_c CHAR$$
(19)

$$TAR \xrightarrow{kIC} GAS$$
 (20)

this sub-model is based on two reactions, primary pyrolysis which represents the degradation of biomass to gas, char and tar and secondary pyrolysis that accounts for the tar cracking reaction to generate more gas.

2) Three first order parallel reactions for the generation of the three macroproducts (reference [22]):

$BIO \xrightarrow{kgas} GAS - WATER$	(21)
$BIO \xrightarrow{kliquids} TAR + WATER$	(22)
$BIO \xrightarrow{kchar} CHAR$	(23)
$TAR \xrightarrow{kTC} GAS$	(24)

in this sub-model primary pyrolysis is represent by three independent reactions which describe the generation of dry gas, liquids and char; an additional reaction takes into account the cracking of tar to generate more gas.

The first kinetic scheme is the most simple; however it completely relies on the choice of experimental parameters (kinetic parameters and macro-products yield). It does not take into account the effect of the operating parameter, since this information can be provided only by choosing different reference kinetics and macro-products distribution.

The second kinetic scheme increases the number of reactions in the model. It is more accurate since, up to a certain limit, takes into account the effect of the operating conditions on the macro-products distribution. One of the main problems with this scheme is that the kinetic parameters are based on the total dry gas and the total condensate yields, respectively (for instance [23]). Therefore one reaction represents the total condensate generation which includes tar and water as well. This is not very useful since in comprehensive models it is required to consider water as a gaseous product. In addition information are required to separate the water and tar contribution to the total condensate yield.

Concerning the kinetic parameters to be used in the two kinetic schemes several options are possible. [18] reviewed a large numbers of publications focused on the evaluation of kinetic parameters for biomass pyrolysis. The aim of the author was to estimate reliable values for intrinsic devolatilization kinetics to be used in detailed particle models which take into account mass and heat transfer terms. It was concluded that kinetic parameters can be grouped in three classes, which vary due to different operating conditions used in the experiments. However, after hyp.8 it is not possible to use intrinsic kinetics and apparent parameters have to be used. The work of [7] was devoted to evaluate the effect of the devolatilization kinetics on the results of the simulation of a fixed bed combustor; it was concluded that the faster the devolatilization rate the shorter is the ignition time and lower the production of un-combusted species (carbon monoxide, hydrogen), conversely the thickness of the reaction zone was not influenced by the devolatilization kinetics. Some of the kinetic parameters examined by [7, 18] are reported in Table 6.3.

	reported in the study of [7,18].		
	Reference	A [s⁻¹]	E [kJ mol ⁻¹]
	[24]	1.516·10 ³	105
	[19]	$3.0.10^{3}$	69
	[23]	5.16·10 ⁶	84
	[25]	3.4·10 ⁴	69
	[26]	1.885.10 ⁶	108
_	[27]	1.483·10 ⁶	88.6

Table 6.3 - Kinetic parameters for a single first	order reaction
reported in the study of [7,18].	

A preliminary study has been carried out in order to evaluate the effect of the kinetic scheme and parameters. The comparison is based on the works of [28, 29, 30]. These lab-scale reactors are modelled as fixed bed reactors with continuous nitrogen flow according to the equation reported in the previous Paragraph; the heating rate is 80°C min⁻¹ which is much lower than that of a full-scale gasifier. Four devolatilization sub-models were compared:

- A first order global devolatilization reaction with experimental coefficients based on the work of [24, 31].
- A set of three parallel reactions based on the work of [23].
- A set of three parallel reactions based on the work of [32].
- A structural model named bioCPD based on the work of [21].

Figure 6.5 shows the comparison of the four sub-models in terms of reaction rate and final char yield.



Figure 6.5 - Comparison of mass-loss rate and final char yields obtained using four different devolatilization sub-models and compared to the char yields achieved in the work of [28, 29, 30].

Noteworthy, even with a very low heating rate the mass loss characteristics predicted by the four sub-models are similar: devolatilization is completed in nearly 350-400 s. The four models lead to two different char yields. The single reaction model lead to the specified value of 33% of the initial dry biomass which similar to the 30% achieved by the [23] set; this value is close to the low temperature yields reported by the experimental works. Conversely the [8] set and bioCPD lead to char yield of 12-15%, which is slightly lower than the high temperature experimental values. Consequently it can be stated that the choice of devolatilization sub-model and kinetics are relatively arbitrary, since theoretical pro and cons exist for each of them. However the devolatilization time scale seems to be poorly affected by the choice of the kinetic parameters, on the other hand the macro-products distribution is largely affected by the choice of the devolatilization sub-model. In this study the kinetic scheme of [8] is used for sake of simplicity. The kinetic parameters of [24] are used in the model.

6.2.2.2.3 Gas speciation

As aforementioned it is necessary to determine the gas composition produced form biomass pyrolysis. This task is somewhat more difficult than determining the macro-products distribution and may be affected by large uncertainties. In comprehensive model of biomass gasifiers two main approaches are used to determine the gas composition of the volatiles.

- 1) Constant coefficients, based on the work of [8] the total gas yield is decomposed in specific yield of each gaseous component (carbon monoxide, methane etc.) by means of coefficients derived from experimental studies [31].
- The matrix developed by [11] which is based on the conservation equations of carbon, hydrogen, oxygen, energy and two empirical parameters.

Again the two approaches were compared, along with bioCPD, with the results of the three experimental works mentioned before. As an example, Table 6.4 compares the predicted water yield with the range of experimental values achieved at three different final temperatures. It can be noted that although the higher complexity of the Thunmann approach and bioCPD, they fail to estimate the final water content. Assuming a constant coefficient obtained from another similar experiment seems to be a more reliable choice, despite the total loss of predictivity and effect of operating conditions. This latter option is used in this study.

Table 6.4 - Water yield predicted by the three sub-models and compared with range of experimental values achieved by three authors [28, 29, 30] at three

_					
-	Nominal	Experimental	Constant	Thunmann	bioCPD
	temperature	Values	coefficients		
	[°C]				
-	420	25-32	25	17.4	1.3
	600	26-33	25	15.5	3.7
	720	24-33	25	14.4	5

6.2.2.3 Heat Transfer

Some of the heat transfer terms were introduced in Paragraph 6.2.1.4. It is still necessary to define the convective heat transfer coefficients and the conductive and radiating heat transfer within the solid matrix.

6.2.2.3.1 Convective Heat Transfer

As far as the convective heat transfer coefficients are concerned, it is necessary to calculate the solid-gas as well as the gas-wall and solid-wall heat transfer coefficients.

For the first one two relations are mainly adopted in comprehensive model of gasifiers and combustors.

The first one is the correlation of [33]:

$$h_{gs} = 2.06 \frac{c_{pg} \rho_g U_g}{\varepsilon} \operatorname{Re}^{-0.575} \operatorname{Pr}^{-0.667}$$
(25)

however [8] reports that since this correlation was developed for non-reacting packed bed, it may lead to values that exceed those encountered in reacting gasifiers. Therefore it can be multiplied by a correction factor can be in the range (0.02-1).

Another correlation which is widely adopted is that of [34], where the heat transfer coefficient is determined from the Nusselt number, which can be calculated as:

$$Nu = 2 + 1.1 \cdot \text{Re}^{0.6} \text{Pr}^{0.333}$$
(26)

no corrections for these correlations are suggested by the authors who use it.

In this study the heat transfer coefficient is evaluated from the [33] relationship, given the more critical information provided by the literature.

Concerning the gas and solid to wall heat transfer coefficient the approach of [35] is followed.

6.2.2.3.2 Conductive Heat Transfer

Conductive heat transfer is often represented with a Fourier law or grouped with radiative heat as a function proportional to the temperature cubed.

In any case the main issue to face is the choice of the effective thermal conductivity of the bed, which depends not only on the bed material conductivity but also on the particle packing factor and void fraction.

$$q_{cond} = \lambda_s \cdot \frac{d^2 T_s}{dz^2}$$
⁽²⁷⁾

Different options for the evaluation of the effective conductivity can be found in the literature. [4] multiplied the solid thermal conductivity by the void fraction; instead [8] adopts the correlations proposed by [36].

Some authors (for instance [10]) neglects the conductive heat term. In this study the treatment of [8] is retained.

6.2.2.3.3 Radiative Heat Transfer

As reported by [4] radiation plays an important role in igniting and sustaining combustion in the bed. This heat transfer mechanism is often coupled with conductive heat transfer into an effective conductivity term and expressed as proportional to the temperature cubed (for instance [8] and [2]).

Starting from the work of [4], which proposed hyp.8, the two flux model developed by Schuster and Schwarzschild [5] has been widely applied [6,7,10] in representing radiative heat transfer in packed bed. This latter model is used in this study.

The two fluxes radiative model is based on two radiation intensities moving in opposite directions within the bed:

$$\frac{1}{2}\frac{dI^{+}}{d\tau} = \left(1 - \varpi\right) \cdot I_{b} - I^{+} + \frac{\varpi}{2}\left(I^{-} + I^{+}\right)$$
(28)

$$-\frac{1}{2}\frac{dI^{-}}{d\tau} = (1-\varpi)\cdot I_{b} - I^{-} + \frac{\varpi}{2}(I^{-} + I^{+})$$
⁽²⁹⁾

Where I_b is the black body intensity which can be calculated as:

$$I_b = \frac{\sigma}{\pi} \cdot T_s^4 \tag{30}$$

Assuming a scattering coefficient (ϖ) equal to zero (hyp.8) it is possible to estimate the absorption coefficient as:

$$\kappa = -\frac{\ln \varepsilon}{d_p} \tag{31}$$

hence the two fluxes can be written as:

$$\frac{1}{2}\frac{dI^{+}}{dz} = -\frac{\ln\varepsilon}{d_{n}} \cdot \left(\frac{\sigma}{\pi} \cdot T_{s}^{4} - I^{+}\right)$$
(32)

$$\frac{1}{2}\frac{dI^{-}}{dz} = -\frac{\ln\varepsilon}{d_{p}} \cdot \left(\frac{\sigma}{\pi} \cdot T_{s}^{4} - I^{-}\right)$$
(33)

finally the total radiative flux within the bed can be calculated as:

$$q_{rad} = \pi \cdot \frac{d(I^+ - I^-)}{dz}$$
(34)

6.2.2.4 Mass Transfer

Similarly to convective heat transfer the two most common correlations for the calculation of the mass transfer coefficient are those of [33] and [34].

The first one has been used and discussed in the works of [2] and [8], can be written as:

$$k_m = 2.06 \frac{\rho_g U_g}{\varepsilon} \operatorname{Re}^{-0.575} Sc^{-0.667}$$
(35)

As reported by [8] it is often necessary to multiply this equation with a corrective factor or limit the maximum value which can be reached.

The second correlation allows deriving the mass transfer coefficient from the Sherwood number which can be calculated as:

$$Sh = 2 + 1.1 \cdot \text{Re}^{0.6} Sc^{0.333}$$
(36)

as for convective heat transfer no comments are reported in the literature for this correlation.

Again the [33] relationship is used in this study due to the critical analysis reported in the work of [8].

6.2.2.4 Particle evolution

As pointed out in the comment of hyp.5 the description of biomass particles has to be dramatically simplified both due to the great complexity of detailed mathematical models and the lack of experimental data to apply them.

Therefore simplified models of particle evolution have to be used and the particle consumption is attributed only to heterogeneous reactions.

First of all it is necessary to assume the impact of each phenomenon on the particle size. Drving and devolatilization are often assumed to have a negligible impact on the particle size (for instance [8]), which is therefore reduced only due to char oxidation and gasification reactions. This assumption is rather far from reality since, as reported in Chapter 3 and 4, it was observed that devolatilization may have a large impact on the particle size. On the other hand, introducing the devolatilization term in the particle evolution sub-model increases the complexity of the calculation. As a consequence the particle evolution represents the "char" particle evolution. As reported by [2] the two most common sub-models of char particles evolution are the shell progressive model and the ash segregation model. In the first one the ash are assumed to remain intact. The gasifying agent is then required to diffuse through the gas film boundary layer and the ash layer. The ash in the ash segregation model is assumed to crumble and fall away from the char particle with the gasifying agent required to diffuse only through the gas film boundary layer. In the case of biomass fuels the ash content is generally low; as a consequence it not likely that a layer of ash may remain after conversion of the organic material, therefore the ash segregation model seems to be more realistic and it is used in this study. The use of the ash segregation model implies that the particle diameter shrinks due to char conversion, therefore the density of the bed and the void fraction remain constant causing a reduction of the bed velocity. Therefore it is necessary to modify equation 13:

$$\rho_{char0} \frac{d(U_s)}{dz} = -(R_c + R_{g1} + R_{g2} + R_{g3})$$
(37)

and the solid velocity can be correlated to the particle diameter as reported by [9]:

$$d_{p} = d_{p0}^{3} \left(\frac{U_{s}}{U_{s0}}\right)^{\frac{1}{3}}$$
(38)

this allows calculating the specific particle surface of the bed as:

$$a_s = 6 \cdot \left(\frac{1 - \varepsilon}{d_p}\right) \tag{39}$$

Noteworthy since the char density is considered constant, there is no need for an additional equation for evaluating the solid velocity as stated in Paragraph 6.2.1.4.

6.2.2.6 Heterogeneous reactions

The reaction rate of heterogeneous reactions can be expressed according to the ash segregation model as:

$$R_{j} = \frac{a_{s}}{\frac{1}{k_{m}} + \frac{1}{k_{j}}} \cdot C_{i}$$
(40)

i = O2, CO2, H2O, H2. *j* = C, G1, G2, G3.

Therefore the reaction rate is assumed to have a linear dependence on the oxidizing/gasifying species concentration. The two resistances in the denominator are the mass transfer coefficient to take into account the diffusion of reactants in the outer film of the particle, and the intrinsic chemical kinetics of the char.

It is worthy to note that this expression is independent of the char density or particle diameter, as a consequence there is no effect associated to the particle conversion (for instance the reduction of active sites) and the paradox of a negative particle diameter can be reached. Therefore it was necessary to introduce a procedure which limits the particle conversion. Two options are possible:

- use a logic cycle (IF-THEN-ELSE) which sets to zero the reaction rate when the particle diameter is below a critical value [2];
- introduce a corrective function which is almost equal to 1 when the particle diameter is large and goes to zero as the particle diameter approaches a critical value;

The latter option is retained in this study and the corrective function is expressed as:

$$f = \exp\left(\alpha \cdot \frac{d_p - d_{p0}}{d_p}\right) \tag{41}$$

where α is a tuning parameter.

The calculation of the mass transfer coefficient has been presented in Paragraph 6.2.2.4. As far as the intrinsic kinetics are concerned this is usually expressed with an Arrhenius-type relationship multiplied by the solid temperature:

$$k_{j} = A_{j} \cdot T_{s} \cdot e^{\left(\frac{-E_{j}}{R \cdot T_{s}}\right)}$$
(42)

Recently [37] reviewed the kinetics of heterogeneous char reactions involved in biomass gasification. Here only a brief resume of the kinetic parameters used for heterogeneous reactions in comprehensive gasifier models is presented.

6.2.2.6.1 Carbon oxidation

Carbon oxidation is the most widely studied heterogeneous reaction, assuming char as pure carbon the reaction can be written as:

$$C + \gamma O_2 \rightarrow (2 - 2\gamma)CO + (2\gamma - 1)CO_2 \tag{43}$$

where γ is an empirical coefficient which depends mainly on the solid temperature, and can be calculate from several correlations such as those of [38, 39, 40]. For simplicity it is possible to assume that the only product of char oxidation is carbon monoxide [3] or carbon dioxide [4,8]. Concerning the kinetic parameters for carbon oxidation two sets are usually employed and reported in Tab. 6.5. Notably the set of [41] represent a faster reaction rate than the [42] set on the temperature characteristic of the reaction front (> 600°C) and it is more sensitive to temperature variations. Notably the set of [41] was derived from a study on the combustion of cellulosic paper while the set of [42] from woodchips combustion.

 Table 6.5 - Parameters for intrinsic kinetics of carbon oxidation used in comprehensive biomass combustor and gasification models.

	gennedigter anna g	
Reference	A [m k ⁻¹ s ⁻¹]	E [K]
[41]	5.67·10 ⁹	19294
[42]	1.74	9000

In this study the hypothesis of [3] is retained and the kinetic parameters of [41] are adopted.

6.2.2.6.2 Carbon dioxide gasification

The gasification of the char with carbon dioxide, often referred as the Boduard reaction, can be written as:

$$C + CO_2 \xrightarrow{kg1} 2CO \tag{44}$$

Table 6.6 reports some kinetic parameters used for the calculation of the intrinsic kinetic constant of carbon dioxide gasification. The only set achieved for biomass char is that proposed by [43] which is used in [8] and [9]. Other authors adopt kinetic parameters obtained for fossil fuels and derived by [44]. The comparison of three set in the temperature range typical of char gasification (> 800°C) shows that kinetic set of [43] produces the fastest reaction rate, while the set of [44] for coal the slowest. In this study the kinetic parameters proposed by [43] are used.

Table 6.6 - Parameters for intrinsic kinetics of gasification with carbon dioxide used in comprehensive biomass combustor and gasification models.

Reference	Fuel	A [m k ⁻¹ s ⁻¹]	E [K]
[43]	Wood	10′	26095
[44]	Lignite	3.42	15600
[44]	Coal	589	26800

6.2.2.6.3 Steam (water) gasification

The gasification of the char with water can be written as:

$$C + H_2 O \xrightarrow{kg2} CO + H_2 \tag{45}$$

The kinetic parameters of this reaction are often considered as equal to those of the Boduard reaction [2,8]. [45] assumed that this reaction is faster than the Boduard reaction and multiplied the pre-exponential factor by 1.67. This coefficient is used in this study to correct the pre-exponential factor of [43].

6.2.2.6.4 Hydro-gasification

The gasification of the char with hydrogen can be written as:

$$C + 2H_2 \xrightarrow{kg3} CH_4 \tag{46}$$

According to [2] this reaction is negligible at atmospheric pressure. Therefore it is common to describe its kinetics with the same activation energy of carbon dioxide gasification but reducing the pre-exponential factor by three orders of magnitude [8]. This assumption is retained in this study.

6.2.2.7 Homogeneous phase reactions

The main homogeneous reactions occurring in a gasification system are reported in Table 1.1. These involve the combustion of methane, tar, carbon monoxide and hydrogen, as well as reforming of methane and tar and the water gas shift-reaction. In comprehensive model of gasification systems the kinetic expression of the gas phase reaction are usually represented with global reaction rate. This approach is justified by the very different time-scale of the gas-phase reactions compared to the heterogeneous reactions; noteworthy the homogenous reactions are sometimes represented implying the equilibrium condition [2]. Most of the authors assume an immediate ignition of the combustion reactions as the oxygen contacts the volatile compounds, according to the flaming pyrolysis description proposed by [46]. However [7] included a mixing term in the evaluation of the reaction rate, stating that volatiles and oxygen have to mix before they react. Homogenous phase reaction rates are derived from studies which are independent of gasification systems. For sake of simplicity only five reactions are considered in this study: the combustion of methane, tar, carbon monoxide and hydrogen, and the water-gas shift reaction.

6.2.2.7.1 Hydrocarbons combustion

(-)

Hydrocarbons combustion can be expressed according to the general reaction:

$$C_n H_m + \frac{n}{2}O_2 \rightarrow \frac{m}{2}H_2 + nCO \tag{47}$$

where hydrogen and carbon monoxide are the products of the reaction. Since hydrogen combustion is faster than this reaction (it is often described with an infinite reaction rate [3]), it can be included in the global reaction as follows:

$$C_n H_m + \left(\frac{2n+m}{2}O_2\right) \rightarrow \frac{m}{2}H_2O + nCO$$
(48)

where the combustion products are water and carbon monoxide.

Conversely carbon monoxide combustion is a slower than oxidative demolition of hydrocarbons, therefore it is important to take it into account as a separate reaction; it may play an important role in the simulation of the homogenous phase as reported by [8]. After an extensive survey of the bibliographic sources for the choice of the kinetic parameters, it was concluded that the most referenced source is the work of [47]. This work report [48] two sets of kinetic parameters (Table 6.7) for long-chain hydrocarbons and cyclic hydrocarbons, respectively. The reaction rate proposed by the authors is:

$$R_{j} = \varepsilon A_{c} e^{\left[\frac{-E_{c}}{R \cdot T_{g}}\right]} T_{g} P^{0.3} \left[C_{hydrocarba}\right]^{0.5} C_{oxygen}$$
(49)

As mentioned before two main hydrocarbon species are assumed to be produced from biomass devolatilization: methane and tar. Most of the authors use the kinetic parameters for cyclic hydrocarbon to describe the methane combustion [3, 8, 10], except for [4] which group all the volatiles into a fictitious compound. Concerning tar many authors adopt the same kinetic parameters of methane [3, 8], except for [10] which applies the kinetic parameters from cyclic hydrocarbon: notably this imply that tar are more reactive than methane. For sake of computational simplicity the methane and tar combustion equations are simplified according to [9], posing the hydrocarbon exponent equal to 1; this practice allows reducing the computational cost and failure of the numerical solver. In this study the kinetic parameters for cyclic hydrocarbons are used both for methane and tar combustion; the exponents are taken equal to 1 for sake of computational simplicity.

Hydrocarbon	A [(m ³ kmol ⁻¹) ^{0.5} (s K) ⁻¹]	E[K]
Cyclic	9200000	9650
Long Chain	59.8	12200

Table 6.7 - Kinetic parameters for hydrocarbon combustion [47].

<u>6.2.2.7.2 Carbon monoxide combustion</u> Carbon monoxide oxidation can be written as:

$$2CO + O_2 \xrightarrow{kc3} 2CO_2 \tag{50}$$

This reaction is the slowest step of hydrocarbon combustion as well as the one with the largest heat of reaction.

The reaction rate of carbon monoxide can be expressed as:

$$R_{c3} = \varepsilon A_{c3} e^{\left(\frac{-E_{c3}}{R \cdot T_g}\right)} T_g C_{co} \left[C_{oxygen}\right]^{\alpha} \left[C_{water}\right]^{0.5}$$
(51)

Two values for the oxygen exponent are used in the literature. The first one reported in [48] is 0.25; the second one proposed by [49] is 0.5. Most of the authors of fixed bed gasification of combustion models [3, 8, 10, 40] use 0.25. Concerning the kinetic parameters three sets (Table 6.8) can be found in the literature, reported by [40, 48, 49], respectively. A direct comparison is possible only between the set of [40, 48], notably the latter is represent a slower kinetic over the temperature range of fixed bed gasifiers (473-1473 K). The kinetic parameters reported by [49] are used in this study; the exponents are taken equal to 1 for sake of computational simplicity.

Table 6.8 - Kinetic parameters for carbon monoxide oxidation.

Reference	Unit A	А	E [J kmol ⁻¹]
[48]	[(m ³ mol ⁻¹) ^{0.75}] s ⁻¹	3.98e+17	20000
[49]	[(m ³ mol ⁻¹)] s ⁻¹	1.3e+11	15105
[40]	$[(m^3 mol^{-1})^{0.75}] s^{-1}$	7.31e+14	34740

<u>6.2.2.7.3 Hydrogen combustion</u> Hydrogen oxidation can be written as:

$$2H_2 + O_2 \xrightarrow{kc4} 2H_2O$$
 (52)

This reaction is often assumed to be infinitely fast (for instance [3]). However, for the sake of computational simplicity, it is common to try to describe this reaction with very fast kinetics ([8, 10]). In this study this approach is retained and the reaction rate for hydrogen oxidation is represented as:

$$R_{c4} = \varepsilon A_{c4} e^{\left(\frac{-E_{c4}}{R \cdot T_g}\right)} C_{hydrogen} C_{oxygen}$$
(53)

The fast reaction rate is represented with a large frequency factor $(10^{11} \text{ m}^3 \text{s}^{-1} \text{mol}^{-1})$, and low activation energy $(42 \cdot 10^3 \text{ Jmol}^{-1})$. This treatment is retained in this study.

6.2.2.7.4 Water-gas shift

The water-gas shift reaction can be written as:

$$H_2O + CO \leftrightarrow H_2 + CO_2 \tag{54}$$

This reaction is very important in determining the final syngas composition as highlighted in the experiment of [50] and the model of [8].

Conversely to the combustion reactions, it is very important to consider the equilibrium of this reaction which rather sensitive to temperature.

It is possible to represent this reaction with two approaches:

- One kinetic expression for the forward reaction and an equilibrium constant [45];
- Separate kinetics for the forward and backward reactions [40].

In this study the latter approach is retained and based on the kinetic parameters proposed by the excellent works of [51, 52]. The reaction rate is expressed as:

$$R_{wg} = \varepsilon \left[A_f e^{\left(\frac{-E_f}{R \cdot T_g}\right)} C_{co} C_{water} \right] - \varepsilon \left[A_b e^{\left(\frac{-E_b}{R \cdot T_g}\right)} C_{co2} C_{hydrogen} \right]$$
(55)

The kinetic parameters for the two reactions are reported in Tab. 6.9.

Table 6.9 - Kinetic parameters for forward and backward water gas shift reactions.

	Unit A	А	E [J kmol ⁻¹]
Forward	[(m ³ mol ⁻¹) ^{0.75}] s ⁻¹	3.98e+17	20000
Backward	[(m ³ mol ⁻¹)] s ⁻¹	1.3e+11	15105

6.3 Gasifier simulation

6.3.1 Simulation software and implementation

The model described in the previous Paragraphs was implemented and simulated with the software gPROMS developed by Process System Enterprise (PSE).

The main feature of this software is the capability to write down equations in an electronic sheet more or less like on piece of paper (as represented in Fig. 6.6). This work has been dealing with the gPROMS model builder utility which is based on two main entities the "model" and the "process", as represented in Fig. 6.6. The model is an environment for declaration of parameters, variables, boundary conditions as well as typing equations. Each model can be coupled with one or more process which are instances of the same set of equations but which can be characterized by different values of parameters, input variables, solution parameters and initial conditions. gPROMS model builder allows describing distributed domains and carry out dynamic simulations.



Figure 6.6 - Graphical representation of the main features of the gPROMS model builder utility.

6.3.2 Simulation parameters

Some parameters have to be defined in order to carry out the simulations.

First of all the macro-products and the gaseous species yields, which are reported in Tab. 6.10 and 6.11. The macro-products distribution as well as the tar composition and tar cracking yields are equal to those used by [8]. The yields of the volatiles generated from primary pyrolysis are corrected in order to achieve a global composition of the biomass similar to WSP.

<i>i</i> a	ble 6.10 - Macro	o-proaucts a	istribution a	na ultimate co	omposition [%wt]
	Component	Yield	С	Н	0
	GAS	48	17.4	10.8	71.8
	TAR	19	44.6	5.0	50.4
	CHAR	33	100	0	0
	BIOMASS	-	49.8	6.1	44.1

Table 6.10 - Macro-products distribution and ultimate composition [%wt].

Table 6.11 - Gaseous species distribution of volatiles produced from primar	y
pyrolysis and secondary pyrolysis.	

Reaction	Compound	Yield
	CO	9
	CO_2	11
R _{P1}	CH_4	2
	H ₂ O	24
	H ₂	2
	CO	9.5
R _{TC}	CO_2	5.7
	CH_4	3.8

As a consequence it is possible to define the bulk densities of the three constituents of the biomass, reported in Tab. 6.12.

Table 6.12 - Bulk densities of the biomass constituents according to the initial total bulk density, the initial moisture content and the char yield assumed from [8].

Constituent	Bulk density [kg m ⁻³]
Total	665
ρ _{moi0} = 12%⋅Total	80
ρ _{biomass0} = Total – Moisture	585
$\rho_{char0} = 33\%$ ·Biomass	193

The solid is modelled with as uniform distribution of spheres with initial diameter equal to 0.02 m. Table 6.13 and 6.14 lists the thermo-chemical properties used in the simulations. Specific heats and heats of reaction are considered constant in the simulations. The solid thermal conductivity was considered constant as well and taken as 10% of pure oak wood (0.017 W m⁻¹ K⁻¹).

simulation of the model.					
Solid phase	J kg⁻¹ K⁻¹	Gas phase	J kmol ⁻¹ K ⁻¹		
Moisture	4180	CO	33190		
Biomass	3191	CO_2	54180		
Char	1683	H ₂ O	41250		
		H ₂	30210		
		CH_4	72810		
		N ₂	32700		
		O ₂	34860		
		TAR	71300		

Table 6.13 - Specific heats of solid and gaseous components used in the simulation of the model.

Solid phase	J kg⁻¹	Gas phase	J kg⁻¹
М	-2.3·10 ⁶	R _{TC}	4.2·10 ⁴
R _{P1}	-4.2·10 ⁵	R _{C1}	17.5·10 ⁶
R _c	$2.5 \cdot 10^7$	R _{C2}	50.2·10 ⁶
R _{G1}	-9.3·10 ⁶	R _{C3}	10.1·10 ⁶
R _{G2}	-9.3·10 ⁶	R _{C4}	142.9·10 ⁶
R _{G3}	-9.3·10 ⁶	R _{WG}	1.5·10 ⁶

6.3.3 Simulation strategy

6.3.3.1 Geometry

The first aim of the model is to evaluate the effect of air introduction in the middle of the domain. To do this (see Paragraph 6.2.1.2) the solid phase in the gasifier is schematized with two consecutive PFRs, while the gas phase is schematized with the sequence PFR-CSTR-PFR. The CSTR is located in correspondence of the nozzle outlet inside the gasifier. The total height of the gasifier modelled is 1 m and the air inlet is positioned at 0.35 m from the top of this portion. The schematization is reported in Fig. 6.7. The first couple of PFRs cover the space from the top of the portion to 0.35 m from the top. Here the second solid PFR starts. Concerning the gas phase the first discretization element after 0.35 m is modelled as a CSTR to allow for an additional inlet which could not be represented with a full PFR. The second gas PFR begins immediately after the CSTR. This representation (namely throat-less) allows for a separate definition of the boundary conditions as well as for the reactions. For instance there is no need to activate the combustion reactions in the portion above the air inlet. The second aim of the model is to evaluate the effect of throat on the model results. To do this the section of the gasifier has to be introduced in the equations of Paragraph 6.2.1.4 as an additional equation. The presence of the throat is schematized with a further partition of the gasifier geometry (namely throated) which is represented in Fig. 6.7. Three zones (1, 2, 3) can be identified in the discretization; this partition is retained also in the throat-less configuration. The presence of the throat is introduced by defining the gasifier diameter as a function of the axial coordinate z.



Figure 6.7 - Representation of the gasifier geometries implemented in the model.

6.3.3.2 Solution procedure

gPROMS allows specifying the parameters for the solution of differential algebraic equations (DAE), which are the number of discretisation intervals, the order of approximation and the type of spatial discretization method.

In this study the domain is meshed with 300 intervals with uniform distribution. This value was identified as the optimal trade-off between simulation stability and repeatability of the results and leads to cell a length of nearly 3 mm.

The system of differential equation is solved with a first order backward finite difference method.

6.3.3.3 Boundary conditions

gPROMS allows for definition of the system boundary conditions, which can be set in the model section, and input values, which can be assigned in the process section. The boundary conditions in the model are related to the radiative heat flux and wall temperature. Concerning the two radiative intensities the boundary values have to be specified at the top and at the bottom of the reactor, respectively. The values are:

$$I_{top}^{+} = \frac{e \cdot \sigma \cdot T_{s.top}^{-4}}{\pi}$$
(56)
$$I_{bottom}^{-} = \frac{e \cdot \sigma \cdot T_{s.bottom}^{-4}}{\pi}$$
(57)

The temperature of the gasifier wall is considered equal to 300 K, despite the presence of the recuperative jacket described in Chapter 5.
6.3.3.4 Initial conditions, ignition and simulation sequence

The simulation is carried out in the following steps:

- the bed is initially composed of char, the temperature of the gas and solid i. is 300 K and the feeding are char and air at 300 K and 343 K, respectively;
- the ignition with the flare described in Chapter 5 is simulated by providing ii. heat to the throat section of the gasifier for 100 s:
- subsequently the external source of heat is set to zero and simulation is let iii. evolving until steady state conditions are reached:
- iv. once steady state conditions are approached the constituent BIOMASS is added to the solid feeding and the simulation is let running until steady state conditions are reached:
- once steady state conditions are approached the constituent MOISTURE is v. added to the solid feeding and the simulation is let running until steady state conditions are reached.

6.3.3.5 Input values

The input values of the simulation are the gas and solid velocity as well as the gas and solid inlet temperatures. Table 6.15 reports the input values for the simulation of the WSP reference case. The gas velocity values depend on the presence of the throat, the input used both for throat-less and throated configurations are reported. The first PFR has to be provided with a small gas flow-rate for numerical reasons.

Table 6.15 - Input values used in the reference case.								
Input	Velocity [m s ⁻¹]	Temperature [K]						
Solid	2.9·10 ⁻⁵	300						
Air throat-less	2.8·10 ⁻²	343						
Air throated	7.5·10 ⁻²	343						
Gas PFR	1·10 ⁻⁴	300						

Table 6.15 Input values used in the reference acce

6.3.3.6 Assigned coefficients

For sake of numerical simplicity and due to the uncertainties reported in Paragraphs 6.2.2.3 and 6.2.2.4 related to the values determined with the semiempirical correlations the heat transfer and mass transfer coefficients as well as the factor α are assumed and taken as constant in the simulation, after a preliminary evaluation of the order of magnitude in mean conditions. Table 6.16 reports the values of the parameter used in the simulation and varied in the three zones reported in Fig. 6.7.

Input	Unit	Т	hroat-les	S	Throated			
		1	2	3	1	2	3	
h _{sg}	$W m^{-2} K^{-1}$	10	50	25	10	50	25	
h _{sw}	$W m^{-2} K^{-1}$	30	30	30	30	30	30	
h _{gw}	W m⁻² K⁻¹	20.1	20.1	20.1	20.1	20.1	20.1	
k _m	m s⁻¹	0.0045	0.0045	0.0045	0.0045	0.0045	0.0045	
α	-	1	1	1	1	1	1	

Table 6 16 - Values of the specified coefficients

6.4 Model results

The first aim of the model is to represent the gasifier with air introduction in the middle of the gasifier. Consequently the first set of simulations is devoted to address this issue.

6.4.1 Case study

6.4.1.1 Variables distribution

The simulations allow to determine the gas species distributions (Fig. 6.8a) as well as the gas and solid temperature (Fig. 6.9b) and reaction rates distribution (Fig. 6.10c) along the gasifier axis. The comparison of the three figures leads to the identification of five zones along the gasifier axis.

The first one ranges from 0 to 300 mm, almost nothing happen in this zone. The temperature is equal to the inlet temperature and no reactions can take place; due to this fact it was chosen to switch off R_{P1} and M before the air inlet in order to reduce the computational cost and increase the simulation stability.

The second zone ranges from 300 to 350 mm where a steep temperature gradient can be identified in the proximity of the air inlet. It would have been a more representative choice to let R_{P1} and M active in this zone but this would have increased the numerical stability of the simulation. From 0 to 350 mm no gas composition is reported in Fig. 6.8a, actually the composition is 100% nitrogen which is not reported for sake of clarity. The temperature gradient increases the solid temperature from 30 to nearly 800°C.

The core of the gasifier ranges from 350 to 400 mm, immediately after the air inlet. The solid phase is subjected to a steep temperature gradient, as it approaches the air inlet. Here the solid temperature further increases from 800°C to 1050°C (peak temperature). As consequence devolatilization starts and volatiles, tar and char are formed. Combustible volatiles are quickly burned (R_{c1} - R_{c4}) in this zone due to the high oxygen concentration, as consequence the gas the solid temperatures dramatically increase. As the char is formed it is readily ignited (R_c), nevertheless the gas phase oxidation is more important than the char oxidation. In addition the high temperature promotes the cracking of tar forming additional methane and carbon monoxide (R_{P2} not reported in Fig. 6.8c). All the exothermic reactions take place from 350 to 400 mm since oxygen is readily consumed in this zone. As the oxygen concentration decreases the combustible species concentration increases due to residue biomass devolatilization and char gasification. This latter zone can be identified as the oxidation zone of the gasifier. Notably biomass devolatilization and volatiles oxidation occur simultaneously, according to the flaming pyrolysis description.

The following zone (400-600 mm) is characterized by the lack of oxygen but still rather high temperatures (from 1000 to 550 °C), thus it can be identified as the reduction and gasification zone. The water and carbon dioxide concentrations increase up to 400 mm due to carbon monoxide and hydrogen combustion, subsequently their concentrations start to decrease as they are consumed due to gasification reactions (R_{G1} and R_{G2}) forming hydrogen and carbon monoxide; the same can be reported for methane which is not included in the figures for sake of clarity. Finally at 600 mm all the processes are completed and the gas reaches a stable composition, the temperature slowly reduces due to thermal dispersion down to nearly 200°C.



Figure 6.8 - Simulation results for the test case: (A) volume fraction of gas species, (B) gas and solid phase temperature profiles, (C) reaction rates distribution along the gasifier axis.

6.4.1.2 Comparison with experimental data

The results of the simulation of gasification tests with WSP are compared with the experimental results reported in Chapter 5 in order to assess the validity of the model. The validation of the model is based on three parameters:

- gas composition;
- maximum solid temperature and position of the temperature peak;
- specific gas production.

Table 6.17 reports the comparison of these data.

The best results are achieved for the specific gas production which matches the experimental value and the maximum solid temperature which is in the range of values reported in Chapter 5. However it must be noted that a better validation of thermal profile could be achieved by measuring the temperature profile inside the gasifier. As far as the gas composition is concerned there is some discrepancy between the experimental and the simulated values. In particular the hydrogen, carbon dioxide and methane contents are lower than the experimental values; conversely the carbon monoxide content is higher than the experimental value.

The air flow-rate and consequently the ER were varied In order to analyze this discrepancy. It was found that the ER 0.21 results in a gas composition more similar to the experimental values; however the maximum temperature and the specific gas production are completely out of range. As expected, the lower the ER the lower the temperature and the gas specific production. Moreover the lower the ER the lower the carbon monoxide content and the higher the carbon dioxide and nitrogen contents, while hydrogen and methane remain almost constant.

These results highlight that the equivalence ratio used for the simulation is consistent with the experimental value, reporting similar temperature and specific gas productions, in addition the comparison of the gas LHV of the experimental and simulated syngas are very close (5.6 Vs. 5.55 MJ m_n^{-3}). It can be concluded that the overall energy and mass balance fit fairly well and the reason of the disagreement can be related to the gas species balance. This is likely to be since these balances are more affected from kinetics and input parameters. In particular the macro-product distribution as well as the pyrolysis gas distribution can be a source of error since it is specified a priori.

A further indication of the validity of the representation is the position of the oxidation zone (in the proximity of the air inlet) and the flaming pyrolysis regime, which were observed during the experimental tests (see Chapter 5).

Data	ER	H_2	CO	CO_2	CH_4	TAR	N_2	Ts	PS
set		[%]	[%]	[%]	[%]	[%]	[%]	[°C]	$[m_n^3 h^{-1}]$
Exp.	0.29	17.0	21.5	12.1	2.8	-	46.7	~1100	2.2
Sym.	0.29	15.7	27.5	7.2	1.1	0	48.5	1050	2.2
Sym.	0.21	17.1	23.2	9.9	1.4	0	48.2	837	1.6
Sym.	0.17	17.6	18.4	12.6	1.7	0.8	48.8	747	1.2
Sym.	0.15	17.4	15	14.2	1.8	1	50.3	708	1.1

Table 6.17 - Comparison of simulation and experimental results.

6.4.2 Parameter Sensitivity

In order to assess the impact of the parameters, some kinetics or assigned values were changed and compared to the reference case. Tab. 6.18 reports the comparison of the gas composition, maximum solid temperature and specific gas production for the reference case and the other simulations.

First of all it was chosen to vary the carbon monoxide oxidation kinetics, since it was recognized that this reaction has deep impact on the (see Fig. 6.8C) oxidation zone and contributes to determine the peak temperature. The same simulation was then carried out with the kinetics proposed by [40]. However, the results are completely identical to the reference case except for maximum temperature which is very slightly lower.

The analysis was further carried out by switching the product of the char oxidation from carbon monoxide to carbon dioxide. This change affects the simulations, in particular the availability of carbon monoxide in the gas phase is greatly reduced and consequently the temperature of the oxidation zone is reduced to 957°C. The lower the temperature of the oxidation zone the lower the hydrogen and carbon monoxide content as well as the specific gas production due to depression of the gasification reactions.

In addition the effect of some assigned parameters was tested, in particular the effect of α . In the reference case this parameter is set to 1 throughout the gasifier length, this implies assuming that there no difference in the way the char conversion slow down the reaction rates of heterogeneous reactions. This parameter was varied according to two hypotheses:

- In section 2 the devolatilization rate is fast and the evolving volatiles block the diffusion of oxygen and gasifying agents to the char; therefore the reaction rate is more depressed in section 2 than in section 3 where devolatilization is complete and the char has a more open structure (as proposed by [12,13].
- 2) In section 2 the air inlet and the steep temperature gradient improve the gas velocity and therefore the mass-transfer coefficient, moreover the newly char in section 2 is more reactive than in section 3, where reactivity is reduced due to burn-out and annealing.

These two situations are represented by setting α equal to 2 in section 2 and 1 in section 3, and 1 in section 2 and 2 in section 3, for the first and second hypothesis, respectively. The results shows that this setting affects only slightly the simulation results, in both cases a reduction of the total reactivity lead to lower hydrogen, carbon dioxide and carbon monoxide contents, as well as a lower specific gas production.

reference simulation and variation of some parameters.									
Data	Note	H_2	CO	CO_2	CH_4	N_2	Ts	PS	
set		[%]	[%]	[%]	[%]	[%]	[°C]	[m _n ³ h ⁻¹]	
Sym.	-	15.7	27.5	7.2	1.1	48.5	1050	2.17	
Sym.	R _{C3} [40] kinetics	15.7	27.5	7.2	1.1	48.5	1047	2.17	
Sym.	R _C CO ₂ product	14.8	24.9	8.5	1	50.7	957	2.07	
Sym.	α sec.2→2 α sec.3→1	15.3	26.9	7.5	1.1	49.1	1050	2.14	
Sym.	α sec.2→1 α sec.3→2	15.2	26.1	7.1	1.1	49.5	1065	2.13	

Table 6.18 - Parameters sensitivity: comparison of the results obtained from the reference simulation and variation of some parameters.

6.4.2 Heat transfer

As stated in Chapter 2 the purpose of developing this model is to gain a tool which can aid the interpretation of the gasifier behaviour. For instance, the relevance of the heat transfer mechanisms can be compared.

Fig. 6.9a reports the temperature profile obtained from the simulation of the gasifier with carbon dioxide as product of the char oxidation and Fig. 6.9b the comparison of the convective, conductive and radiative heat transfer of the solid phase along the gasifier axis. Noteworthy the conductive and radiative fluxes occur within the solid phase, thus their sign is related to the direction, while the convective heat occurs between the phases and the sign is determined by the temperature gradient.

The temperature profiles are qualitatively similar to those of Fig. 6.8 but shifted to lower temperatures. Among the three heat fluxes conductive heat is the less important, its scale is almost negligible compared to the others; therefore the assumption of the packed bed thermal conductivity is not a major issue since this term does not affect the simulation. This result is similar to the findings of [4].

As the solid approaches the air inlet it immediately heat up the incoming cold stream. Subsequently as volatiles combustion occur the gas reaches higher temperatures than the solid phase (1200 Vs. 950°C) and the solid receives heat from the exothermic reactions and in a short time the two phases reaches a thermal equilibrium.

As can be seen from Fig. 6.9b the shape of the radiative heat flux is rather symmetrical with the centre positioned in the proximity of the air inlet. The radiative flux propagates both in the positive and negative directions, and it is the only flux which effectively propagates counter-current to the solid flow. Therefore it is fundamental in providing a source of ignition for the incoming solid and determining the position of the reaction front and peak temperatures.



Figure 6.9 - (A) gas and solid phase temperature profiles and (B) heat transfer fluxes within the solid phase obtained from the simulation of the reference case with carbon dioxide as product of the char oxidation.

6.4.3 Throated configuration

The throat-less configuration was used to simplify the domain geometry and calculation, so to address the capabilities and sensitivity of the model.

Subsequently an attempt has been made to evaluate the effect of the throat on the simulations.

The implementation of the throat in the model equations is carried out by defining two additional variables gasifier diameter and cross-section. These variables are function of the gasifier axis according the geometry of the gasifier.

Noteworthy it is necessary to assume the effect of the throat on the gas and solid flows. Given hyp.1, it can be simply assumed that as the cross-section is reduced the gas velocity increase according to the continuity equation. This assumption cannot be confirmed a priori for the solid flow. As matter of fact the restriction can have three different effects on the solid flow:

- 1) the solid flow behaves just like a gas or a liquid therefore its velocity increase in the restricted section of the gasifier;
- the solid velocity is mainly governed by char consumption and discharge frequency from the bottom grid, apart from these two parameters the solid bed is fixed and its velocity is not affected by the restriction;
- 3) the solid flow is slowed down by the restricted section, just like when woodchips or wood pellets are poured in a funnel, the particle pack above the opening blocking each other.

Assumptions 1 and 2 were tested in this study. It is worthy to note that assuming 1 equals to introduce the variable "Section" inside the spatial derivative, while considering it constant and thus out of the derivative when assuming 2; consequently when assuming 1 the volumetric flow is maintained, while for 2 is reduced.



Figure 6.10 - Shifting of the solid temperature profile obtained from the simulation of the reference case with carbon dioxide as product of the char oxidation and assumption 1 for the solid motion in the throat.



Figure 6.11 - (A) Effect of the throat on the gas velocity: comparison of the throatless and throated configuration from simulation of the gasifier with carbon dioxide as char oxidation product; (B) Shifting of the solid temperature profile obtained from the simulation of the reference case with carbon dioxide as product of the char oxidation and assumption 1 for the solid motion in the throat.

Fig. 6.10 reports the evolution of the solid phase temperature profile during the simulation of the gasifier with assumption 1. It can be noted that no steady state is reached and the mild reacting front propagates throughout the gasifier length and finally exit from the domain. The mass flow in the restricted section is higher than in the throat-less configuration, but the radiating flux moving in the negative direction is the same. As a consequence no stable ignition can be reached. The initial char bed ignites right after the throat (where the solid and gas velocity slow down), but as the biomass approaches this hot zone the volatiles generation further increase the gas velocity and the reacting front is pushed away from the gasifier.

As far assumption 2 is concerned, a stable reacting front can be achieved with the initial char bed (see Fig. 6.11B). However as the biomass enters the throat the reacting front is again pushed away from the reactor with no proper ignition of the biomass. This is a consequence of the high gas acceleration in the throat due to a combination of the restricted section and the steep temperature gradient. Fig. 6.11A compares the gas velocity profiles along the axial coordinate of the gasifier in the throated and throat-less configuration, it can be seen how the restricted section speeds up the gas velocity; at the end of the throat is nearly five times that of the throat-less configuration. As observed form Fig. 6.8 and Fig. 6.9 the volatiles combustion heat up the solid phase with convective heat transfer, thus the hot solid phase can provide heat to the incoming fresh biomass due to radiative heat transfer. This ignition mechanism is compromised in this case since, as the gas velocity increases the volatiles combustion takes place far from the air.

Therefore it can be concluded that both assumption 1 is not representative of the gasifier behaviour, since it leads to the formation of the char bed outside of the throat due to high solid velocity. Assumption 2 seems to fit better with reality, however also the gas flow plays an important role in ignition and stabilization and still deserve further investigations.

6.5 Summary

This Paragraph has reported about the development of a 1-D model of the CRIBE gasifier, operated and tested as reported in Chapter 5.

Particular attention has been paid to the critical evaluation of the sub-models and kinetics to be used in the model as a consequence of a broad review of experimental articles. The model is based on nine hypotheses whose validity is discussed.

The main purpose of developing such a model (see Chapter 2) is providing an interpretative tool to carry out modelling aided experiments as already been done with the Drop Tube Reactor in Chapter 3.

However coupling experiment and modelling at the pilot scale is much more complex than at laboratory; in particular the gasification process of a moving bed is far more complex than representing a single particle moving into a Drop Tube. Therefore the model of the gasifier had to be developed with some simplifications, in particular the representation of the solid flow as well as the particle evolution is very difficult to be taken into account and the sub-model complexity does not guarantee enough reliability.

The innovative approach of this study is the attempt to include the effect of air inlet in the middle of the gasifier and the throat. To do this a preliminary study was carried with a simplified cylindrical geometry, with a CSTR positioned at the nozzle outlet to represent the air inlet into the domain. This representation of the gasifier has been simulated with different operating parameters and a limited sensitivity analysis has been carried out. The results of the simulation of the reference case (the gasification of WSP in test 2 and 3 reported in Chapter 5) fits fairly well with the experimental values, except for the gas composition which is not completely matched. This is ascribed to the numerical values of some kinetic parameters as well as the imposition of the pyrolysis gas composition. However, it can be noted that this representation differs from the real gasifier since the throat is omitted. The simplified version of the model is used for evaluating the gas species distribution, reaction rates, temperature profiles and heat transfer mechanisms along the gasifier axis. It was found that a stable reaction front is achieved as a combination of volatiles combustion, which provides most of the heat, and heat transfer within the solid phase through radiation.

An attempt was made also to include the throat in the model. This poses an additional difficulty since the effect of the restriction on the solid phase flow is to be assumed. Simulations were carried out in order to assess the impact of two assumptions (solid phase moving as a gas or insensitive to the restriction). It was found that the first assumption leads to ignition of the initial char bed outside of the throat and no steady state was reached; therefore the acceleration of the solid velocity is not a realistic representation. With assumption 2 it was possible to form a stable reacting front in the initial stage with the char bed; however, as the biomass enters the throat the reacting front soon propagates toward the bottom of the gasifier and no steady state is reached. This implies that also gas generation is not modelled properly; in particular excessive velocity may be predicted by the simulation with consequent shifts of the volatiles combustion far from the air inlet.

Although the model is still not complete, it is a useful starting point for addressing the gasifier behaviour. Several developments are possible, in particular:

- implementing a different devolatilization model which can take into account variation of the operating conditions, this could be done also off-line according to a recursive procedure: a simple model can be used for achieving the solid temperature profile which can be post processed to determine the macro-products and gas species distributions;
- performing a broader sensitivity analysis of the model;
- evaluating the effect of the operating conditions and possibly validate this effect with experimental data;
- activating the devolatilization and drying process also in the first solid PFR;
- evaluating the effect of the throat; to this purpose it could be beneficial to perform simple experiments of the solid flow in a restricted section, in addition the effect of the gas flow in the throat deserves further investigations about the velocity profile;
- finally, among the nine hypotheses presented hyp.1 is believed to be most important to be removed: as highlighted in Chapter 5 the pressure drop across the gasifier bed plays a very important role in determining the gas velocity and the actual equivalence ratio; therefore the inclusion of the momentum equation for the gas velocity is a "must" for further developments.

CONCLUSIONS

This Thesis focused on the development of experimental systems and modelling tools for the study of biomass gasification. This aim was pursued by carrying out four different activities related to biomass pyrolysis and gasification. The main conclusions achieved by the four activities are reported.

A CFD model of a Drop Tube Reactor was developed to evaluate the effective residence time and particle thermal history. These results were used for elaborating suitable global high heating rate kinetics through a specifically developed procedure. Biomass particles in fast pyrolysis runs were found to be more reactive than in low heating rate runs (in thermogravimetric balance). Furthermore, kinetics differed significantly from those obtained assuming the strong hypothesis of constant particle temperature.

A tar sampling system was developed and tested with a fixed bed pyrolysis reactor and the collected condensate was characterized by means of four different laboratory techniques (TGA, TG-FTIR, UA, GC-MS). The different water content of the four fractions indicated that the system can effectively fractionate the condensate according to the boiling point. However, both the sampling system and the pyrolysis plant have to be improved; in particular it is mandatory to equip the pyrolysis reactor with a solid feeding system and couple the gas analysis of the micro-GC with FTIR-analysis. The condensate analysis showed that TGA is a useful preliminary tool for a first screen of the condensate properties. However, TG-FTIR and GC-MS are the most powerful techniques allowing the estimation of the water content and the qualitative composition of the fractions.

A pilot scale gasification facility based on a fixed bed downdraft gasifier has been developed and tested. Gasification tests of two pelletized biomass (wood sawdust pellet and a mixture of wood sawdust and sunflower seeds residues) as feedstock were carried out. The gasification of these biomass fuels produced a stable syngas composition with an average lower heating value close to 5.6 MJ m_n^{-3} . However the gasification of pelletized biomass poses some difficulties: the high pressure drop across the gasifier bed and the variable resistance to flow during the tests lead to a de-rating of the syngas flow-rate and difficult control of the process. In addition the char fragments into dust which is not recovered from the collection tank and dramatically increases the suspended solids in the water. The average operating and performance parameters derived from the balances were:

- Average Biomass loading rate ~50 kg h⁻¹.
- ER ~0.3.
- Specific gas production ~2.3.
- CGE ~70%.

Sampling of the gasifier bed from the air nozzles revealed partially devolatilized particles supporting the flaming pyrolysis hypothesis. The particle size and shape was very similar to WSP, while it is likely that SRP fragment into dust before reaching this point.

The gasifier produced a broad range of tars from class 1 to class 5, the lack of insulation of the first part of the gasifier clean-up line led to intense condensation onto the piping walls and in the cyclone. The particles collected from the cyclone are heavily mixed up with tars, therefore their handling and disposal has to follow strict safety and environmental procedures.

A modelling activity was carried out to develop an interpretative tool of the downdraft gasifier behaviour. The innovative approach of this study is the attempt to include the effect of air inlet in the middle of the gasifier and the throat. To do this a preliminary study was carried with a simplified cylindrical geometry, with a CSTR positioned at the nozzle outlet to represent the air inlet into the domain. The results of the simulation of the reference case (the gasification of WSP in test 2 and 3 reported in Chapter 5) fits fairly well with the experimental values, except for the gas composition which is not completely matched.

The simplified version of the model is used for evaluating the gas species distribution, reaction rates, temperature profiles and heat transfer mechanisms along the gasifier axis. It was found that a stable reaction front is achieved as a combination of volatiles combustion, which provides most of the heat, and heat transfer within the solid phase through radiation.

An attempt was made also to include the throat in the model. This posed an additional difficulty since the effect of the restriction on the solid phase flow is to be assumed. Simulations were carried out in order to assess the impact of two assumptions (solid phase moving as a gas or insensitive to the restriction). It was found that both assumptions are not representative of the gasifier behaviour since the reacting front propagates toward the bottom of the gasifier and no steady state can be reached. However, a stable char burning bed can be achieved with the second assumption which seems to be more realistic, and suggests that gas generation and acceleration are not properly simulated by the model.

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LIST OF PUBLICATIONS

International Journals

- E. Biagini, M. Simone, L. Tognotti. Characterization of high heating rate chars of biomass fuels. Proceedings of the Combustion Institute. Volume 32, Issue 2, 2009, Pages 2043-2050.
- M. Simone, C. Galletti, E. Biagini, L. Tognotti. Evaluation of global biomass devolatilization kinetics in a drop tube reactor with CFD aided experiments. Fuel. Volume 88, Issue 10, 2009, Pages 1818-1827.
- M. Simone, M. Bientinesi, C. Nicolella, L. Petarca. Integration of a small biofuel refinery in a rural context. Chemical Engineering Research and Design. Volume 87, Issue 9, 2009, Pages 1891-1205.
- 4. M. Simone, E. Guerrazzi, E. Biagini, C. Nicolella, L.Tognotti. Technological barriers of biomass gasification. International Journal of Heat and Technology. Volume 27, Issue 2, 2009, Pages 127-132.

In preparation for International Journals

- 1. M. Simone, F. Barontini, C. Nicolella, L. Tognotti. Gasifiication of pelletized biomass: assessment of a pilot scale downdraft gasifier.
- M. Simone, N. Nassi o Di Nasso, C. Nicolella, L. Tognotti. LCA applied to the gasification of woodchips derived by the maintenance of the S. Rossore natural reserve.
- 3. E. Biagini, M. Simone, C. Nicolella, L. Tognotti. Process modelling of a downdraft biomass gasifier.
- 4. A. Mancini, F. Barontini, M. Simone, G. Ragaglini, F. Triana, C. Nicolella. Biofuels production in Tuscany: case study analysis of sunflower cultivation and conversion.

International Conferences

- F. Barontini, M. Simone, G. Ragaglini, A. Mancini, S.D'Alvano, F. Triana, C. Nicolella. From crop to biofuels: a case study of sunflower crude oil production in Tuscany. Submitted to 19th European Biomass Conference, 6-10 June, Berlin.
- M. Simone, F. Barontini, C. Nicolella, L.Tognotti. Gasification tests of pelletized biomass-residues in a downdraft gasifier. Submitted to 19th European Biomass Conference, 6-10 June, Berlin.
- 3. M. Simone, F. Barontini, A. Ierna, C. Nicolella, L.Tognotti. Biomass TAR: assessment of a sampling device and a characterization methodology. Submitted to 19th European Biomass Conference, 6-10 June, Berlin.

- E. Biagini, M. Simone, C. Nicolella, L. Tognotti. Comparative process study of biomass gasification for power and chemical production. Submitted to 19th European Biomass Conference, 6-10 June, Berlin.
- M.Simone, F. Barontini, C.Nicolella, L.Tognotti. Evaluating the performance of a downdraft biomass gasifier. Accepted at 11th European Combustion Meeting, 28 June- 01 July 2011, Cardiff.
- M.Simone, C.Nicolella, L.Tognotti. Gasification of woodchips from the San Rossore natural reserve maintenance for CHP application: a case study analysis. Accepted at Icheap 10, 8-11 May 2011, Florence.
- 7. M.Simone, E.Biagini, C.Nicolella, L.Tognotti. Biomass Gasification: experimental and modelling activities at CRIBE. XXXI Meeting of the Italian section of the combustion Institute. 27-30 June 2010, Ischia.
- M.Simone, E.Biagini, C.Nicolella, L.Tognotti. Development of pilot scale facilities for testing secondary generation fuels production processes.18th European Biomass Conference, 3-7 May 2010, Lyon.
- E.Biagini, L. Masoni, E. Bargagna, M. Simone, G. Pannocchia, C.Nicolella, L.Tognotti. Advanced process models for biomass gasifiers.18th European Biomass Conference, 3-7 May 2010, Lyon.
- 10. M.Simone, M. Bientinesi, C.Nicolella. Environmental impact of oil-based biofuels production processes. Icheap 9, 10-13 May 2009, Rome.
- 11. M.Simone, M. Marcucci, E.Biagini, C.Galletti, L.Tognotti. Characterization of solid fuels in oxy-fuel conditions. Icheap 9, 10-13 May 2009, Rome.
- M.Simone, E.Guerrazzi, E.Biagini, C.Nicolella, L.Tognotti. Barriere Tecnologiche nella Gassificazione delle Biomasse. Aige 2, 4-5 September 2008, Pisa.
- M.Simone, E.Biagini, C.Galletti, L.Tognotti. Qualification of a lab-scale drop tube reactor for evaluating high heating rate devolatilization kinetics. XXXI Meeting of the Italian section of the combustion Institute. 17-20 June 2008, Turin.

PROJECTS AND COLLABORATION

This Thesis is involved in the following projects:

- 1. Integrated Systems for Hydrogen Production and Use in Distributed Generation FISR foundings.
- 2. Fattoria dell'Energia Enel foundings.
- 3. CRIBE Fondazione CariPisa foundings.

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> Horizon is unlimited but all is a deep lake, Where the drops seem to be dressed of a new red My eyes discover marks of a new world, Where his smell is covered by his crimes and vices Dark Stain as a never ending fight.

Finally I want to report a picture I discovered at the very beginning of my PhD. I used to start my spot-presentations at the GRICU students forums with the little story about the gasification teenager and it really worked: I was awarded for two years as the best presenter! Thanks to Erik Rensfelt who is probably the author of the picture.

THE HUMAN ANALOGY: GASIFICATION, A TECHNOLOGY IN ITS TEENS



- No longer a beautiful prodigy child
- Now has pimples and a few scars
- Obsessed with himself and things not appealing to the adult world
- Results are not to expectations
- Spends money and wants (absolutely needs !) more of it
- Says this with an unsteady voice

Mistakes can be learned from, but only if there is a second chance