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Experimental investigation of small-scale gasification of agricultural and forestry residues

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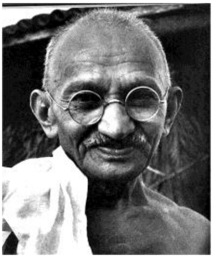
The best way to thank them all will be to observe in years coming the spread of biomass gasification plants in Italy as well as in the rest of the world.

Hiih... E che so' quelle?
Quelle sono le nuvole.
E che so' 'ste nuvole?
Mah...
Quanto so' belle... quanto so' belle... quanto so' belle...

"Che cosa sono le nuvole?" (1967)
Pier Paolo Pasolini



"Live simply so that others may simply live."

Mohandas Karamchand Gandhi

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Abbreviations

IISc	Indian Institute of Science, Bangalore, India	
UniFi	University of Florence	
RE-CORD	Renewable Energy Consortium for Research and Demonstration	
CFB	Circulating Fluidized Bed	
PCFB	Pressurized Circulating Fluidized Bed	
K	Kinetic model	
TE	Thermodynamic equilibrium model	
NN	Artificial Neural Networks model	
sTE	Stoichiometric Thermodynamic equilibrium model	
nsTE	Non-Stoichiometric Thermodynamic equilibrium model	
E	Energy	
Q_u	Useful Heat	
PS	Particle Size	
PG	Producer Gas	
SV	Superficial gas Velocity	
E_{PG}	Heat of combustion of Producer Gas	
LHV	Low Heating Value	[kJ]

EF	Equivalent Ratio
BFB	Bubbling Fluidized bed
PFD	Process Flow Diagram
SFC	Specific Fuel Consumption
SCADA	Supervisory Control And Data Acquisition
STD	Standard
EROEI	Energy Return On Energy Invested
EF	Energy Utilization Factor
IGCC	Integrated Gasification Combined Cycle
ESP	Electro Static Precipitator

Nomenclature

A	Surface	[m^2]
T	Temperature	[K]
c_p	Constant pressure specific heat	[J/kgK^{-1}]
m	Mass flow rate	[$kg\ s^{-1}$]
p	Pressure	[Pa]
t	Time	[s]
u	Velocity	[$m\ s^{-1}$]
V	Volume	[m^3]

W	Power	[MW]
K	Thermal conductivity	[W m^{-1} K^{-1}]
c_i	Molar concentration	[mol/m^3]

Greek

λ	air/fuel ratio	[-]
ρ	Density	[kg m^{-3}]

Subscripts

f	Fuel
stoic	Stoichiometric
el	Electrical

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Summary

Main objectives of the work have been to:

- adapt, install, commissioning of a 70kWe small scale innovative biomass gasifier inclusive of engine for power production
- develop numerical model for case study energy analysis
- experimental analysis on particulate and tar concentration of Producer Gas
- evaluate potential and efficiency of agro-residues energy conversion

A small scale innovative gasifier plant has been installed and operated at University of Florence facilities during a joint collaboration project with the Indian Institute of Science, Bangalore. The plant comprises of innovative features, most important of those is the reactor capability to generate high quality gas in comparison to other fixed bed downdraft design. Different test run have being practiced feeding the system with different kind of biomass, including compacted agricultural residues, in order to evaluate the technical feasibility and the system performance on low intrinsic value feedstock.

An extensive state of art of numerical modelling of biomass gasification process has been carried out with scope of figuring out possible solutions for the specificity of the case study. Consequently has been elaborated a model for system performance prediction end efficiencies evaluation to be coupled with experimental data gathering.

Relevant main parameters like air excess ratio, particle size, temperature and mass and energy flow rates have been monitored. Primary measures for tar removal have been studied in detail and the superficial gas velocity has been found to be a relevant parameter influencing T and tar decomposition inside the reactor. The producer gas composition has been characterized using Thermo Scientific c2V-200 micro gas chromatograph and the tar and particle concentration with on line sampling methods UNI CEN/TS 15439:2008. Very low tar concentration coupled with LHV up to 5 MJ/kg have been recorded at cold end in numerous experimental records.

Specific fuel consumption in the range of 1.16 kg/kWe has been achieved, amounting to almost 19% plant net efficiency. A complementary activity has been implemented on the agro-residue chain. The feasibility of supply and energy potential of 4 hectares of vineyards and 4 hectares of olive grove have been analysed and tested.

1. Biomass from agricultural and forestry residues

This chapter introduces waste biomass as an energy source. It focuses on specific contexts where thermochemical conversion is the preferred option. Circumstances and logistics make low energy density source very different and dependent to various site conditions. For this reason the Italian, Tuscany and Florence area data are reported and evaluated.

After a brief note on population-energy interrelation in the first section, pruning and forestry residues are introduced and the gross energy potential explained.

1.1 Introduction

Sustainability issues in the use of biomass to energy have been raised in the last years. Moreover, the expected decline in production of fossil fuels, particularly conventional crude oil [1], brought to the adoption of some new energy sources which have negative environmental effects (i.e. tar sands, shale gas). Since social condition and fuel are coupled (see Figure 1-1), an urgent solution worth both for energy supply and sustainability is strongly needed in the next decades.

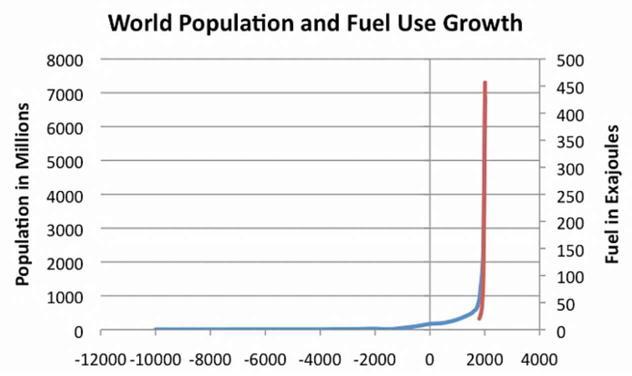

Figure 1-1: World population during last 14,000 years (blue), overlaid with fossil fuel use (red), **[2]**

Land and energy have historically always been related, because solar energy in all its form is proportional to the area of soil reaching sunlight. The industrialized society of today is unique historically in that access to biomass does not impose the ultimate limit: humans have learned to decouple industrial activities from biological productivity by exploiting fossil resources in the form of petroleum, coal and gas [3]. Quote from a dystopian action movie "gasoline is our land" [4] is moderately true.

Waste biomass, like wind and solar and other renewables, can be a step towards restoring the land and energy relation since it is not over-exploitable.

Commercial viability of decentralised small scale production could be improved by integrating bioenergy production with other production systems or in a closed loop operation where waste from one process is used as an input in the production of other product [5]. An alternative could be to integrate bioenergy production with other unrelated production systems where bioenergy is produced from waste residues and also used in supporting the production system creating the waste. This creates production cycles of energy and other non-energy products with less waste to the environment [6].

1.2 Pruning residues

In Italy biomass sources for energy production derive from various activities such as exploitation of forest stands, residues from agriculture, new forest plants specialized in production of biomass for energy purpose and residue from wood industry. Total gross amount is reported in Table 1-1.

Table 1-1: Values of residues (t/ha) and ratio of residue/product (wet basis) in Italy **[7]**

PLANTS	RESIDUE (T/HA)	RESIDUE/PRODUCT
Vineyard	2.9	0.2-0.8
Olive trees	1.7	0.5-2.6
Apple trees	2.4	0.1
Pear trees	2.0	0.1
Peach trees	2.9	0.2
Citrus tress	1.8	0.1
Almond trees	1.7	1.9
Hazel trees	2.8	1.9

Particularly attention has to be given to pruning residues from tree crops whose disposal is expensive and valorisation can be profitable. Furthermore residues removal avoids inoculation of organisms that cause infectious disease such as fungi, oomycetes, bacteria, viruses etc. Usually agro-wastes are cleaned out with open burning technique, but some years ago the Italian legislation[1] limited the practice to selected periods.

The amount of agro-residues in Tuscany (see Table 1-2) and Italy (see Table 1-1) is reported.

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[1] Decreto legislativo n. 152 del 3 aprile 2006

Table 1-2: Residues from agricultural activities (t/y) in Florence and Tuscany **[8]**

	VINEYARDS	FRUIT	OLIVE GROVES	POPLAR	CHEST NUT	TOTAL
Florence	29,520	1,440	63,274	1,480	7,462	103,17
Tuscany	102,744	11,549	183,974	11,040	34,144	343,45

Olive tree

More than 2000 years ago Pliny the Elder asserted that Italy was the major olive and olive oil producer in the world [9]. Due to its historical presence olive tree is deeply integrated in land use and culture of regions "*La vita, la terra, il tempo. L'ulivo è il segno del loro possesso, ne è metafora e sacralità*" [10].

Figure 1-2: Untouched olive residues long after pruning, Castellina in Chianti, Italy

Despite in many cases olive residues from pruning are not valorised (cf. Figure 1-2) energy valorisation of agricultural and forestry residual biomass is not a new practice. As an example, Figure 1-3 shows a particular use of olive grove pruning residues for construction materials production.

Figure 1-3: Brick-kiln powered by bundles of olive branches (left) and relative clay model before firing (right) **[11]**

Grape Vine

The grape vine has been used as a symbol since ancient times. In Greek and roman mythology gods of the grape harvest and winemaking were present and wild and mystic festivals, named Bacchanalia, were dedicated to.

The vine is also used as a symbol In Christian iconography, in the Gospel according to John (15:5-8) is reported Jesus Christ own statement, “I am the vine.” The vine as symbol of the chosen people is employed several times in the Old Testament, Pope Benedict XVI on 19 April 2005 when elected defined himself “humble labourer in the vineyard of the Lord”

Vine grape agricultural by-product is generated in large amounts in the wine making regions of Mediterranean countries, with an estimated yearly production ranging from 1.0 to 3.0 ton/ha/Year [7] [12]. Operations of pruning are carried out in periods and with variable cadence in function of the specific cultivations and the time of vegetative fallow.

Numerous are cases where wine production residues (i.e. Vinasse) are collected and valorised, but usually not for energy conversion. The possibility of recovering vine-branches for their energetic utilization is related to the possibility of proceed in the collection of material, and for this reason it is in function to the density of the plant, to the modality of trimming and the following plant growth (the plant breeding form) and the disposition (degree of fragmentation and slope) of the ground.

NON-ENERGY TECHNIQUES FOR TREATMENT OF WASTE BIOMASS FROM PRUNING

The *first* one is to chip the residues directly in the field along the alleyways and provide their subsequent burial. Residues in this way decompose and releases minerals and part of the carbon with favourable repercussions on the soil amendment and quality. This simpler solution can be covered only when the vineyard is healthy. Otherwise residues constitute a source of infection, inoculum and spread of diseases such dead arm, root rot or apoplexy in the case of the vine grape.

The *second* one is carried out with piles collection and then combustion in accordance with the legal requirements of each country or region. In Tuscany the practice is allowed before May 31 and only during particular hours of the day. In some part of the world the bonfires of agro-wastes have important cultural implications and significance, in the celebration held every 16th of May in Salento where vineyard pruning residues staked in a 25 height pile are burned (see Fig. 1-4).

Figure 1-4: The “Focara” in Novoli, Southern Italy

The *third* one is the composting process by means of different techniques and equipment depending on context but basically pursued by shredding the plant matter, adding water and ensuring proper aeration by regularly turning the mixture. Worms and fungi further break up the material.

1.3 Forestry residues

Forest residues can be defined as all above-ground biomass left on the ground after timber harvesting operations (e.g. branches, tops, small unmarketable logs and undergrowth trees). On average 10 to 15 % of the total above ground biomass is left behind as forest residues during regular harvesting activities (20–30% in the first commercial thinning but only 4–5% in the final cutting) [13].

Forest residues have a great biomass potential. Especially in Europe where, because of the high degree of utilization of industrial wood processing, residues sources of woody biomass are becoming scarce. In Italy, an amount of potentially available biomass (assuming a 15% recovery rate) is estimated in 1,318,613 m^3 [14].

If more accurate forest waste pre-treatment activities are implemented, the recovery rate can significantly increase. Milling and briquetting are estimated to make exploitable another part of usually unrecovered residues, comprehended between 20 to 30% of total amount. Usually in Tuscany this amount consists of pine needles, leaves and small twigs. Furthermore, the possibility to wait the more convenient gathering period when sun and air drying lead to very low moisture content (see Figure 1-5) is an additional interesting benefit of this kind of wastes.

Figure 1-5: Dry non-exploited residues, Iesa, Tuscany.

Further data on this kind of waste are given in section 2.3.

2. Feedstock supply and preparation

In this chapter an overview of all supply chain aspects is reported, with help of data from an experimental campaign of pruning residues valorisation (sections 2.1, 2.2). Inclusion of supply side activities is justified by following reasons:

- Pre-commercial technologies cannot avoid the context they are acting
- Intrinsic features of the 70 kWe power plant (see section 3.2)
- Some financial support derived from projects focused on supply chain
- Literature lack on connection among energy conversion aspects and supply chain issues

Bio-energy production cannot focus only on technical aspects of the conversion plant; a comprehensive analysis of systems must include a supply chain perspective on activities carried out *before* the energy conversion of biomass. The evaluation, even in the case of residues, must comprehend all the agro-chain aspects from an agronomical, energetic, economic, environmental and sustainability point of view. Summarizing, this aspects are:

- harvesting and collecting biomass
- storage throughout the bio-energy chain
- transport in the bio-energy chain
- pre-treatment techniques
- design of the bio-energy production system
- emission and process waste

The overall purpose of biomass supply chain for energy use is basically twofold:

- Feedstock costs are to be kept competitive [15].
- Continuous feedstock supply has to be ensured [16]

Furthermore biomass pre-treatment technologies available at the moment for small scale gasification are presented in Chapter 2.3.

2.1 The project VISPO

Introduction

Data gathering of all the aspects of agro-chain is very difficult, and often boundary conditions not well defined.

Figure 2-1 depicts how biomass is moving through various main operations along the supply chain for ensuring constant and competitively-priced feedstock supply for energy conversion plants. The idiosyncratic combinations of different components of the chain can make direct comparisons between different bio-energy systems difficult [17].

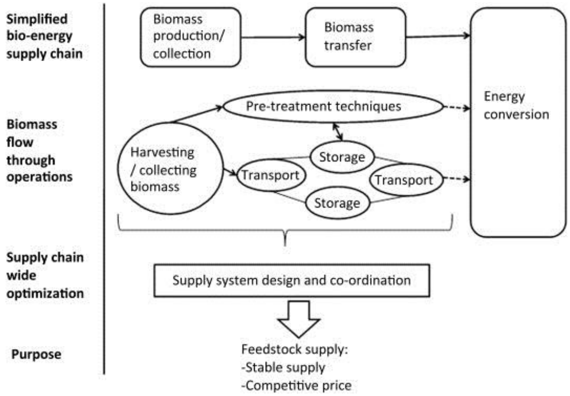

Figure 2-1: Facilitating biomass flow along the bio-energy chain **[18]**

Agro-residues context can be significantly simpler because the very low energy density of biomass collected cannot sustain complex chains and large numbers of intermediaries. Nevertheless, numerous agro-energy experiences have often led to clash with various difficulties resulting in a non-competitive price of the final product.

The project specifically implemented differs from previous experience because offers a full micro-structure of integrated supply chain and main part of the added value remains to the farmer. The name of the project is VISPO; it is funded by the

Region of Tuscany by means of the Leader+ initiative financed by EU structural funds. The aim of the project, whose acronym in Italian is "Valorizazzione Innovativa Scarti potatura Olivo" which means “Innovative Valorisation of Olive Pruning Scraps”, is to analyse the opportunities from agro-residue short energy chains to set up innovative applications aiming at environmental, economic and social sustainability. Partners in the project are UniFi as a scientific body, two farms and a foundation for the protection of the Chianti Classico region.

Table 2-1 [19] reports the potential of waste focused by VISPO in Italy, and the main features (Table 2-2, [20]) relevant for energy conversion.

Table 2-1: Average values of waste residues and ratio of residue/product in Italy

Plant	Residue (Tons per Hectare)	Residue/Product (w.b.)
Grape Vine	2.9	0.2-0.8
Olive	1.7	0.5-0.8

Table 2-2: Availability and energy characterization of pruning olive and vine shoots

Residue features	Measure unit	Olive residue	Vine residue
Production	Ton/Hectare*year[2]	0.8-1.6	0.6
Bulk Density	Kg/m^3	150	260
Moisture content	% d.b.	30	40
LHV	kcal/kg	4420	4300

It should be noted, however, that past experience has shown a great variability of values as for tables as before. Territorial logistics, geography, orographic and the extension of the single vineyard or olive grove can significantly affect the timing, the degree of mechanization and thus the total economical and energy cost of the project. Large improvement potential can be achieved with best practices and fine tuning on the basis of past experiences.

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[2] As received

In this respect the author remarks that Table 2-1 values should be distinguish between biomass potentially available and recoverable for energy purposes. This is a generally accepted practice for fossil fuel reserves, distinguished in technically and economically recoverable resources.

Supply basin 1: The Grassi Farm

The first farm enrolled in VISPO project is “Azienda Agricola Giacomo Grassi”, Location Dudda, Greve in Chianti (FI), Italy. The base land consists of approximately 25 hectares.

16 hectares are dedicated to olive groves for a total of about 5,000 olive trees with varieties typical of the area as the main Frantoio, Leccino and Moraiolo to which are added the minor varieties such as olive White, Pendolino, Maurino, Leccio the Horn. Total average yearly production ranges strongly depending on weather conditions and water supply between 9 and 12 tonnes of oil.

4.5 hectares are dedicated to vineyards, 80% is the Cultivar Sangiovese type and the remaining 20% with minor grape varieties such as Colorino, Pugnitello, Foglia Tonda, Ciliegiolo, Canaiolo, Malvasia Nera and Mammolo.

3 hectares in total of Grassi farm cultures have been enrolled in VISPO project, in Table 2-3 main features of experimental study dedicated area are presented.

Table 2-3: Olive grove and vineyard features of Grassi Farm

	Vineyard A	**Vineyard B**	**Olive grove**
Age (Years)	10	15	15
Row width (m)	2.7	2.7	-
Area (hectare)	1	1	1
Residue [Kg/y]	900	900	1700
Cane training system	Guyot simple	Guyot simple	-
Cultivation type	Sangiovese	Sangiovese	-
Pruning time [h]	50	50	25

VINEYARD PRUNING

The total number of wine grape plants involved is about 15,000. The Farm combines manual pruning among rows and mechanic pruning with a tractor powered forage harvester (Figure 2-2).

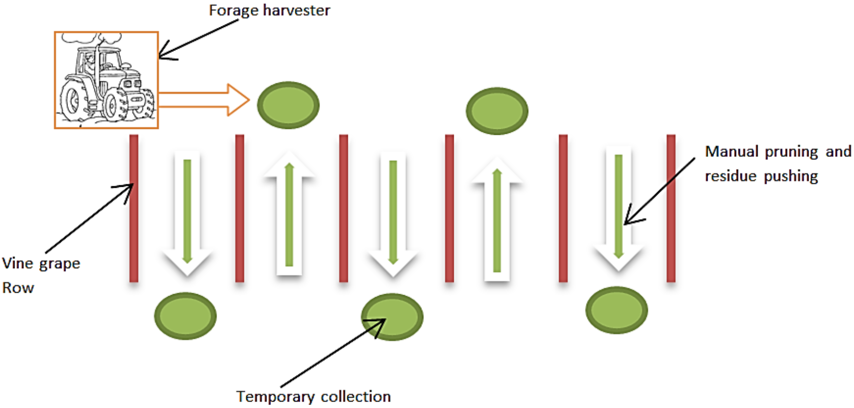

Figure 2-2: Wine grape residue collection technique at Grassi Farm

Both vineyards A and B have a surface inclined by almost 30° and the distance between the rows is 2.7 meters. The Azimuth angle is 30° east, very convenient position because it makes the plant not having open pores during the hours when sunlight is greater[3].

Residue amount depend, other than weather conditions and water availability, by the cane training system as well. Furthermore, extraordinary activities (i.e. grape renewal) during life of vineyard (that can exceed 30 years) can lead to additional

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[3] Nourishment of the plant is based on the evaporation of water, made possible by pores.

amounts of residues. Renewal is necessary in case of plant disease; a common case of vine grape ailment is presented further on this chapter.

OLIVE GROVE PRUNING

Both summers of 2011 and 2012 have been particularly dry and this has influenced both product (oil) and co-product (pruning residues, pomace) amounts. Since grass is present in the olive grove, mowing has been necessary before pruning to avoid mouldering due to humidity.

Olive tree distance is 3 meters in-row and 6 metres the between. After pruning, residues have been manually pushed in windrows among olive rows. Manual pushing (orange arrow) and harvesting have been accounted as an energy cost of VISPO (Figure 2-3).

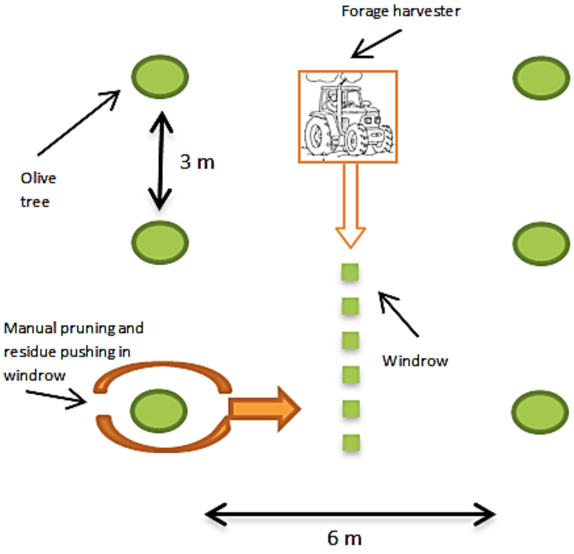

Figure 2-3: Olive grove residue collection technique at Grassi Farm

Supply basin 2: Montepaldi Farm

Montepaldi is a farm in the heart of Chianti Classico (City of San Casciano Val di Pesa). Montepaldi is a limited liability company owned by University of Florence. By its very nature it is dedicated to experimentation and research, and is therefore the ideal place to focus on innovative biomass-related issues. It covers an area of over 300 hectares which consists of arable land, forests, vineyards, olive groves and related processing facilities such as wine and olive press. The activity is mainly related to the production of the wine (1,850 tons of grapes and 1,200 hectolitres of wine on a yearly average), oil and agriculture. In Table 2-4 the land being part of experimental activity is reported.

Table 2-4: Olive groves and vineyards made available to VISPO Project by Montepaldi Farm

	Pruning technique	**Crane training system**	**Hectare**	**Grape Vine Type**
Vineyard A	Manual pruning	Cordon	1	Sauvignon Blanc, 15 years old
Vineyard B	Bar trimmer and (as a second step) manual pruning	Cordon	1	Sangiovese, 15 years old
Olive Grove A	Manual pruning	Cordon	1.5	Leccino
Olive Grove B	Manual pruning	Cordon	1.5	Leccino

VINEYARD PRUNING

Montepaldi farm is equipped with special bar trimmer (Figure 2-4) which is very useful for a first gross pruning of large areas and then the grape is manually adjusted (Figure 2-5). Fully manual pruning has been carried out when mechanical activity was not possible for orographic reasons.

Figure 2-4: Bar trimmer on February 12, 2012 in VISPO Project Vineyard

After pruning almost 2000 kg of biomass residues were windrow disposed as in Figure 2-5 waiting for tractor-powered forage harvester. Then agro-residues were taken to the experimental area of UniFi very closed to the pruning site.

Figure 2-5: Manual pruning after bar trimmer (left) and windrow (right)

OLIVE PRUNING

The hectare of cultivation provided to the experiments produced approximately 1000 kg of biomass. Pruning has been managed entirely manually since orography could not admit mechanical devices and tractor. The presence of leafs during pruning period of olive tree[4] (Figure 2-6) brings to different results in ash content and other biomass features.

Figure 2-6: Cutting waiting for harvester (left) and detail of leaf presence (right)

On the other hand, during grove managing operation, large branches of the plant are removed and as a consequence a very high quality biomass is generated (Figure 2-7).

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[4] Seasonal leaf loss for Grape Wine is, as for majority of plants, in autumn.

Figure 2-7: Olive tree logs

OTHER TYPES OF BIOMASS

As first assessment a sample (VM2-A) of grape vine plant affected by “Mal dell’Esca” or apoplexy has been conserved and analysed (Appendix B – Laboratory analysis for details). This disease, very common, is the consequence of the attack of three different types of fungi causing in sequence the obstruction of xylem followed by oxidation and death. The only remedy is the complete cutting of plant and the substitution with a new one (vine yard renewal).

Being a very common disease affecting usually from 5% to 15% of vineyard plants each year, energy valorisation can brought to interesting results.

2.2 Experimental analysis of the agro-residue chain

Unifi has an experimental area inside Montepaldi Farm, where numerous biomass conversion and research plants are present. Works of collecting, storing, analysis, pre-treatment and finally energy conversion have been implemented. Biomass residues features have been monitored starting from the day of the pruning. Different kind of storing conditions has been simulated, part of residues has been collected indoor, part outdoor with different sun exposition in order to replicate most of possible storing circumstances.

Biomass collecting and storage

Transport of agro residue to the UniFi area is done by means of truck, in the case of Grassi farm the distance to be covered is 30 km.

Agro residues has been piled open air in numerous heaps with intention of reproduce a common procedure that is to leave biomass residues for a few months at the collecting site to significantly reduce their water content [21]. Furthermore, the short harvesting and pruning period and the low density over the territory naturally induce the need of storage in order to ensure continual supply of feedstock for bio-energy plants [22]. Agro-wastes conditions have been monitored, the evolution of biomass features during storing time and in different parts of pile has been recorded, particularly has been analysed the efficiency of sun drying.

Size and shape condition of biomass as received was not suitable for direct energy conversion, the forage harvester during load can chip the residues but not in a complete and homogeneous mode. Among chunks there was, in the case of grape vine, vine stocks exceeding 10 cm length (Figure 2-8 and Figure 2-9).

Figure 2-8: Size and shape detail of vine stock as received

Also for olive grove residues some problems related to the size have been registered since small branches are not chipped during mechanical harvesting and also for the presence of leafs.

Figure 2-9: Olive tree pruning residue as received

Laboratory Analysis

Analysis has been pursued by RE-CORD laboratory following technical standard as below:

- UNI EN 14774-3:2009: Solid Biofuels - Determination Of Moisture Content - Oven Dry Method - Part 3: Moisture In General Analysis Sample
- UNI EN 14775:2010: Solid biofuels - Determination of ash content
- UNI EN 15104:2011: Solid Biofuels - Determination Of Total Content Of Carbon, Hydrogen And Nitrogen - Instrumental Methods
- UNI EN 15289:2011: Solid biofuels - Determination of total content of sulphur and chlorine

List of samples analysed is reported in Table 2-5 for olive tree and Table 2-6 for vine grape pruning residues. Details of each single analysis are reported in "Appendix B – Laboratory analysis".

Table 2-5: Details of samples of olive grove pruning residue

Sample ID	Type, Origin and date	Storing	Sample date	Note
OM1-A	Olive tree, Montepaldi Farm, April 2012	Open air	May 8, 2012	External part of heap, sun and air exposed
OM1-B	Olive tree, Montepaldi Farm, April 2012	Open air	May 8, 2012	Internal part of heap
OM1-C	Olive tree, Montepaldi Farm, April 2012	Open air	October 8, 2012	External part of heap, sun and air exposed
OM1-D	Olive tree, Montepaldi Farm, April 2012	Open air	October 8, 2012	Internal part of heap
OM1-E	Olive tree, Montepaldi Farm, April 2012	Chipped, Open air	October 8, 2012	External part of heap, sun and air exposed
OM1-F	Olive tree, Montepaldi Farm, April 2012	Chipped, Open air	October 8, 2012	Internal part of heap
OM1-G	Olive tree, Montepaldi Farm, April 2012	Indoor	October 8, 2012	
OM2-A	Olive tree log, Montepaldi Farm, April 2012	Indoor	May 8, 2012	

Table 2-6: Details of samples of Vineyard residue analysed

Sample ID	Type, Origin and date	Storing	Sample date	Note
VM1-A	Vine grape, Montepaldi Farm, March 2012	Open air	May 8, 2012	External part of heap, sun and air exposed
VM1-B	Vine grape, Montepaldi Farm, April 2012	Open air	May 8, 2012	Internal part of heap
VM1-C	Vine grape, Montepaldi Farm, April 2012	Open air	October 8, 2012	External part of heap, sun and air exposed
VM1-D	Vine grape, Montepaldi Farm, April 2012	Open air	October 8, 2012	Internal part of heap, humification undergoing
VM1-E	Vine grape, Montepaldi Farm, April 2012	Chipped, Open air	October 8, 2012	External part of heap, sun and air exposed
VM1-F	Vine grape, Montepaldi Farm, April 2012	Chipped, Open air	October 8, 2012	Internal part of heap
VG1-A	Vine grape, Grassi Farm, May 2012	-	May 17, 2012	Collected during pruning
VG1-B	Vine grape, Grassi Farm, May 2012	Open air	October 8, 2012	External part of heap, sun and air exposed
VG1-C	Vine grape, Grassi Farm, May 2012	Open air	October 8, 2012	Internal part of heap
VM2-A	Grape stems, Montepaldi Farm, April 2012	Open air	November 9, 2012	
VM3-A	Grape affected by Apoplexy disease, Montepaldi Farm, April 2012	-	March 27, 2012	Only branch, no leafs

Energy analysis of pruning activities

Table 2-7 indicates major outcomes of energy analysis during VISPO campaign. Two specific vineyards demonstrate to have a highly energy potential, both are inclusive of energy expenditure due to 30 km transport of biomass residues to the UniFi experimental area.

Results are interesting since most of the logistics carried out are not taken into account, since farmers work is necessary in any case. The EROEI, the ratio of the amount of usable energy acquired from a particular energy resource to the amount of energy expended to obtain that energy resource [23], of the complete process (biomass pre-treatment excluded) demonstrate being 1:19 for Case study A.

Table 2-7: Summary of energy analysis recorded during VISPO project

	Vineyard A – Grassi Farm	**Vineyard B – Grassi Farm**
Area [hectare]	1	1
Residue collection time [h]	2	2
Diesel fuel [litre/ton of residue]	18.5	21
Residue [kg]	900	1050
Energy recovered (HHV, ad) [MJ]	11,700	13,200
EROEI[5]	1:19	1:16

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[5] Energy expenditures for biomass collecting have been calculated as 615MJ: 16.65 litres of Diesel fuel (LHV 36.94 MJ/litre). Manual operations of pruning are not taken into energy account.

Forestry residue supply basin

In the surroundings of the gasifier plant there is a wide mountainous area covered by forests and woodlands. Most common trees are oak, holm oak, pine and strawberry tree. Pine trees are usually cut as a whole with community permission since are not an autochthonous specie.

Residue deriving by surface maintenance is very abundant and operations are taken in charge by different Mountain Communities of the region. During last year's many actors of forestry operations were hit hard by rise of petroleum fuel prices creating a crisis for the sector. Labour cost, mass and volume of biofuels, capacity of the carriers are key variables primarily dependent on the travel distance as well as cost of diesel fuel [24].

The forest area being addressed as supply basin of the 70kW$_e$ plant covers 10.000 hectares in the proximity of Iesa hamlet, Monticiano administrative council. The highest quality part of cut shrubbery is employed as household firewood and the rest is chipped and used as feedstock in energy plants.

2.3 Biomass pre-treatment for energy conversion

Energy valorisation case study

Scope of this section is an overview of pre-treatment activities carried out on the feedstock used for the 70 kWe gasifier case study. Other techniques (an overview in Table 2-8) economically non-viable for small scale aims or for other technical reasons will not be considered.

Table 2-8: Major biomass pre-treatment techniques **[18]**

Techniques	Definition
Ensiling	Ensiling is “the process of creating silage via anaerobic fermentation”
Pelletisation	Pelletisation may be described as “drying and pressing of biomass under high pressure to produce cylindrical pieces of compressed and extruded biomass”
Torrefaction	Torrefaction is “a thermal pre-treatment technology performed at atmospheric pressure in the absence of oxygen. Temperatures between 200 and 300 °C are used, which produces a solid uniform product with very low moisture content and a high calorific value compared to fresh biomass”
Pyrolysis	Pyrolysis means “the direct thermal decomposition of biomass in the absence of oxygen. Temperatures employed in pyrolysis are 400–800 °C. The products are gas, liquid and solid char, and their relative proportions depend on the pyrolysis method, the characteristics of the biomass and the reaction parameters”

Briquetting

The first option has been milling and briquetting the waste biomass collected during VISPO project. Manual loading and unloading of the biomass and separated drying process has been carried out.

The briquetting machine plant used (Figure 2-10, left) can make stick shape briquette of different diameter and different shape from biomass of agro-forest origin (Figure 2-10). Ultimate analysis of samples is reported in “Appendix B – Laboratory analysis”.

Figure 2-10: Briquette machine during operation (left) and close-up of briquette of milled forestry residues (right).

Chipping

The second solution has been an additional size decrease of chunks with a mobile chipper. In Figure 2-11 are visible the vine grape branches on the left meanwhile the chipped material is thrown rightward (on the background the pickup vehicle for transport of chipper). Optionally a mechanical screening by means of manual or vibrating devices can be used to further selection of preferred size biomass.

Figure 2-11: Small woodchipper during the pre-treatment at UniFi area

Other two bigger machineries have been employed for larger quantities and to produce larger size chips as requested for tests.

The first machine used is a disc chipper Model H 880/250, Pezzolato S.p.A.; it is manually fed and requires two operators and a power of 59 kW. The size of machine is definitely bigger than the purpose of small scale gasification since can process 2 to 4 tons of biomass per hour.

The second, larger (up to 30 tons of biomass per hour) machinery is the JENZ HEM 561 model. It is a chipper intended to be used also for chipping whole trees (up to 560 mm in diameter) and needs a power drive of 240 kW.

Residues drying by cogeneration

Biomass for test has been dried in a separate site. However, energy and mass balance demonstrates that the power system generate enough waste heat in the exhausts potentially exploitable for drying. Table 2-9 reports requirements for drying purposes. Feeding rate and moisture content of feedstock at reactor gate are set to fixed values, and accounting for different yearlong conditions.

Table 2-9: Drier mass and energy balance

	VALUE	UNIT
Wet biomass flow, minimum	88	kg/h
Wet biomass flow, minimum	79	kg/h
Moisture, maximum	45	% wt. d.b.
Moisture, maximum	30	% wt. d.b.
Moisture at reactor	15	% wt. d.b.
Dry biomass flow at reactor	70	kg/h
H2O to be evaporated, maximum	18[6]	kg/h
H2O to be evaporated, maximum	9	kg/h
Heat requirement, maximum	18	kWth
Heat requirement, maximum	9	kWth

The waste heat from the engine is usually available from 5 sources:

- cooling water of engine jacket
- lubrication oil
- air intake of intercooler (first stage)
- exhaust gases
- radiated heat and intercooler (second stage)

Energy Utilization Factor is defined as:

$$\frac{(E_{el} + Q_u)}{E_{PG}}$$

and usually set 0.7-0.9 [25], while Cummins evaluate this factor up to 88.1 [26]. For conservative reasons EF has been set to the value of 0.8.

Table 2-10 reports main energy balance of the case study. Average producer gas flow rate at nominal condition has been set to 249.5 kg/h and the heat of

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[6] Conservatively considered 4.186 kJ/kg_H_2O

combustion to 266.7 kW. An average exhaust mass flow of 585.2 kg/h results in 66kWth[7] of recoverable heat.

Table 2-10: Engine energy balance

	VALUE	UNIT
EUF	80	%
E_{PG}	266.7	Kw
E_{el}	70	kWe
Q_u	143.4	kWth
Heat in exhaust	66	kWth

Additional waste heat can be derived from PG along the streamline to engine. It is a common practice, usually for heating water for buildings energy requirements. In this specific case exploitable heat is present before gas cooler. Hot water from gas cooler is cooled down by a wet cooling tower, thus this heat is considered unrecoverable. In Table 2-11 main values of energy recovery are reported, the minimum temperature of PG is set 300°C to avoid substantial variations in physical properties.

Table 2-11: Heat recovery potential from Producer Gas

DATA	VALUE	UNIT
PG specific density	1.162	kg/Nm^3
PG flow	211	Nm^3/h
PG specific heat capacity	1.319	$kJ/Nm^3/°C$
PG T inlet	455	°C
PG T outlet	300	°C
Heat recovered	12	kWth

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[7] The specific heat capacity of gases has been considered constant to the value of 1,030 [kJ/kg*K], the temperature of exhaust 420°C

3. Small scale biomass gasification technologies

This chapter illustrates the power production technologies available for the conversion of biomass by means of gasification. Conversion technologies other than gasification are available (i.e. Organic Rankine Cycle, Externally fired gas turbines) but usually are employed on larger scale than this case study.

In the first section an extended state of the art of biomass gasification systems is implemented. Section 3.2 deals with the innovative gasification power plant developed for this work.

3.1 Classification and state of art

The lower energy density of biomass fuels compared to fossil fuels makes transportation a relevant cost factor in bio-energy systems pushing towards smaller applications [27]. Even more so in case of residues, whose specific to land area amount is lower than other biomass sources.

Small scale biomass gasification is one of the best affordable technologies for lignocellulosic wastes and in the upcoming years is thought to be the as one of the major technologies for complementing the energy needs of the world [28]. The main advantages are that the feedstock for thermochemical conversion can be any type of biomass including agricultural residues, forestry residues, non- fermentable by-products from bio refineries, by-products of food industry, by-products of any bioprocessing facility and even organic municipal wastes [28].

Gasification science – the basics

Gasification reactions (except shift reaction) are strongly endothermic and need heat supply in order to be performed. An external heat source is avoided in gasifiers which employ air or oxygen as the gasifying agent, since O_2 reacts with part of the char and the other products of the pyrolysis supplying the heat required. Partial combustion reactions are:

$$\mathrm{C} + {}^{1}/_{2}\,\mathrm{O_2} \rightarrow \mathrm{CO} \qquad \Delta H_{298K} = -\,111\ \mathrm{MJ/kmol} \qquad (3.1)$$

$$\mathrm{C} + \mathrm{O_2} \rightarrow \mathrm{CO_2} \qquad \Delta H_{298K} = -\,394\ \mathrm{MJ/kmol} \qquad (3.2)$$

$$\mathrm{CO} + {}^{1}/_{2}\,\mathrm{O_2} \rightarrow \mathrm{CO_2} \qquad \Delta H_{298K} = -\,284\ \mathrm{MJ/kmol} \qquad (3.3)$$

$$\mathrm{H_2} + {}^{1}/_{2}\,\mathrm{O_2} \rightarrow \mathrm{H_2O} \qquad \Delta H_{298K} = -\,242\ \mathrm{MJ/kmol} \qquad (3.4)$$

$$\mathrm{CH_4} + 2\mathrm{O_2} \rightarrow \mathrm{CO_2} + 2\mathrm{H_2O} \qquad \Delta H_{298K} = -\,36\ \mathrm{MJ/kmol} \qquad (3.5)$$

The water steam can be produced during the drying and pyrolysis of the feedstock or introduced as a gasifying agent or even generated according to reversible water gas reactions. Water gas reactions together with the Boudouard equation are the main endothermic reduction reactions involved in the process. These reactions increase the concentration of carbon monoxide and hydrogen in the producer gas, especially at higher temperatures and lower pressures:

- WATER–GAS REACTION: $C + H_2O \rightarrow CO + H_2$ (+131.4 kJ/mol) (3.6)
- WATER–GAS REACTION: $C + 2H_2O \rightarrow CO_2 + H_2$ (+90.2 kJ/mol) (3.7)
- BOUDOUARD REACTION: $C + CO_2 \rightarrow 2CO$ (+172.6 kJ/mol) (3.8)

Several other reduction mechanisms occur during the gasification process; some of the most important reactions are listed below.

- WATER GAS SHIFT $CO + H_2O \rightarrow CO_2 + H_2$ (-41.1 kJ/mol) (3.9)
- METHANE PRODUCTION: $2CO + 2H_2 \rightarrow CH_4 + CO_2$ (-247.3 kJ/mol) (3.10)
- METHANE PRODUCTION: $CO + 3H_2 \rightarrow CH_4 + H_2O$ (-206.1 kJ/mol) (3.11)
- METHANE PRODUCTION: $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$ (-165.1 kJ/mol) (3.12)
- METHANE PRODUCTION: $C + 2H_2 \rightarrow CH_4$ (-74.8 kJ/mol) (3.14)

The equilibrium of reactions which determine to a large extent the final gas composition is strongly influenced by the temperature, as depicted in

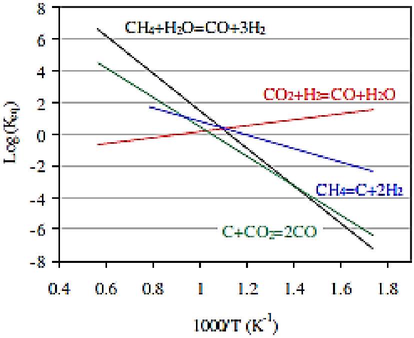


Figure 3-1: Equilibrium constant of main gasification reaction **[29]**

Gasification technology

There is no univocal classification of biomass gasifier at the moment; continuous technological improvements make any state of art out to date very soon. Moreover, the gasification process consists of various different steps, each of those subjected to a wide spectrum of available technologies. Main stages of biomass gasification can be defined as upstream, gasification and downstream processing (see Figure 3-2).

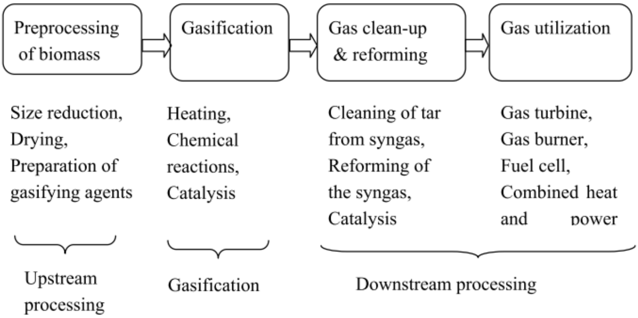


Figure 3-2: Processes involved in biomass gasification **[28]**

The core process is the gasification. Three distinct categories distinguished by reactor operating conditions are presented in Figure 3-3.

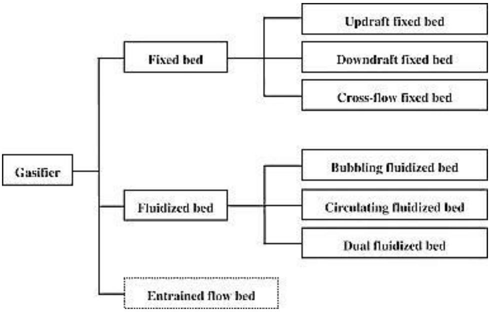


Figure 3-3: General categories of biomass gasifiers **[30]**

If small scale applications are addressed, the fixed bed category is considered as the most suitable one. In Figure 3-4 principal reactor design are plotted in relation to thermal capacity.

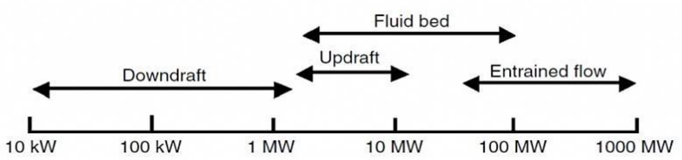
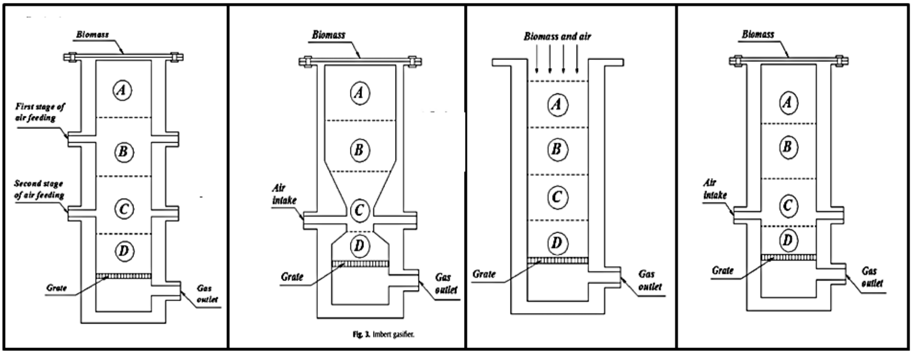


Figure 3-4: Range of applicability for biomass gasifier types **[31]**

Amongst downdraft fixed bed gasifiers (the most suitable type for small scale application) a wide variety of design is still present. A further categorization has been outlined considering 3 important design features:

- Top of reactor: open or closed during process
- Throat: with constriction (Imbert type) or not
- Stage air supply: 1 or 2 or more

Basing on combination of 3 features, in Figure 3-5 are illustrated 4 of main technological solutions available nowadays.



- Closed top
- Throatless
- Double air

- Closed top
- Throat
- Single air

- Open top
- Throatless
- Single air

- Closed top
- Throatless
- Single air

Figure 3-5: Comparison of main gasifier reactor design

Top of reactor

First open top gasifiers were developed firstly by Chinese for rice hulls gasification [32]. Top of reactor choice is addressed to both practical and thermochemical issues. The atmosphere-exposed reactor has the advantage of easier biomass charge and possibility to continuous feeding, while the closed one can handle biomass charge only in a batch mode.

From the thermochemical point of view the open or closed top has influence on air injection and thus oxidation and T distribution along reactor. Closed top has the advantage of a more control on air injection, being possible to fix the exact position of the oxidation zone. On the other hand, the open top directs the gasification agent to the whole cross-sectional area of reactor, leading to wider and homogeneous areas of reactions and avoiding as much as possible channelling phenomena.

Throat

Throated designed reactors are also named Imbert type, from French inventor George Imbert which developed this kind of gasifier around 1920 (Figure 3-5, second from left). Main reason of the Imbert design is explained by high thermal cracking behaviours originated by pyrolysis gases forced to flow through high temperature passage. This is the reason because the oxidation agent is always injected in the constriction point. The disadvantage is the physical limitation of biomass flowing down the reactor, biomass has to be properly sized to avoid bridging or other blocking phenomenon. This kind of reactor is generally employed for woody biomass of uniform size and shape.

Throatless design allows unrestricted movement of the biomass down the gasifier, easier than in the throated type [31], hence enhancing the biomass flowing through reactor and avoiding stoppage by bridging or other occlusive circumstances. Another advantage, from a constructive point of view, is given by simplification in manufacturing process, a very important issue in small scale plant economy.

Air supply

As in Figure 3-5 there are multiple choices on how to inject air into the reactor, the position and number of nozzles is fundamental because the temperature, equivalent ratio, tar cracking and other parameters strongly depend on it. The open top solution, allowing gasification agent entering the reactor, is considered as being the first stage of air injection.

3.2 The innovative technology

UniFi selected, among all different technology packages of biomass gasification, a specific design developed by a laboratory of the leading Indian University, IISc. The choice has been made because of the specific system design, long experience of the developer, results achieved, sustainability goals of system and specific biomass addressed.

The Combustion, Gasification and Propulsion Laboratory (CGPL)

The CGPL is a laboratory at the IISc, Bangalore, whose activities on biomass gasification started on 1982 and, so far, over 500.000 plant working hours has been reached. Quoting the official website, CGPL "*is involved in innovative research and developmental activity in the field of Bio-resource in addition to frontier work in Aerospace propulsion. Besides fundamental studies, this laboratory has developed techniques of gasifying a wide range of biomass including agro-residues. These techniques have been perfected into small independent power plants, which could serve thermal or electricity needs of industry or rural society.*" [33].

By means of an Italy-India cooperation and technology transfer project a 70kWe biomass gasifier system has been designed, adapted, manufactured, installed, commissioned and tested.

Following a description of the main components of the gasifier system is implemented. Special attention is given to the reactor being the most innovative feature of the system: *simultaneously* open top, throatless and double stage air supply.

The reactor

This kind of reactor (see Figure 3-6) has been designed to overcome some problem of the throated one, especially when processing low density biomass like agro-residues. The throat constitutes a hazard to biomass flow and can cause unwanted phenomena as bridging and channelling [34].

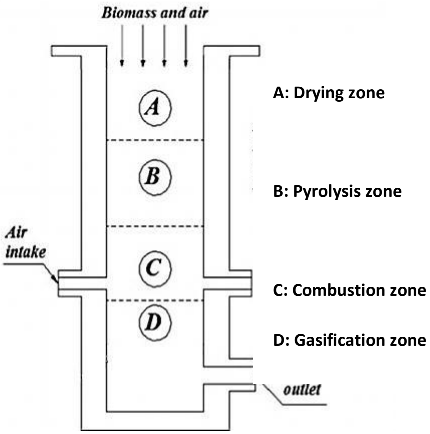


Figure 3-6: Unique design manufactured by IISc

Such a reactor arrangement makes possible to enlarge the high temperature area because of the re-burn feature made possible by second stage of oxidising zone. Improvement in respect of classical Imbert type is visible confronting Figure 3-7 and Figure 3-8 where the high temperature area along the vertical axis and along cross-section is highlighted.

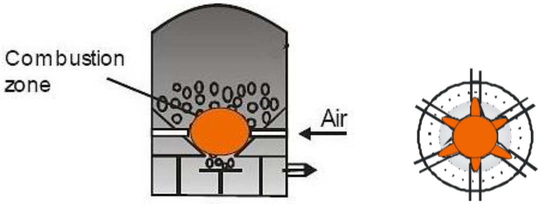


Figure 3-7: Scheme of Imbert gasifier. Section side (left) and top view of reactor (right)

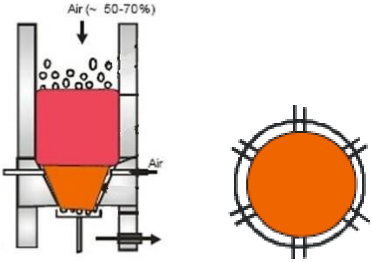


Figure 3-8: Scheme of IISc gasifier. Section side (left) and top view of reactor (right)

The major modification has been applied to the air injection sector of the reactor. The novelty in the design arises from dual air entry, from top and also nozzles, which permits establishing a flame front moving towards the top of the reactor, thus ensuring a large thermal bed inside the reactor, to improve the gas residence time [35]. The area of propagation of flame front it's visible in Figure 3-8. The advantages of such a reactor are first of all a higher residence time of volatiles in the high temperature area; detailed measurements have shown that the fraction of higher molecular weight compounds in the hot gas from an open top design is lower than in closed top design [36] [37] [38].

Furthermore, the insulation of reactor has been improved (Figure 3-9) since usually small scale reactors performance well only at rated values, when reducing flow rate the gas quality deteriorates. This problem at lower power level is generally related to heat generation vs. heat loss rate [39]. The heat loss through the reactor (however well designed) would be unfavourable for small power level systems.

Figure 3-9: Refractory bricks and char extraction screw

Finally, a mention to the char bed features made possible by the design reactor. Uniform distribution of high temperature across the char bed and presence of reactive char have been addressed to improve tar cracking also in the reduction zone. Dasappa et al. asserts that condition favourable, even if not the best required, for activation of charcoal are present in the reactor [32].

Overview of the system

Table 3-1 summarize some of the main features of the technology package installed at UniFi facilities.

Table 3-1: Main features of UniFi gasifier

Capacity	70 kg/h
Power generation	70 kWe gas engine
Gasifier turn down ratio	1 : 0.35
Gas average calorific value	4.604 kJ/Nm^3
Cold gas Tar	<15 mg/Nm^3
Cold gas particulate	<15 mg/Nm^3
Gas temperature	Nearly ambient
Type of equipment	Major operations automated
Max dimensions of biomass	50 X 50 X 50 mm
Allowed moisture content	less than 15% on dry basis (approximate)

PG cleaning system

The gas cleaning system is composed by:

- Cyclone
- Heat exchanger
- Series of water scrubbers
- Fabric filters
- Treatment for contaminated water (dust and organic compounds)

Figure 3-10 shows a scheme of treatment.

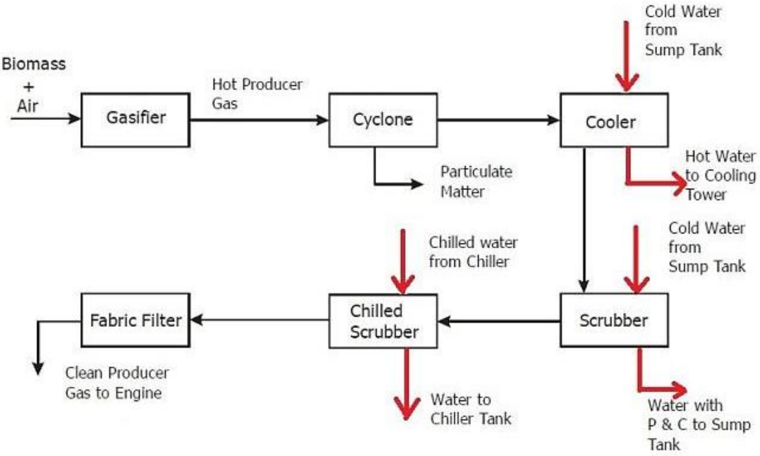


Figure 3-10: Gas conditioning scheme

The hot gas enters the cyclone for dust removal, then a cooler and a scrubber using direct water sprays. A second chilled water scrubber is present; it uses the principle of condensate nucleation to remove dust and fine contaminants along with a gas drying by cooling below ambient temperature. A separate circuit is provided for the dehumidifying scrubber with low temperature water [35]. A fabric filter with pore size of 5 µm is also used to remove any residual contaminant and a blower provides necessary suction for meeting the engine requirements.

As water is being used for scrubbing, a closed loop system of water usage (highlighted in red in Figure 3-10) and treatment for contaminated water is employed. This expedient avoids using large quantities of water.

The engine

The gasifier is equipped with Cummins single fuel gas genset Model G 855 G (Table 3-2). It is a Natural gas, spark ignited engine adapted for 100% PG operation. IISc chose the PG alone mode of operation after having better performance because of better combustion of homogeneous mixture of gaseous species [40]. The maximum working hours are rated as 6,000 per year.

Table 3-2: Main details of Cummins Engine Model G-855G

Cylinder #	6 (in-line)
Bore [mm]	140
Stroke [mm]	152
Displacement [litre]	14
Compression ratio	8.5:1

Carburettors for other conventional gaseous fuels are not suitable due to widely different stoichiometric air–fuel requirements than PG. The stoichiometric air–fuel ratio varies between 10 and 6 (on a volume basis) for fuels such as natural gas and biogas/land-fill gas based, while for producer gas is on average 1.2–1.4 (on a volume basis).

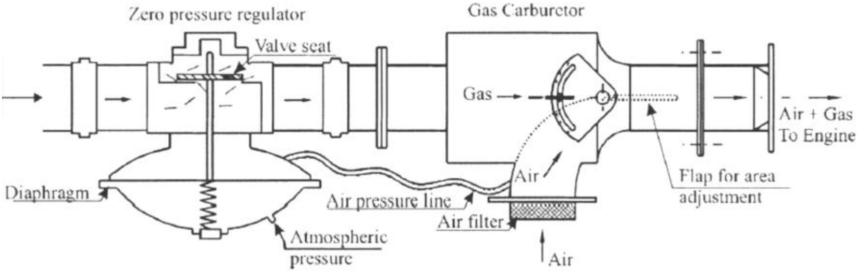


Figure 3-11: Schematic of zero-pressure regulator and gas carburetor.

Solution has been found in coupling the operation with a zero-pressure regulator (Figure 3-11) which ensures a gas pressure (downstream of the pressure regulator) identical to that of air pressure, which is achieved by connecting the air pressure line (downstream of the air filter) to the upper chamber of the regulator. This arrangement ensures that the air–fuel ratio is set irrespective of the total mixture flow rate [41].

The single air fuel has the great advantage of complete independency on diesel fuel, especially advantageous in rural electrification context. On the other hand the limitation of this solution is that, if exhausts are coupled with drying of biomass, sufficient amount of dry biomass has to be properly stored on site for start-up purposes.

4. State of art of modelling

The complex nature of gasification has not been yet completely understood; in the last years innovative models try to explore new aspects of this process with various methodologies and different goals.

An attempt to select and evaluate models suitable for gasification system available at UniFi facilities has been developed, together with the development of a new one particularly fit for the case study. This chapter reports all reviewed models and describe the rational of the approach along with aggregate data analysis and conclusions.

4.1 Selection

A selection of models of biomass gasification has been carried out basing the search on the following criteria:

- Suitability for fixed bed gasifiers
- Goals of model
- Implementation capabilities

40 articles been selected and catalogued from academic journals, out of these 11 of have been further excluded for various reasons. The complete list of articles is in Annex to this chapter.

4.2 Model Classification

Each model selected has been classified following categories as in Table 4-1.

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Table 4-1: List of model categories

GASIFIER TYPE	GOAL	REACTION	MODEL TYPE	MODEL EQUATIONS	CHEMICAL REACTIONS
– Downdraft – Open top downdraft – Spouted bed – Inverted downdraft – Multistage – PCFB – Fluidized – Batch/ other – Various	– Experimental comparison/validation – Performance prediction (one or more parameters) – Parametric analysis – Experimental data gathering (no model)	– Drying, Pyrolysis, Oxidation, Reduction – Pyrolysis, Oxidation, Reduction – Reduction only	– Stoichiometric thermodynamic equilibrium – Non-stoichiometric thermodynamic equilibrium – Kinetic – Fluid dynamics – Only experimental data gathering – Multiple (separated/coupled/modified)	– Energy conservation – Mass conservation – Ideal gas – Continuity equation – Transport equation – Petrovic and Thodos correlation – Eckert correlation – No equation (gibbs free energy minimization) – Other correlations – N.A.	– Water-gas ($C+H_2O=CO+H_2$) – Boudouard ($C+CO_2=2CO$) – Shift ($CO+H_20 \leftrightarrow H_2+CO_2$) – Methane ($C+2H_2=CH_4$) – Methane reforming ($CH_4+H20 \leftrightarrow CO+3H_2$) – Pyrolysys_other – Combustion_other – Langmuir-Hinshelwood correlation – No reactions (gibbs free energy minimization) – N.A.

EQUATION TYPE	SIMULATION TOOL	INPUT	OUTPUT
– Linear ordinary differential (any order) – Non-linear ordinary differential (any order) – Both linear and non-linear – Partial differential – Other correlation	– Fortran – RAND – Modelica Language – Matlab-Simulink – Comsol Multiphisics – SIL simulation language – HSC chemistry – PSR (Gri-mech) – N.A.	– Ultimate analysis – Proximate analysis – HHV/LHV – Moisture content (db/wb) – ER – T reduction – Heat (generation/loss/of pyrolysis) – Carbon conversion – CH_4 conversion – Char bed length – Phisical parameters – Char reactivity factor – GC – Pyrolysis factor – Gasifier geometry (throath angle/diameter, insulation thickness, size, tuyeres distribution..) – Prior model output	– GC out – GC along reaction zone – HHV/LHV – Conversion efficiency (energy/exergy) – Endothermic heat in Reduction zone – Char out – T out – W_{th} – Gas flow (mass/volume) – Char reactivity – Cold gas efficiency – T reduction zone – Boudouard reduction rate – Pressure drop – Flame front velocity – D-P-O-R zone lenght

4.3 Results analysis

Some results of models selection and classification as for categories of Figure 4-1 are presented in form of following pie charts.

Gasifier type

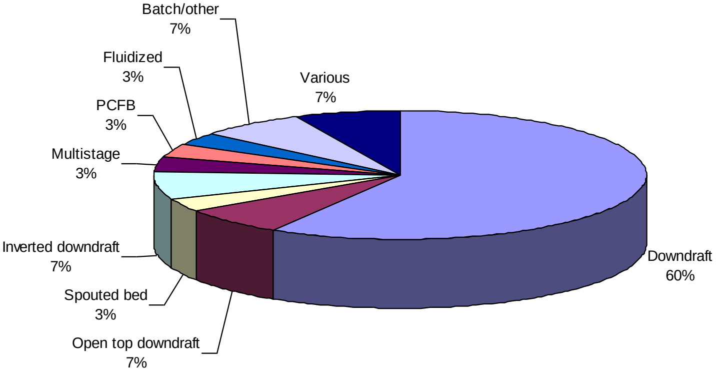

Figure 4-1: Percentage of each type of gasifier

Goal

Figure 4-2 illustrates the share of each single goal on the total of models analysed. Amongst goals the author highlight that "performance prediction" category is often related to system efficiency only, while reliability of gasifiers is an important issue as well. It is not possible a direct simulation of reliability, but indirectly (i.e. cracking behaviour of reactor) could indicate issues of gas quality thus a prediction on the amount of operating hours.

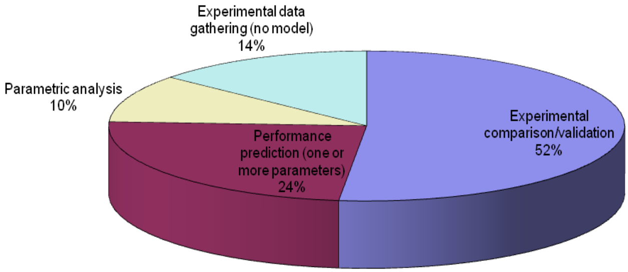

Figure 4-2: Graph of different goals for each model analysed[8]

Thermo-chemical reactions

Models that include more than a reaction of the gasification process (79% of the survey) not necessarily address all reactions. Outputs from other models or experimental data (i.e. pyrolysis plants) are often used as input (Figure 4-3).

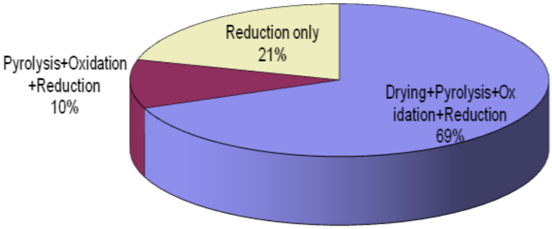

Figure 4-3: Graph of thermochemical reaction share.

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[8] The “parametric analysis” subdivision refers to sensitivity analysis based on input and output parameters of models.

Model type

Three main thermochemical modelling types for gasification can be found in literature: Kinetics (K), Thermodynamic equilibrium (TE) and Artificial Neural Networks (NN). Thermodynamic equilibrium models can be further divided into Stoichiometric (sTE) and Non-Stoichiometric (nsTE, minimization of Gibbs free energy). Other software packages are present like Aspen Plus® **[42]** or Cycle Tempo **[43]**. The survey includes K, sTE and nsTE only because of the selection criteria listed in section 4.1. Table 4-2 reports main features of each single category included in the survey.

Table 4-2: A scheme reporting pros and cons of model types analysed

MODEL TYPE	STRENGTHS	WEAKNESSES
sTE	Can be coupled to experimental parameters or correlations	Inclusion of chemical reactions
nsTE	Description of the chemical reaction non required. Only chemical species as input/output	Independent on reactor design.
K	Can take into account specific characteristics of the gasifier	Computational and implementation effort
Software, Computer programs, libraries	Can take into account system component (i.e. scrubber, separator)	Not always flexible on input/output choice

In Figure 4-4 the share of each model type as defined in Table 4-2. “Multiple” category indicates hybrid models coupling more than one type, while “fluid dynamics” collect CFD studies (gasification reactions not always present).

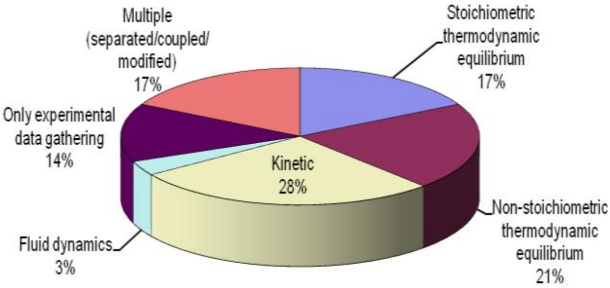

Figure 4-4: Graph with percentage for any model type

Input

Selection of models was implemented trying to exploit specific UniFi gasification plants features. In Figure 4-5 the presence of inputs in models is visually depicted.

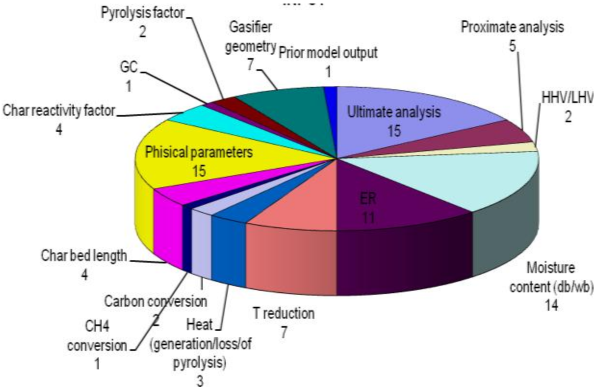

Figure 4-5: Pie Graph of inputs

"Pyrolysis factor" is a coefficient to measure the completeness of volatiles oxidation and reduction during process: it can vary from 0 (no pyrolysis products) to 1 (pyrolysis products only) (cf. models in 3.7 e 3.26). "Physical parameters" includes: P,T air preheating, u, PS, devolatization, $m_{biomass}$, m_{PG}, k, Pressure drop, C_i.

Simulation tool

An overview of simulation tools for modelling is presented in Figure 4-6. In most of the cases the numerical computing environment is not specified by authors.

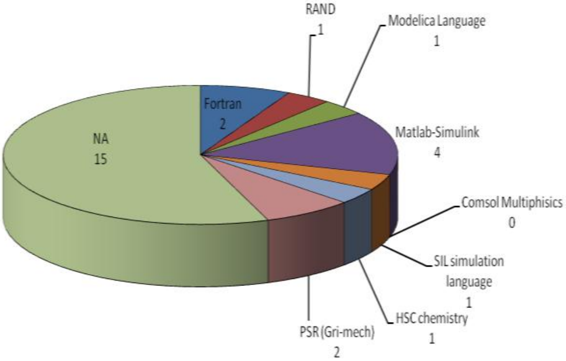

Figure 4-6: Simulation tools share

Output

Capability of predict the GC is confirmed as the major goal of models (see Figure 4-7), closely related to GC is the process efficiency output (second-law efficiency included). On the other hand, modelization of tar formation and removal mechanisms is rare, especially in outputs.

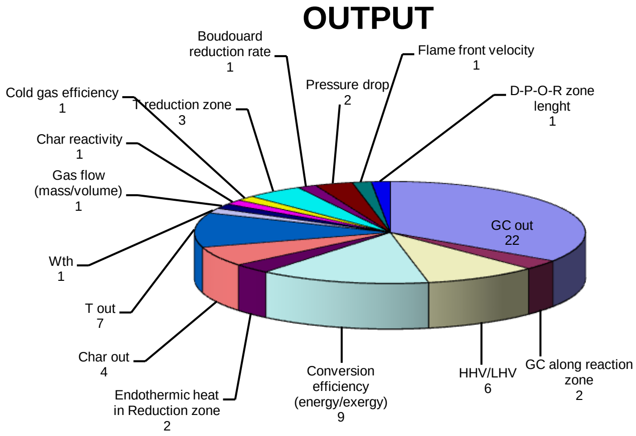

Figure 4-7: Pie Graph of outputs

4.4 Conclusions

The complete references of articles are reported in the Annex A of this chapter. Brief comments on suitability of each single model to the UniFi case study can be found in Appendix C – Gasification models review.

Models 3.17 and 3.18 are the most suitable among sTE type; they can easily be coupled with experimental data by means of corrective coefficients and address issues in line with case study purposes (i.e. high temperature zone).

As for nsTE the 3.22 and 3.13 are the preferred ones because both are validated on open top reactors, in line with the scope of the study, and shows compatibility with other models or software.

Among K models 3.26 is the best option because includes the reactor design parameter, and is potentially compatible with models and experimental data on pyrolysis.

As a conclusion model 3.13 has been used as the basis for the development of a new nsTE model. The numerical computation analysis has been then coupled with experimental records in order to achieve predictive capabilities on system performance. Outcomes of this approach are reported in section 6.4.

Annex A

[3.1] A.K. Sharma, Equilibrium and kinetic modelling of char reduction reactions in a downdraft biomass gasifier: a comparison, Solar Energy 52(2008), pp. 918–928.

[3.2] D.L. Giltrap, R. McKibbin and G.R.G. Barnes, A steady state model of gas–char reactions in a downdraft gasifier, Solar Energy 74 (2003), pp. 85–91

[3.3] B. Gobel, U. Henriksen, T.K. Jensen, B. Qvale and N. Houbak, The development of a computer model for a fixed bed gasifier an its use for optimization an control, Bioresour Technol 98 (2007), pp. 2043–2052

[3.4] L.D. Zhong, W.H. Mei and Z. Hong, Kinetic model establishment and verification of the biomass gasification fluidised bed, Proceedings of the 8th International Conference on Machine Learning and Cybernetics Baoding, July 12–15 (2009).

[3.5] P.C. Roy, A. Datta and N. Chakraborty, Modelling of a downdraft biomass gasifier with finite rate kinetics in the reduction zone, Int J Energy Res33 (2009), pp. 833–851

[3.6] T.H. Jayah, L. Aye, R.J. Fuller and D.F. Stewart, Computer simulation of a downdraft wood gasifier for tea drying, Biomass Bioenergy 25 (2003), pp. 459–469

[3.7] B.V. Babu and P.N. Sheth, Modeling and simulation of reduction zone of downdraft biomass gasifier: effect of char reactivity factor, Energy Convers Manage 47 (15–16) (2006), pp. 2602–2611

[3.12] M. Ruggiero and G. Manfrida, An equilibrium model for biomass gasification processes, Renew Energy 16 (1999), pp. 1106–1109.

[3.11] Z.A. Zainal, R. Ali, C.H. Lean and K.N. Seetharamu, Prediction of performance of a downdraft gasifier using equilibrium modeling for different biomass materials, Energy Convers Manage 42 (2001), pp. 1499–1515

[3.13] C.R. Altafini, P.R. Wander and R.M. Barreto, Prediction of the working parameters of a wood waste gasifier through an equilibrium model,Energy Convers Manage 44 (2003), pp. 2763–2777

[3.14] X. Li, J.R. Grace, A.P. Watkinson, C.J. Lim and A. Ergüdenler, Equilibrium modeling of gasification: a free energy minimization approach and its application to circulating fluidized bed coal gasifier, Fuel 80 (2001), pp. 195–207.

[3.15] A. Melgar, J.F. Pérez, H. Laget and A. Hornillo, Thermochemical equilibrium modelling of gasifying process, Energy Convers Manage 48 (2007), pp. 59–67

[3.16] R. Karamarkovic and V. Karamarkovic, Exergy and energy analysis of biomass gasification at different temperatures, Energy (2009)

[3.17] H.-J. Huang and S. Ramaswamy, Modeling biomass gasification using thermodynamic equilibrium approach, Appl Biochem Biotechnol 154(2009), pp. 193–204

[3.18] S. Jarungthammachote and A. Dutta, Thermodynamic equilibrium model and second law analysis of a downdraft waste gasifier, Energy 32(2007), pp. 1660–1669

[3.19] S. Jarungthammachote and A. Dutta, Equilibrium modeling of gasification: Gibbs free energy minimisation approach and its application to spouted bed and spout-fluid bed gasifiers, Energy Convers Manage 49 (2008), pp. 1345–1356

[3.8] Di Blasi, Dynamic behaviour of stratified downdraft gasifiers, Chem Eng Sci 55 (2000), pp. 2931–2944.

[3.9]Siva Kumar, S.; Pitchandi, K.; Natarajan, E.,Modeling and Simulation of Down Draft Wood Gasifier, Journal of Applied Science, vol. 8, Issue 2, p.271-279

[3.10] D.H. Lee, H. Yang, R. Yan and D.T. Liang, *Prediction of gaseous products from biomass pyrolysis through combined kinetic and thermodynamic simulations,* Fuel *86 (2006), pp. 410–417.*

[3.20] An Experimental Data Based Correction Method of Biomass Gasification Equilibrium Modeling, L. Damiani and A. Trucco, J. Sol. Energy Eng. 132, 031011 (2010), DOI:10.1115/1.4001463

[3.21] P. Baggio, M. Baratieri, L. Fiori, M. Grigiante, D. Avi and P. Tosi, *Experimental and modeling analysis of a batch gasification reactor,* Energy Convers. Manage. *50 (2009), pp. 1426–1435*

[3.22] Sharma, A.Kr. *Equilibrium modeling of global reduction reactions for a downdraft (biomass) gasifier (2008) Energy Conversion and Management, 49 (4), pp. 832-842*

[3.23] T. B. Reeda, R. Waltb, S. Ellisc, A. Dasd, S. Deutche a, *SUPERFICIAL VELOCITY - THE KEY TO DOWNDRAFT GASIFICATION1. The Biomass Energy Foundation,*

[3.24] Sharma, A.Kr. *Modeling fluid and heat transport in the reactive, porous bed of downdraft (biomass) gasifier (2007)* International Journal of Heat and Fluid Flow, *28 (6), pp. 1518-1530.*

[3.25] Effect of biomass particle size and air superficial velocity on the gasification process in a downdraft fixed bed gasifier. An experimental and modelling study (2008) Fuel Processing Technology, *89 (11), pp. 1076-1089*

[3.26] N. Gao and A. Li, *Modeling an simulation of combined pyrolysis and reduction zone for a downdraft biomass gasifier,* Energ Convers Manage *49(2008), pp. 3483–3490*

[3.27] *Gilbert, P., Ryu, C., Sharifi, V., Swithenbank, J. , Tar reduction in pyrolysis vapours from biomass over a hot char bed ,(2009)* Bioresource Technology, *100 (23), pp. 6045-6051*

[3.28] *Avdhesh Kr. Sharma, Experimental investigations on a 20 kWe, solid biomass gasification system, Biomass and Bioenergy, Volume 34, Issue 12, Pages 1629-1982 (December 2010)*

[3.29] *Barrio M, Fossum M, Hustad JE. A small-scale stratified downdraft gasifier coupled to a gas engine for combined heat and power production. In: Bridgwater AV, editor. Progress in thermochemical biomass conversion. vol. 1. 2001. p. 426–40*

5. Analysis of Tar removal technologies

This Chapter gives an introduction on the focus of the experimental activity described later in Chapter 6. The first section introduces tars, while the second the removal measures of our interest. Third section is dedicated to char influence on tar, since can be of help in understanding some behaviour of UniFi/IISc reactor. Last two sections explain process parameter and their use during experimental campaign.

5.1 Tar definition and formation mechanism

The tar, a complex mixture of condensable hydrocarbons, resulting from the gasification of biomass is an unwanted by-product of the process. The concentration of tar must be controlled and maintained at levels as low as possible, since the possible condensation of organic compounds that constitute it could adversely affect the performance of the system.

So far many definitions have been provided and in 2000 the IEA Bioenergy Task Gasification established to define tar every “hydrocarbons with molecular weight higher than benzene”. There are several methods for the classification of the tar; Milne et al. [44] have devised a division into four classes of products as a result of gas-phase thermal cracking reactions:

- PRIMARY PRODUCTS: characterized by cellulose-derived products such as levoglucosan, hydroxyacetaldehyde, and furfurals; analogous hemicellulose-derived products; and lignin-derived methoxyphenols;
- SECONDARY PRODUCTS: characterized by phenolics and olefins;
- ALKYL TERTIARY PRODUCTS: include methyl derivatives of aromatics, such as methyl acenaphthylene, methylnaphthalene, toluene, and indene;
- CONDENSED TERTIARY PRODUCTS: show the PAH series without substituents: benzene, naphthalene, acenaphthylene, anthracene/phenanthrene, pyrene;

Another widely recognized classification makes a distinction according to the chemical properties, solubility and condensability of compounds and classifies the tar into five distinct classes as for Table 5-1.

Table 5-1: Classification system of Tar from biomass gasification by ECN **[45]**

	Description	**Components**
Class 1	GC undetectable tars. This class includes the heaviest tars that condense at high temperature even at very low concentrations.	gravimetric tars
Class 2	Heterocyclic components (like phenol, pyridine, cresol). These are components that generally exhibit high water solubility, due to their polarity.	pyridine, phenol, cresol, quinoline
Class 3	Aromatic components. Light hydrocarbons that are not important in condensation and water solubility issues.	xylene, styrene, toluene
Class 4	Light polyaromatic hydrocarbons (2-3 rings PAH's). These components condense at relatively high concentrations and intermediate temperatures.	naphthalene; methyl-naphthalene; biphenyl; ethenylnaphtalene; acenaphthylene; acenaphtene; fluorene; phenanthrene; anthracene
Class 5	Heavy polyaromatic hydrocarbons (4-5 rings PAH's). These components condense at relatively high temperature at low concentrations.	fluoranthene; pyrene; benzo-anthracene; chrysene; benzo-fluoranthene; benzo-pyrene; perylene; Indeno-pyrene; Dibenzo-anthracene; Benzo-perylene

The share of most present compounds in biomass tars, according to the classification of Table 5-1, is plotted in Table 5-2.

Table 5-2: Typical composition of tar from biomass **[31]**.

Component	Unit	Value
Benzene	% wt.	37,9
Toluene	% wt.	14,3
Class 3 - other	% wt.	13,9
Naphthalene	% wt.	9,6
Class 4 - other	% wt.	11,4
Class 5 - other	% wt.	0,8
Class 2	% wt.	11,1
other	% wt.	1,0

Li et al. [46] asserts that hydrogen and oxygen contents in tar do not seem to vary with temperature. Carbon, hydrogen and oxygen contents in a sample of biomass gasification tar are showed in Table 5-3.

Table 5-3: Composition of Biomass gasification derived tar **[46]**

Element	Unit	Value
Carbon	% wt.	54,5
Hydrogen	% wt.	6,5
Oxygen	% wt.	39

According to Meng et al. the different behaviour of class 2 to 5 tars can be attributed to different properties such as the distribution of cellulose, hemicellulose and lignin and ash contents. Class 4 and 5 tars are mostly PAH compounds which come from aromatic functional group in the molecular structure of lignin. Furthermore, the author explains that not only behaviour of different tar categories but also the final tar composition depends on the lignocelluloses composition of biomass fuels [47].

Hanaoka et al. showed how the gasification conversions in cellulose, xylan, and lignin were 97.9%, 92.2%, and 52.8% on a carbon basis, respectively [48]. Interesting the proof that tar is accumulated also in the cyclone dust, since laboratory analysis demonstrate solid particles appears to be primarily tar products formed as a result of gas phase condensation reactions, rather than direct carbonization of the biomass feedstock. [49]

Main problems due to tar presence in the PG are related to fouling, corrosion, erosion and abrasion of system components (see Figure 5-1).

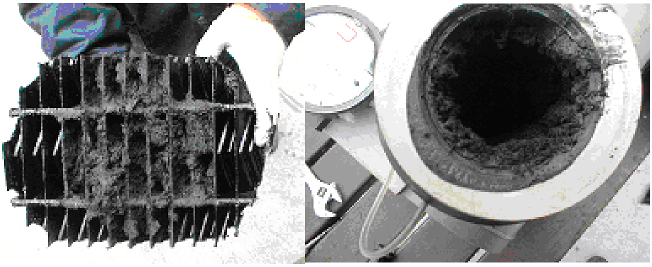

Figure 5-1: Fouling phenomenon on low temperature components.

5.2 Primary cleaning methods

Primary methods for tar removal are methods acting inside the reactor during the gasification process. They can be implemented as:

- Specific design of reactor
- Use of suitable catalyst during gasification
- Optimization of operational parameters

The importance of primary methods lies in the simplicity of the process, no auxiliaries or other energy intensive materials are added to the system. Being biomass a low energy density fuel, the system complexity must be avoided as far as possible [50].

All three methods acts on a series of thermochemical and physical condition influencing tar removal via decomposition in hydrocarbon with smaller carbon number. Li et al. (2009) define four different reaction mechanisms for tar decomposition:

- Cracking: $pC_nHx \rightarrow qC_mH_y + rH_2$. (5.1)
- Steam reforming: $C_nH_x + nH_2O \rightarrow (n + x/2)H_2 + nCO$. (5.2)
- Dry reforming: $C_nH_x + nCO_2 \rightarrow (x/2)H_2 + 2nCO$. (5.3)
- Carbon formation: $C_nH_x \rightarrow nC+(x/2)H_2$. (5.4)

Where C_nH_x represents tar, and C_mH_y represents hydrocarbon with smaller carbon number than C_nH_x. Thermal cracking occurs at >1100°C and produces soot as drawback [51]. Additional benefit of tar cracking is an improving of LHV of gas [40].

On behaviours of tar, due to reactivity during pyrolysis and gasification in different environments, can be remarked that:

- In an inert environment (thermal cracking) the tar radicals may decompose, but they may also react with other tars to form larger tar molecules and ultimately soot. Thus radical formation does not directly result in tar decomposition but initially in even worse (larger) tar molecules.

- In H_2O or CO_2 there is a chance of the radical reacting with one of these two molecules, contributing to tar decomposition and increasing the rate at which it takes place.
- In H_2 the radical can react with H_2 fairly readily, causing a tar molecule to be reformed. In this way, then, H_2 depresses the tar decomposition rate.
- In an $H_2/H_2O/CO_2$ atmosphere the reaction rate of the tar radicals with H_2 is higher than the reaction rate with H_2O or CO_2. Tar decomposition as a result of the tar radicals reacting with H_2O and/or CO_2 is therefore suppressed by the presence of H_2.
- In hydrogasification, aromatic rings may be hydrogenated, causing higher concentrations of CH_4 [52]

5.3 Catalytic activity of char

Enhanced char bed length of IISc reactor improve the residence time of tar in a cracking environment. This section present the theoretical benefit for tar cracking purposes.

Catalytic cracking

The rate of chemical reactions (5.1 to 5.4) can be increased by increasing the temperature or by catalytic action. Biomass-derived tar is very refractory and hard to crack by thermal treatment alone [47]. Two different catalytic actions are possible: primary catalysts are added in the biomass prior gasification and a design modification is not required, while secondary catalyst are added in a specific ad hoc downstream reactor.

Evaluation criteria for a general catalyst are [51]:

- The catalysts must be effective in the removal of tars.
- If the desired product is syngas, the catalysts must be capable of reforming methane.
- The catalysts should provide a suitable syngas ratio for the intended process.
- The catalysts should be resistant to deactivation as a result of carbon fouling and sintering.
- The catalysts should be easily regenerated.
- The catalysts should be strong.
- The catalysts should be inexpensive.

Char as a catalyst

Charcoal is considered catalyst material by many authors [53], [54], [55]. Tar reduction in secondary reactor have shown good performance and results are available since 2000 [56], while solutions of char optimization inside the same reactor, where gasification process occurs, has not been completely explored yet.

The naturally formed char in a downdraft reactor can act as a catalyst but experimentally is very difficult to distinguish its influence on thermal cracking or reforming because of the inevitable presence of steam and carbon dioxide during gasification [57].

Char alone seems to be very effective even at different temperature and different organic compounds. In Figure 5-2 silica and sand are inert and give a comparison of the thermal cracking action with catalytic ones of all the others.

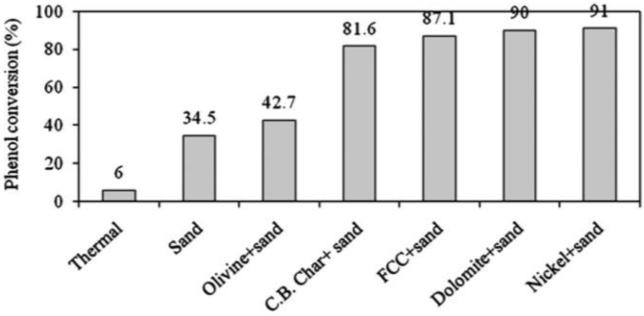

Figure 5-2: Effect of different catalysts on Phenol conversion, T=700°C and Residence Time=0.3s **[53]**.

Mun et. al reported as well the “much lower” tar removal efficiency of olivine compared to char. Because of the presence of inorganics (ash) char is never alone in a gasifier and the catalytic effect may be attributed to them [58]. This last issue is relevant since further experimentation will be presented using agricultural residues as feedstock (high ash content biomass).

Mun et al (2010) indicate a third action of tar removal by char that is simple tar adsorption. Moreover char may be free from poisoning by sulphur, chlorine and volatile alkali and alkaline earth metallic (AAEM) species [57].

Life of char

All catalysts show less surface area for tar adsorption with time, because of the adhesion of the carbonaceous components onto the virgin one during process.

Spent activated carbon shows less activity as well [58], even if above 750°C is possible to avoid a decrease in activity due to carbon decomposition on the char surface [56].

The problem can be overcome by the continuous external supply of the biomass char from the gasifier to the cracker [59]. It was calculated that 96g of char for the complete tar removal of producer gas made by 1 kg of biomass are needed [53], that means a 9.6% of char production from initial biomass inside a gasifier, an amount reachable influencing the gasification parameters of the reactor.

Temperature of operation

Discrepancies on temperature influence on char catalytic activity are present. In most of the cases different outcomes can be related to the general definition of tar, which may lead to different composition of samples. Gilbert et al. compares (Figure 5-3) the product yields of the condensables in the homogeneous (without char) and heterogeneous (with char) bed with increasing the bed length at a fixed temperature of 800°C. For multi ring compound (heavy tars) char activity seem less effective, even for long residence time (that is a function of char bed length) results are not encouraging.

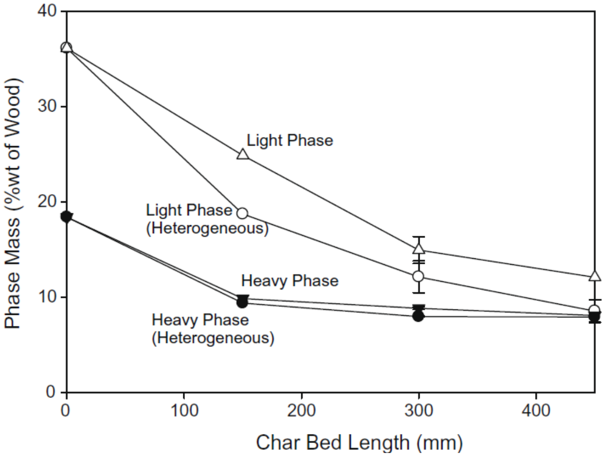

Figure 5-3: Heavy and light tar conversion for different bed lengths **[55]**

The author asserts that a rapid reduction of multi-ring compounds by a longer residence time takes place only at temperatures above 1000 °C. In other works heavy tar removal at temperatures well below 1000°C is reported [60]

Nevertheless, heavy tar removal seems to be the primary limit for char catalytic behaviour. It is a physical limit, since char gasification reactions (increasing with higher temperature) lead to surface decrease of the char (deactivation) [61].

Residence time

The tar removal rate of char, as well as other catalysts, demonstrates to reach a maximum and then a plateau is present (Figure 5-4).

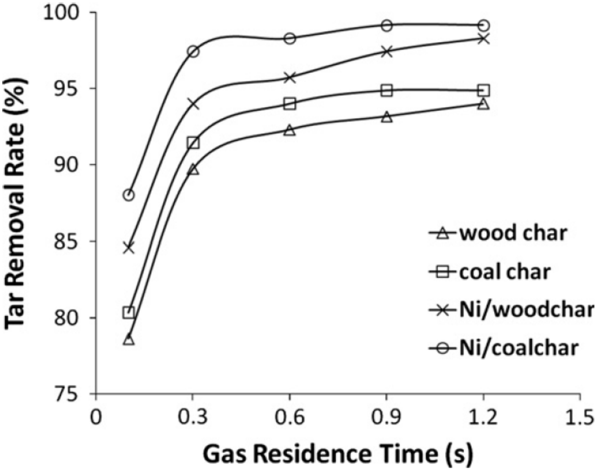

Figure 5-4: Effect of Residence Time on tar removal. T=800°C **[60]**

Activation

One gram of activated carbon has a surface area in excess of 500 m^2, the most widely used technique for estimating surface area is the so-called BET method. Large average pore diameter has to be considered in defining activation as well, since BET method includes micro pores which might not be accessible for the tar component [53]

Among activated carbon the Powered Activated Carbon (PAC) is powder or fine granules less than 1.0 mm in size with an average diameter between .15 and .25 mm and made up of crushed or ground carbon particles. It cannot be excluded that gasifier with stirrer inside the reactor for biomass mixing can improve catalytic activity of char while grinding. Moreover, steam and CO2 content in the producer gas may lead to the continuous natural activation of the biomass char [53].

5.4 Reactor key parameters and relative influence on tar formation

This section presents an insight to five main parameters of the gasification process and their action on thermochemical reactions. Only arguments strictly related to primary cleaning methods are analysed, as a mean to introduce and justify actions taken during experimental campaign.

Parameters are Particle Size (PS), Equivalent Ratio (ER), Superficial gas Velocity (SV), Temperature (T) and Moisture Content. For many aspects these factors are intertwined and discrepancies in literature will be noted.

Particle size

Smaller particles have larger surface areas per unit mass and larger pore sizes which facilitates faster rates of heat transfer [62], this can lead to both higher gas yields and condensable production, because of the faster pyrolysis rate achieved [28]. Experimental results are not univocal: Lv et al. observed that smaller particles resulted in more CH_4, CO, C_2H_4 and less CO_2 which led to higher gas yields, gas energy content and carbon conversion efficiency [63]. Rapagnà reported increases in gas yield and gas compositions of CO, CH_4 and CO_2, when the PS was reduced from largest (1.090 mm) to smallest (0.287 mm). By decreasing the PS from 1.2 mm to 0.075 mm, it was observed that H2 and CO contents as well as gas yield and carbon conversion efficiencies increased whereas the CO2 decreased [64].

Equivalent ratio

The ER is the ratio of the actual air volume supplied per kg of biomass fuel and the volume of air which is necessary for stoichiometric combustion per kg of biomass. ER in biomass gasification is usually between 0.2 and 0.4.

The most important effect is on T: at higher values of ER greater heat is released due to increase of exothermic combustion reactions (Figure 5-5). In the meantime the O_2 increase factor benefits the thermal cracking of the heavier part of tar compounds [65]. This factor is one of the main features of the IISc gasifier where the re-burn stage made possible by the double fire solution acts principally on the mechanism above explained.

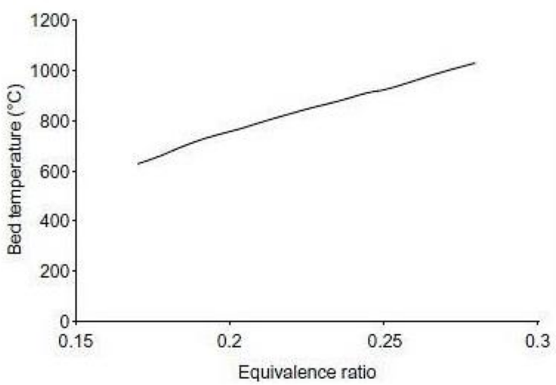

Figure 5-5: Influence on T of ER in a CFB reactor **[66]**

ER increase has of course negative drawbacks on process. The principal is, as showed in Figure 5-6 in a Bubbling Fluidized bed (PFP), heating value decrease because of balance of the reactions moving towards complete combustion. Consequently, the desired temperature inside the reactor must be well evaluated with respect to the value of ER chosen, and a specific trade-off between T and ER for each context should be evaluated.

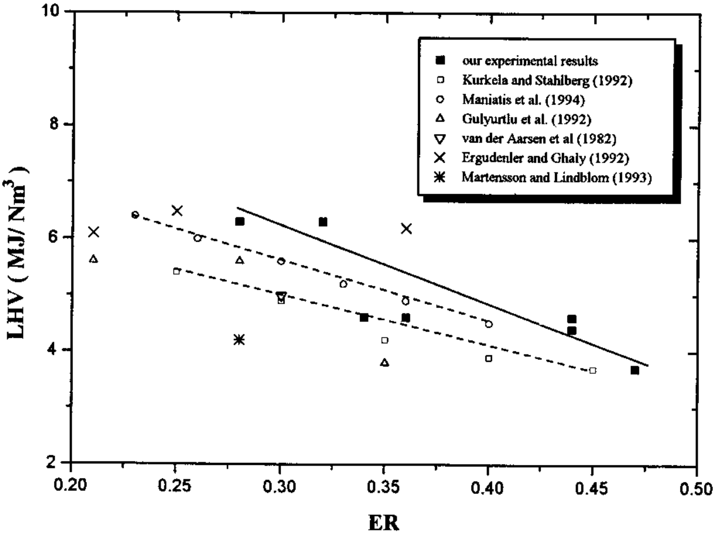

Figure 5-6: LHV of PG with ER in a BFB **[67]**

Superficial gas Velocity

SV is defined as the ratio of the PG production rate at normal conditions and the narrowest cross sectional area of the gasifier reactor:

$$SV\left[\frac{m}{s}\right]=\frac{Q\left[\frac{m^3}{s}\right]}{A\,[m^2]}$$

SV is independent of reactor dimensions, allowing a direct comparison of gasifiers with different power output. Some studies focus on Residence Time which is strictly related to SV but more specific since dependent on reactor geometry.

Table 5-4 reports main SV values for main commercial gasifiers (some of them are coal gasifiers).

Table 5-4: SV of different type of gasifier reactors **[68]**

Gasifier type	***Superficial gas velocity*** **[m/s]**
Imbert	2.5
Biomass Corp.	.95
SERI Air	.28
Syn-Gas air	1.71
Buck Rogers	.23

Since the SV controls the gas stream through the reactor it exerts a great influence on heat flow and subsequent conditioning of tar production and degree of char gasification a well. Yamazaki et al. [69] analysed the SV influence on gas composition of a laboratory scale biomass downdraft gasifier: a remarkable change in gas composition between 0.3 and 0.4 was recorded and out of that range only minor changes occurred (Figure 5-7). SV less than 0.4 has been found not sufficient for running an Internal Combustion Engine due to lower heating value of PG.

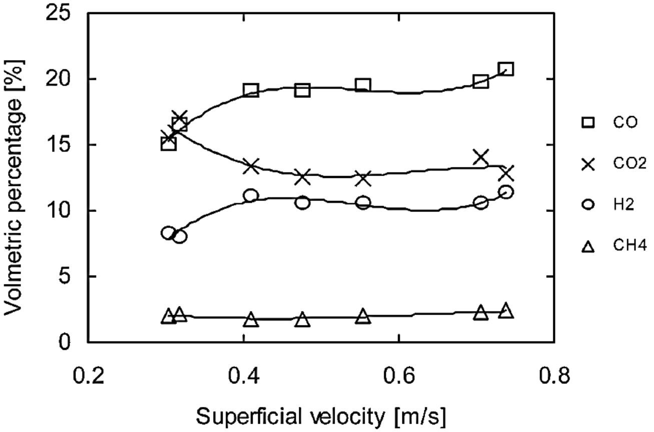

Figure 5-7: Effect of SV on gas composition **[69]**

The relationship between tar yield and SV is a central issue. In Figure 5-8 is plotted the total amount of tar (both GC detachable and not detachable) versus SV. It is visible a twofold effect on tar yield, increasing SV increase T in the reactor leading to an increase on thermal cracking of tar, on the other hand a higher SV decrease the residence time of tar particles in the high temperature area. Trade-off leads to the minimum of tar concentration clearly visible.

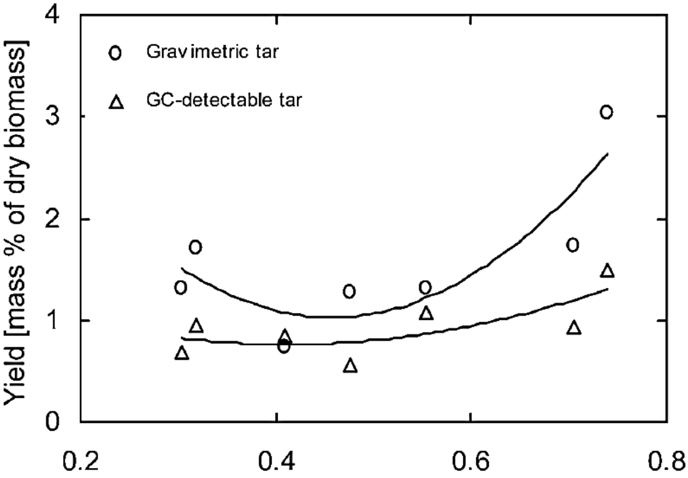

Figure 5-8: Effect of SV on tar yields **[69]**

Temperature

Kinoshita et al. and Yu et al. showed that the proportions of 1-ring and 2-ring aromatics in tar decreased with increasing temperature, whereas those of 3-ring and 4-ring aromatics increased. Furthermore, yields of 1-ring and 2-ring aromatics decreased with increasing residence time, while those of 3-ring and 4-ring aromatics increased [70] [71]. McGrath et al. also re- ported that higher thermal cracking temperature and longer residence time favoured the formation of 3-ring and 4-ring aromatics [72]. The author describes the behaviour of tar components only with temperature, asserting that SV is interlinked with temperature. In Figure 5-9 is clearly visible that SV increasing leads to higher ration of heavy aromatics compounds in the tar [69].

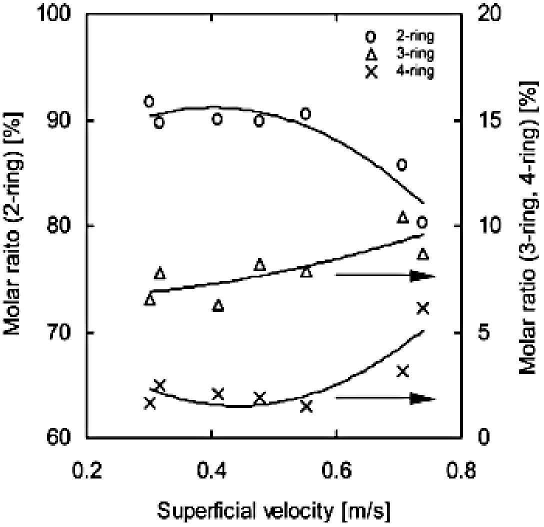

Figure 5-9: SV influence on molar ratio of 2-rins, 3-rings. 4-rings aromatics in condensed tertiary tars

Han et al. [47] reported that an increase in the temperature had a positive effect on the decomposition of class 1 and 2 tars, while the concentrations of class 3 and 5 tars increased with temperature enhancement. On the other hand, favourable effects of high temperatures as above can be counterbalanced by unwanted ash sintering in the reactor [73].

Moisture content

Vaporization of the water molecules contained in the raw material requires heat present in the reactor; this primarily lowers the temperature at which the gasifier operates with same consequences as per the relative section of above.

By means of mathematical models, it was observed that higher moisture content makes predominant the reaction Water-Gas (Equation 1.2) is with respect to the Boudouard reaction (Equation 1.1), with the result of an increased production of CO_2 and H_2 and a decrease of CO [74]. Moreover, as the temperature decreases the equilibrium of the reaction Water-Gas Shift (Equation 1.4) is affected by further increasing the value of CO_2 into the final composition of PG with overall effect of decrease in calorific value of PG since the weak increase of H_2 is not sufficient to compensate for the loss of a significant amount of CO. However, the decrease of the calorific value is less pronounced in case of lower ER operation, downdraft literature cases report that when humidity increases from 0 to 40%, the calorific value of the producer gas decreases of 8.72% to ER = 0.45 and 4.7% to ER = 0.29 [74].

5.5 Methodology

To better exploit the reactor performance on tar cracking activity an extensive investigation on parameters range of variation and their effects on producer gas quality has been implemented. Figure 5-10 illustrates main peculiar measurable factors and the interaction among them, the order of interactions evolves sequentially from top to the bottom of the scheme.

At the top are present elements on which one can act easily during system operation. Mass flow of water scrubber is influencing the pressure downstream the reactor so much that during flare mode the PG gas blower is switched off.

In the middle elements on which is not possible to act directly are reported, they are mutually interrelated and influenced, also with parameters from above. The char bed length, being much extended in the case study reactor, can influence the superficial gas velocity by itself because the friction loss of char can be different from the biomass before being dried and pyrolized.

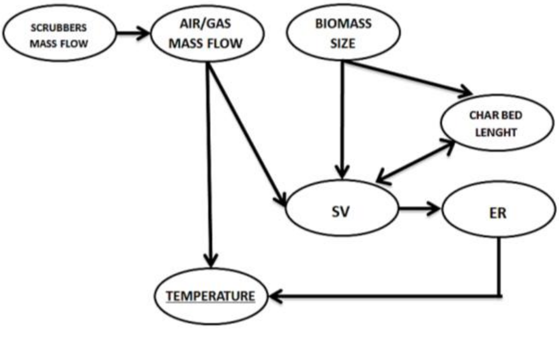

Figure 5-10: Schematic of methodology employed for gas quality improving

Finally, last element, *at the bottom* of Figure 5-10 is the most important parameter as regards primary measure for this peculiar reactor: the temperature in the reactor being intended as distribution across the hot area and maximum value.

A series of experimental test run have been implemented following the methodology as above, trying to explore the interdependence of factors and their consequences on the whole gasification plant.

Primary measures analysis has been the focus of the work also because are the best system options moving towards compactness of gasification plants, being flexible fuel gasifier still lacking on this feature.

The partial load measure are pursued with the purpose of investigating the effect of secondary air supply on the primary measures for tar removal, first of all the temperature of the oxidation zone, an approach already used for only for PG composition studies [75].

As a conclusion, small scale reactors are usually simple systems and control of each single parameter is not possible. The operational parameter to be controlled the most is the airflow injection into the reactor, which as a result influences one or more of key rector parameters. For this reason many authors suggest SV as the most important measure of gasifier performance, as it controls gas production rate, fuel consumption rate, gas energy content, char and tar production rate, and other parameter besides [69] [76] [77] [78] [79]. For all these reasons, and also because IISc/UniFi throatless design (wider cross sectional area) presents SV values different to conventional reactors, particular attention has been addressed to SV during experimental records.

6. 70 kWe case study

This chapter focuses on the biomass gasification plant introduced in section 3.2 and describes all the activities undertaken in design, manufacture, install, commissioning and test campaign. All this outcomes are the finalization of a long way back activity started on 2009 with project AGROGAS, a cooperation and technology transfer collaboration among Italy and India. Among objectives of the project AGROGAS is to:

- Develop and test the technology package by IISc
- Install in Italy a system prototype fed with locally available biomass
- Evaluate the feasibility and modifications needed for proper operation

The project was divided into five tasks:

- Design
- Technology package Transfer to Italy
- Installation and commissioning
- Operation, testing and monitoring
- Assessment of costs and adaptation to standardized EU Certification system and HSE (Health, Safety and Environment)

The project partners were CREAR-UniFi, The IISc, and ENEA (Italian National agency for new technologies, Energy and sustainable economic development).

6.1 Power plant design and manufacturing

The IISc started in 2010 the assessing of a new version of its 100 kg/h co-current fixed bed open top biomass gasifier, specifically for the AGROGAS project. Together with UNIFI a re-design of the technology package has been implemented, downsizing the plant to 70 kWe to specifically address Italian site requirements.

Since the experimental research attention was specifically addressed to thermal cracking action on tar in PG the type of reactor was left unmodified. In fact, open top demonstrate moderate level of cleanliness of the gas produced in particular in respect of the heavy hydrocarbons together with a flexible use of biomass. High thermal performance due to an inner lining of refractory tiles with a high content of aluminium oxide was reached. The lower part of reactor has been provided of automated extraction ash system, very important to guarantee a proper process of char and ash derived by agricultural residue.

Refrigerating tower and the open air tank has been positioned in a more suitable zone, distant to the site where operators are present. A series of additional tank and pumps guaranteed proper operation after these modifications to the system (Figure 6-1).

Figure 6-1: Water treatment section (on the right, in blue) originally thought close to gas gleaning section (on the left)

The plant has been provided of numerous measuring instruments, part of them for system control purposes. Operational safety during operations has been implemented to remarkable levels, and analysis and research activities can rely on a significant amount of data gathered during process.

Figure 6-2 reports the top view of the main stream. On the left different layers of bricks as insulation of reactor are highlighted with different colours. After dust and particulate removal by cyclone the gas is cooed by a water cooler, the same water circuit (cooled by a wet cooling tower) is feeding the first water scrubber. After first scrubber and relative wet cyclone the PG is further cleaned and cooled by a second scrubber fed by a separate chilled water circuit. After that a blower is present and Pre-coated filters are the final step of gas cleaning before engine.

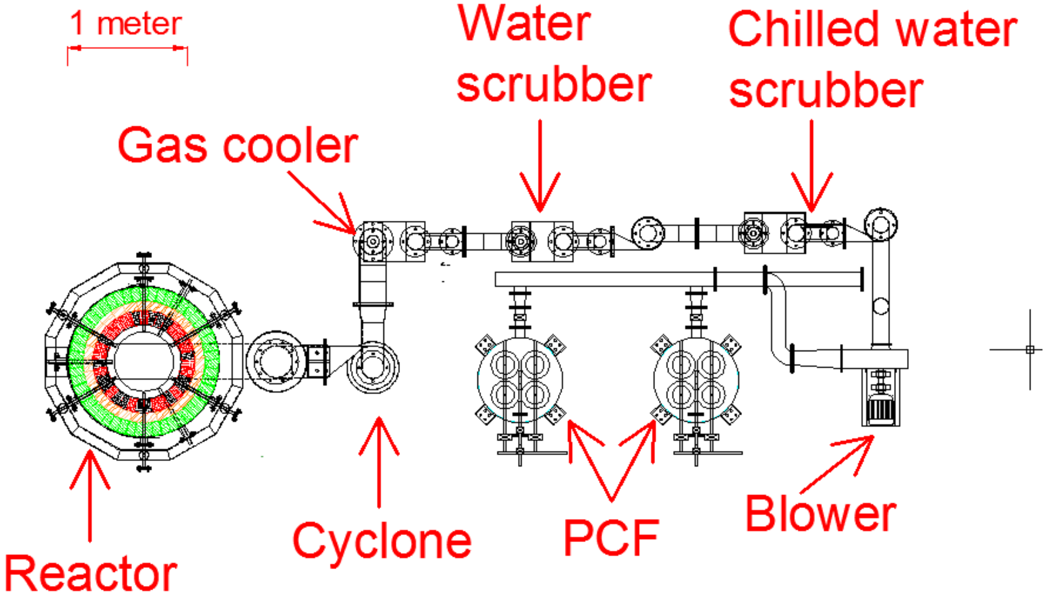

Figure 6-2: PG streamline from Reactor to Pre-coated Filters (PCF)

6.2 Commissioning

A thorough work finalized to conformity of the whole system to the essential Italian requirements has been pursued, and CE marking on power plant was affixed (see “Appendix D –” for the list of directives).

An area within the glassware ColleVilca in Colle di Val D'Elsa (SI) was selected and adapted for system installation, an agreement between ColleVilca and UniFi allowed the small factory to use the excess electricity of plant.

A pre-existing shed of 140 m^2 was employed; the cover is 9.8 m height at maximum level while the infill was absent. The maximum height of the system is 7.2 m at top of reactor.

After the first installation and testing at OVN Bio Energy in New Delhi, the plant, 18.2 tons in total, was dismantled, shipped and then reassembled at the Italian site (Figure 6-3). Following a brief visual report through 7 sequential photos is presented.

Figure 6-3: The plant has been shipped in 3 containers for a total of 36 pallets

The most difficult to position part of system has been the reactor (Figure 6-4); it is the heaviest, almost 5 tons, and more fragile component.

Figure 6-4: Crane elevating reactor for positioning (left). In final configuration the bottom is almost 2 meters above ground level (right)

The very first charge of reactor must be charcoal. After that, commissioning was conducted by wood chips properly dried by sunlight (Figure 6-5) since the drier has been the last part of the plant being installed and operated.

Figure 6-5: Pine wood chips used for commissioning of the plant in Italy

Figure 6-6: Research team and technician at control panel for last check before system start-up.

Gasifier system has to run in flare mode for almost 40 minutes before cranking the engine (Figure 6-6), in order to reach the highest gas quality. Two effective methods (Figure 6-7) for PG quality checking are the colour of the flare and of anisole solution after PG impingement.

Figure 6-7: PG flaring (left), and anisole solution after 30 minutes of tar dissolving.

The video of first run of the engine is available on my blog named “Unforeseen Energy” in the post of January 2, 2013 [80].

6.3 Measuring instruments

Following a brief description of main measure equipment used during tests is presented.

Main data has been monitored and stored along with control management through a SCADA system. On line monitoring and historical data export is made possible by specific software. Measures implemented through SCADA have been: Pressure drop, Temperature, Volume flow, Water line flow. System view and relative acquisition points are visible in Figure 6-10 to Figure 6-12 of next section. A separate control board of engine has been used for monitor and manually record data.

PG composition has been extensively analysed through a portable micro-gas chromatograph, been capable of on line measurements during tests. Both column are porous layer open tubular (PLOT), that is capillary columns where the inner surface is coated with a layer of solid porous material. This layer is usually about 5-50 µm thick as opposed to liquid coated columns where the stationary phase is commonly 0.25- 2.0 µm thick. One column has Divinylbenzene type U, high polarity phase and uses Helium as carrier, while the second Molecular Sieve 5A phase and Argon as a carrier. Following the list of all components detected by two columns employed:

- Air, CO_2, N_2O, H_2S
- Permanent Gases: H_2, Ne, Ar, O_2, N_2, CH_4, CO
- Noble gases: Ne, He, Ar, Kr, Xe
- Specialty gases
- Hydrocarbons C2 isomers
- Hydrocarbons C1-C4
- Biogas
- Fuel Gas
- Natural Gas
- Refinery Gas
- Syngas
- Halogenated Hydrocarbons
- Freons
- Oxygenated Hydrocarbons, alcohols, esters, aldehydes, ketones

For tar concentration measurement a sampling unit for condensing purposes has been developed following UNI CEN/TS 15439:2008 specifications (named also “tar protocol”) as in the scheme of Figure 6-8.

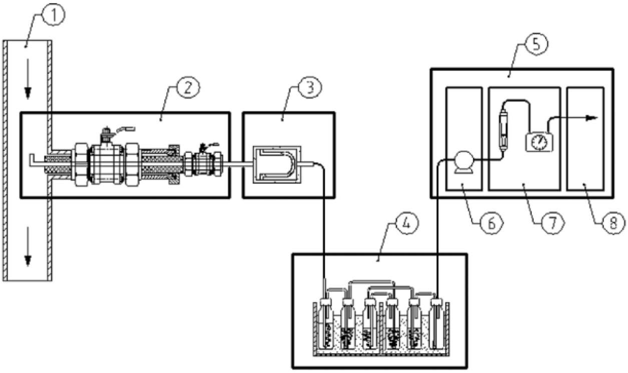

Figure 6-8: Scheme as UNI CEN/TS 15439:2008 technical specification

For any other study RE-CORD analytical and chemistry laboratory has been enrolled being capable of a wide range of analysis, such as:

- atomic absorption
- UV-Vis spectrophotometer
- GC-MS
- GC-FID
- HPLC
- vacuum filtration system
- ionic chromatography
- CHN-S
- TGA
- viscometer
- hydrometer
- calorimeter
- moisture analyser
- ash melting furnace
- pH-meter
- rotavapor
- centrifuge
- knife mill

Finally, a mention to other inspections of tar concentration been visually implemented when not possible to follow all procedures of the technical specification “UNI CEN/TS 15439:2008”. Visual check is an important first evaluation step; it is simple, quick and allows instantaneous system regulation and correction. Tar protocol can be used in a second, very accurate, quantitative step of measurement. In Figure 6-9 a chronological sequence of a gas quality estimate.

Figure 6-9: Thimble filter before the test (left), during gas filtering (centre) and after conclusion (right). White colour on the right attests a very low tar concentration.

6.4 Experimental study

Following a description of tests implemented with different biomass types and different parameters following up the methodology described in section 5.5. Most of the tests have been operated in manual mode in order to adjust parameters in unrestrained mode, although the system can be run in auto-mode as well.

Acquisition points

In Figure 6-10 the rector area scheme and acquisition points is depicted. The quantity of biomass (BIOMASS IN) has been measured at reactor feeding, after drying. For each test the first and last charge was addressed to fill the reactor up to the top, in order to correctly measure the biomass converted during the whole run. The Char being discharged by screw (CHAR OUT) and the P&T matter at cyclone bottom (CYCLONE DUST) close the balance of solid input/output. Main parameters of PG line have been monitored at Reactor (A) and Cyclone (B) outlet.

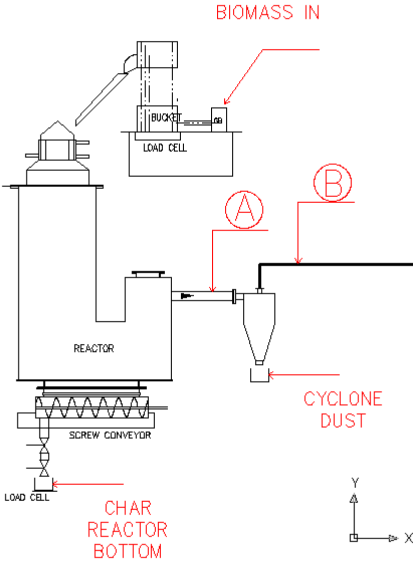

Figure 6-10: Reactor and acquisition points (in red)

Acquisition points for the gas cleaning line (Figure 6-11) have been located at outlet of:

- gas cooler (C)
- wet cyclone of water scrubber (D)
- chilled water scrubber (E)
- blower (F)
- filters (G, H) the last for PG sampling

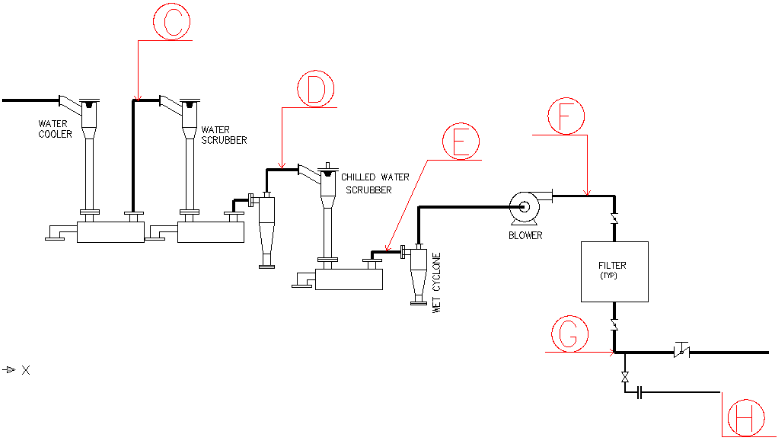

Figure 6-11: Acquisition points in the gas cleaning part of system

Finally, the gross load and exhausts have been monitored as in Figure 6-12

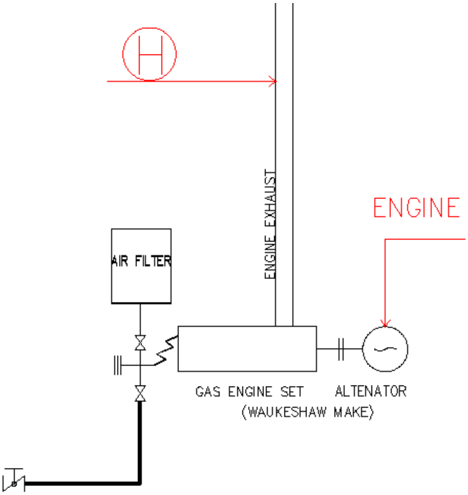

Figure 6-12: Detail of Engine and exhaust line in PFD

Numerous test campaign have been implemented, each of them with specific goals and parameters setting. Biomass features have been considered as parameters as well and are reported in Table 6-1.

Table 6-1: List of biomass types used for tests

ID	BIOMASS ORIGIN	BIOMASS SIZE
A	Woody residues	< 50mmX50mmX50mm
B	Forestry residue	Chips[9]
C	Saw mill waste	50mmX50mmX50mm
D	Pruning residue	Briquettes (∅60mm, length 50mm)

When not defined (last part of this section) steady state only conditions of the system are presented.

Results

A first remark about the influence of size of biomass feed on SV value, mainly due to change of friction loss of flow across reactor. It cannot be seen as a direct correlation, as already noted in scheme of Figure 5-10, since there are two different stages of air injection. Depending on system configuration, around 50% to 70% of total air is entering the reactor from the top, while the rest from nozzles (see Figure 3-8). The amount of air from nozzles is not flowing through the whole reactor, thus particle size of biomass has not direct influence on it. Furthermore, char bed length/size have influence on phenomenon as well.

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[9] Class P45 according to European Specification "CEN/TS 14961:2005, "Solid biofuels - Fuel specifications and classes".

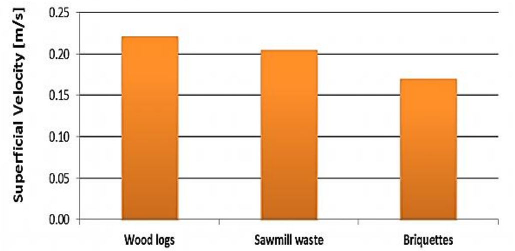


Figure 6-13: Effect of biomass size on SV

In Figure 6-13 the same system configuration and load (rpm of PG blower included) shows SV values against particle size. First of all, the value demonstrates being well below compared to classical Imbert reactor (Cf. Table 5-3). Furthermore it is visible a minor decrease of SV values against biomass size decreasing.

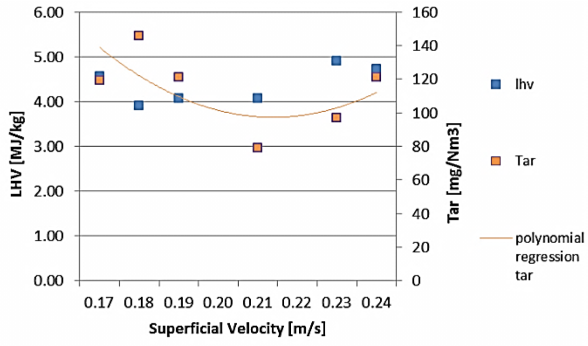


Figure 6-14: SV versus Gas quality and heating value

In Figure 6-14 the SV is plotted versus two major values attesting gas quality: the lower heating value per weight of dry PG and the gross tar concentration. The former is considered as the total amount of condensable matter and measured at the cold end of the gas line. A remarkable result is, first of all, the operational stability of the system which, even at very low SV reached, enhances a heating value fit for fuelling an engine. This is a very important point achievement, especially for double fire or other design allowing an extra amount of oxygen into the reactor. Low tar content together with too low LHV for engine operation has been avoided.

Tar concentration in the gas is the second aspect reported in Figure 6-14. It is not directly being associated to primary measures for removal inside the reactor since there is no distinction among classes and additional gas cooling and cleaning has been put into practice. It is clearly visible, in the fitting curve, a minimum as observed in other similar studies already mentioned (Cf. Figure 5-8).

Tar concentration demonstrates being higher with moisture content increasing, as reported by Figure 6-15. It is a well-known phenomenon, related to lower temperature due to higher energy demand relevant to the drying process inside the reactor. Biomass properties (except moisture content) are slightly different from case to case, and no major variation of system parameters is present. The potential of cleanliness in case of very dry biomass is very interesting; even if, especially for agro-residues, it is a condition achievable only with proper pre-treatment machinery (Cf. section 2.3 for details of pre-treatment work implemented for the case study).

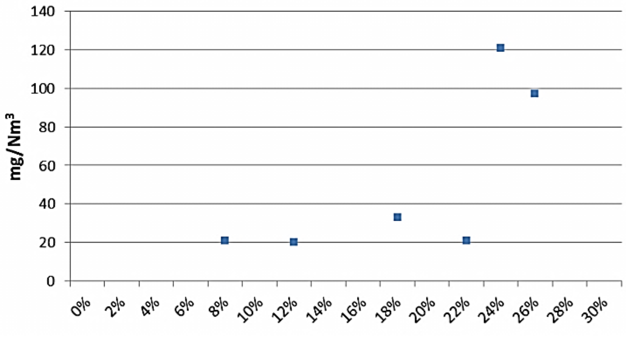


Figure 6-15: Tar concentration against moisture content of biomass feed

More extended data on composition of PG shows (Figure 6-16) only a slight increase in the amount of both CO and H_2 with SV increasing, confirming the possibility to change the process parameters without deteriorating the heating value. This stable performance of reactor leads to smooth operation of the gas engine (at part load for lower SV). This result agrees well with that obtained by Zhang et al. [75].

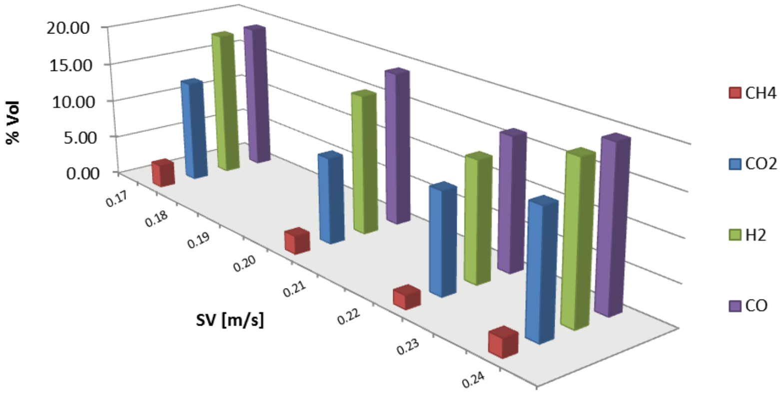


Figure 6-16: PG composition (% v/v) against SV

Heating value has been analysed along with ER as well, even if the open top configuration cannot guarantee an accurate measure of air flow. This last value has been derived from a model implementing mass and energy balance of reactor, including ultimate analysis of feed and char out of system. The trend is decreasing as expected (see Figure 6-17), but the slope is not as high as reported in other studies [67]. This could be explained by the thickness of insulation of reactor, leading to higher temperature even at low combustion rates.

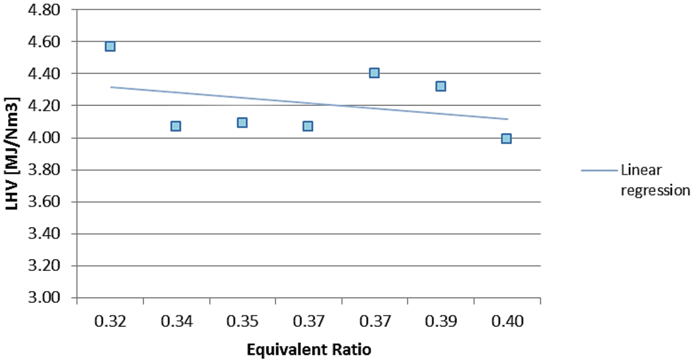


Figure 6-17: Heating value versus ER

Tar collected has been studied, the most abundant hydrocarbons found, and classification according to Table 5-1, are:

- 2,6-Di-tert-butylbenzoquinone
- Di-tert-butylphenol
- Pyrene (Class 5)
- Benzo pyrene (Class 5)
- Fluoranthene (Class 4)
- Benzo fluoranthene (Class 5)
- Phenanthrene (Class 4)
- 1a,9b-Dihydro-1H-cyclopropa[a]anthracene (Class 4)
- Styrene (Class 3)
- Indene (Class 4)
- Naphthalene (Class 4)

It is clearly visible that most abundant compounds are the heaviest ones: Class 4 and 5. This can be explained with high temperature leading to cracking activity of class 2 and 3, as according to other studies [81] [55].

Mass and energy balance

The plant has been subdivided in four main parts:

- Drier
- Reactor
- Gas Cleaning Line
- Engine

All main data acquisition points are used as inputs of a simulation tool. Chemical equilibrium is reached fixing T of reaction (Tc) and supposing the reactor adiabatic. Chemical elements of reaction are supposed 11: O_2, N_2, CO_2, CO, H_20, H_2, OH, NO, NO_2, C, CH_4. Equilibrium is computed through the minimization of the Gibbs free energy method using Ultimate analysis, Moisture content, ER, T_c and P as input. Partial derivatives with respect of mole fraction of each single species are set to 0.

PG composition has been computed and compared with data experimentally recorded. Figure 6-18 plot the comparison for a test with sawmill waste and 0.22 m^3/h as gas flow rate.

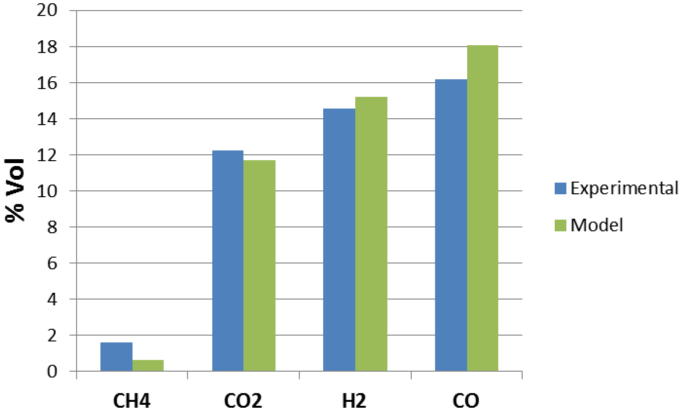
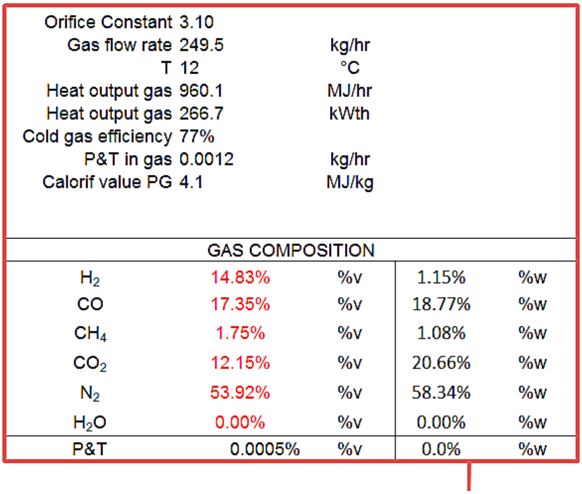


Figure 6-18: Comparison of the predicted and experimentally obtained producer gas composition

Then, an energy balance of input/output with other directly and indirectly measurable values of the system (i.e. solid and condensable from cleaning system components) has been elaborated (Table 6-2 shows PFD of the gas cleaning line). Cold gas efficiency reaches a value of 77% (values of up to 85% have been recorded in previous test by IISc [82]).

Table 6-2: Detail of reactor model computational analysis[10]



Orifice Constant	3.10	
Gas flow rate	249.5	kg/hr
T	12	°C
Heat output gas	960.1	MJ/hr
Heat output gas	266.7	kWth
Cold gas efficiency	77%	
P&T in gas	0.0012	kg/hr
Calorif value PG	4.1	MJ/kg

GAS COMPOSITION				
H_2	14.83%	%v	1.15%	%w
CO	17.35%	%v	18.77%	%w
CH_4	1.75%	%v	1.08%	%w
CO_2	12.15%	%v	20.66%	%w
N_2	53.92%	%v	58.34%	%w
H_2O	0.00%	%v	0.00%	%w
P&T	0.0005%	%v	0.0%	%w

Efficiency of system components has been derived by manufacture manuals. Auxiliaries (See Table 6-3 for the complete list) have been constantly monitored in order to have accurate net efficiency.

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[10] "P&T" refers to particulate and tar. A fixed value of 5 PPM has been set according to previous measures. Tar compounds are not taken into account in the model and the energy content is supposed negligible.

Table 6-3: List of all system auxiliaries and rated power

#	Component	Rated power [kW]	#	Component	Rated power [kW]
1	Flocculator inlet pump	1.13	**10**	PCF Blower	0.75
2	Flocculator outlet pump	0.75	**11**	Char extraction motor	0.75
3	Poly and alum pump	0.75	**12**	Drier blower	2.25
4	Overhead tank pump	0.75	**13**	Bucket elevator motor	0.75
5	Cooler and scrubber pump	5.50	**14**	Drier belt conveyor	0.75
6	Chilled scrubber pump	3.70	**15**	Cooling tower fan	1.12
7	Cooling tower pump	3.75	**16**	Flocculator carbon feeder	0.37
8	Compressor	1.50	**17**	PCF feeder	0.37
9	Gas Blower	2.25	**18**		

Table 6-4 reports average values of the SFC during test run performed with dry wood logs.

Table 6-4: Average SFC against engine load

Run time [h]	Average Load [kWe]	SFC [kg/kWh$_e$]
8	35	1.17
5	34	1.20
6	34	1.18
9	69	1.16
8	71	1.16
10	70	1.15

The system demonstrated to easily cross 18% net electrical efficiency, reaching values of 1.15 kg/kWh$_e$ of Specific Fuel Consumption for this particular kind of biomass.

Unsteady conditions

Due to uncommon higher thermal mass of reactor a few consideration on unsteady measures have been taken into account. Furthermore, reactor demonstrated to well retain heat from previous tests, allowing easier start up procedures. In Figure 6-19 temperature of PG exiting the reactor (green line) shows a very smooth ascending trend also when engine was operated (black dotted line, control board of engine is keeping constant the load). A slightly descending trend (purple squares) of feeding rate is clearly visible and associated to cold gas efficiency raise. No major variations have been recorded on all numerous pressure sensors displaced along gas line, in blue is reported the reactor outlet pressure (left axis, mmH_20).

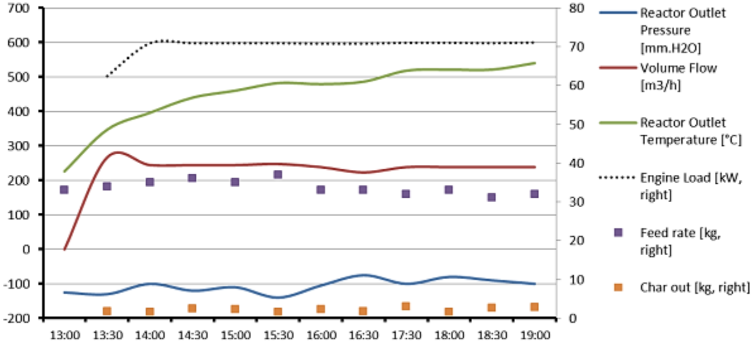

Figure 6-19: Main parameters during system start-up

A test (no engine operation) associated to briquettes is plotted in Figure 6-20. Thermal mass effect of reactor is visible also in this run, since T is well above ambient at the start. Flare T is the purple line, when the main flare is switched off the PG passes across filters and burned to a secondary flare (T of this flare are not present). Unstable PG outlet Temperature is deriving from system parameters check-up (Cf. Volume Flow of PG, the red line). Despite steady state reaching in last minutes of the record, the reactor outlet T is below values recorded in other tests, this can be related to lower LHV and quality of biomass.

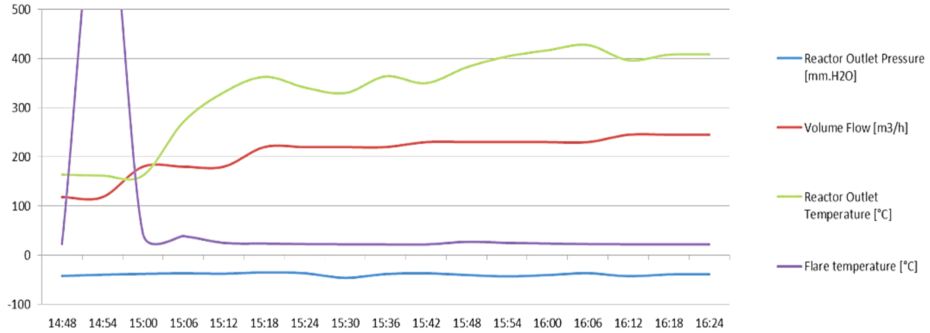

Figure 6-20: System start-up for briquettes gasification

7. Investigation on tar revalorization

Aim of this chapter is to evaluate some possible outcomes regarding an energy valorisation of tar as a by-product of biomass gasification. The work derives from a collaborative activity among UniFi and a manufacturing company of gasifiers. Scope of collaboration has been to figure out possible valorisation solutions for by-products of commercial gasifiers manufactured by the company. Results has been inserted in the present document because describe real issues about tar management after removal from PG streamline. Most of research on secondary measures for tar removal is equipment-focused, that is addressed on performance of components but lacking in tar disposal issues.

In the first section the feasibility study about an additional gasification stage is illustrated. The reactor was specifically designed and sized for being added and operated next to the primary gasifier generating the by-product. The second section collects laboratory analysis on same tar upgrading for fuel use.

Other kinds of non-energy valorisation or treatment are not the purpose of this chapter even if biomass tar has interesting potentials. It could partially cover, in future, the demand now assured by coal tar as an important feedstock for carbon-based chemicals and materials. Nowadays, about one sixth of the total world requirement of aromatic hydrocarbon, nearly 3.0×10^7 ton/year, can only be obtained from coal tar [83].

7.1 Re-gasification

To find useful information on gasification of tar-like compounds an extensive literature review has been implemented on scientific journals, company reports, technical papers, Ph.D. thesis and other academic publications. Neither commercial nor experimental by-product gasifier as the project proposal outlined by UniFi has been found. However, in some articles it was possible to observe interesting best practices, plant component description and assessment along with general useful considerations. These precedents let assert that thermochemical degradation of biomass derived tar by means of gasification is a feasible technical choice.

Literature review

The investigation initially found only articles about the upgrading of the tar by catalytic reforming or steam addition, currently the main methods for upgrading of the heavy hydrocarbons from thermochemical processes. Small scale and air as gasification agent (mandatory condition for the small scale case study) solutions has not been found. Hence the decision to focus on substances with chemical and/or physical properties similar to the compounds received from manufacturer, in particular:

- heavy refinery residues;
- pyrolysis oil;
- Black liquor.

Finally 47 articles have been selected and analysed, in “Appendix E – Gasification of tar-like compounds” is reported the complete list with details and articles are grouped by specific subject.

Heavy refinery residue

Heavy residues arising from crude oil refining consist mainly of substances from the bottom of the distillation columns. The complex mixture of high molecular weight hydrocarbons presents boiling point ranging between 350 and 650 °C. In general are typically formed by a small part of heterocyclic compounds containing sulphur, nitrogen and oxygen, and by large amounts of aromatic hydrocarbons, aliphatic and naphthenic, whose molecules are made up of a number of carbon atoms between 20 and 50 [84]. Chemical-physical characteristics of these compounds vary greatly depending on process and type of crude oil, nonetheless it can be expected that values are within limits given in Table 7-1.

Table 7-1: Chemical-physical characteristics of products of oil refineries **[84,85,86,87]**

	Unit	**Value**
Viscosity @ 100 °C	cSt	6 to 1500[11]
Density @ 15 °C	Kg/m^3	950-1010
Pour Point	°C	<30
Carbon	%wt.	83-87
Hydrogen	%wt.	9-10
Oxygen	%wt.	<1
Ash	%wt.	<1
Water	%wt.	<1
Sulphur	%wt.	<2-7

Kinematic viscosity shows how both tar and heavy oil residues present semi-solid phase at room temperature. Data of sample tar from manufacturing company is presented in Table 7-4. In recent years, different crude oil distillation sites have been equipped with a system for the gasification of heavy residues. In Italy 3 IGCC plants which process up to 150 ton/h of heavy residues are present.

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[11] 6-100 cSt for topping residual arising from the fractionation tower at atmospheric pressure and 600-1500 cSt for residues resulting from the vacuum column fractionation.

Bio-oil

The pyrolysis oil, also known as bio-oil, is a product derived from thermochemical decomposition of biomass at temperatures of about 500°C in inert atmosphere with subsequent cooling. Pyrolysis oil is a kind of tar containing high levels of oxygen. In Table 7-2 chemical and physical properties of typical pyrolysis oil are reported, although its features vary depending on the type of biomass and process.

Table 7-2: Fast-pyrolysis Bio-oil features **[88,89]**

	Unit	Value
Carbon	% Wt.	56
Hydrogen	% Wt.	6
Oxygen	% Wt.	38
Nitrogen	% Wt.	0-0,1
Water	% Wt.	25
Ash	% Wt.	0-0,2
LHV	MJ/kg	17
Density	Kg/m^3	1200
Viscosity @ 40 °C	cSt	30-90
pH		2,5

Studies about using bio-oil as a raw material for gasification reactors are present. Fluidized bed reactors are preferred over those fixed bed because of carbon deposits forming during process. The phenomenon is less disturbing in fluid beds because coke formed is distributed over the entire length of the bed [90].

Interesting tests have been implemented by submitting in a 5 MW entrained flow bed a mixture of 70% pyrolysis oil and the remaining 30% char (usually a complementary by-product of tar from biomass gasification). The char added modifies the gasifying matter (see Figure 7-1) moving toward more suitable chemical and physical features [91].

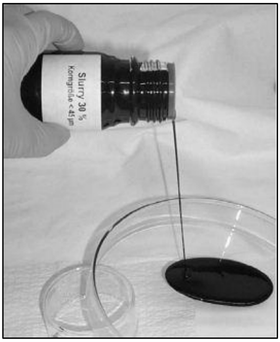

Figure 7-1: 70% bio-oil e 30% char mixture gasified

Another experiment concerning a mixture of 80% of pyrolysis oil and 20% of char has been conducted by using a lab scale fluidized bed gasifier [92]. A cooling tube so as to maintain the temperature of atomizer below 80°C has been used. This measure has been implemented in order to avoid carbon formation, which is the principal reason of obstructions.

As regards fixed bed reactors an important outcome available in literature has been conducted by Panigrahi [93]. Results are limited by the maximum temperature of 800 °C reachable by micro reactor externally heated.

Black liquor gasification

Black liquor is a by-product of the process of extracting fibres from wood; it is mainly produced by paper production industry. It is perhaps the largest source of biomass-derived energy available at industrial level, with an energy potential of approximately 89 GWth globally [94].

Paper mills' black liquor is usually valorised as fuel in a recovery boiler. Over the last years are present studies about viability of black liquor as a feedstock in a gasification process, in particular black liquor in IGCC plants. Table 7-3 shows main values of the by-product; viscosity is not present since strong variations (up to 5000 cSt) depending on T and solid concentration are reported.

Table 7-3: Black liquor physical and chemical data **[94]**

	Unit	Value
HHV	MJ/kg (d.b.)	14
Density	Kg/m^3	1020
Carbon	%w. (d.b.)	34
Hydrogen	%w. (d.b.)	3
Nitrogen	%w. (d.b.)	/
Sulphur	%w. (d.b.)	5
Oxygen	%w. (d.b.)	34
Sodium	%w. (d.b.)	22
Potassium	%w. (d.b.)	1

Among plants for black liquor gasification, bubbling fluidised bed reactors with superheated steam demonstrated to be the most interesting for review purpose. These are low temperatures installations been put into operation between years 2003 and 2004 by paper production companies Georgia-Pacific and Norampac.

Recycling of tar in the same gasifier

The Research Centre of the Netherlands (ECN) has focused on the possibility to continuously recycle the tar removed by the primary stream of producer gas in the very same gasification reactor [95]. The installation consists of a CFB gasifier, two cyclones for ash and dust removal, two wet scrubbers, a wet Electrostatic Precipitator, a booster and a gas engine. In particular, the recycled mixture is composed by tar and water, due to the presence of water scrubbers in the downstream cleaning process.

The plant is fed by 94 kg/h of biomass pellets (12% moisture content) before recycling and 81 kg/h pellets plus 27 kg/h of tar/water mixture during recycling.

The concentration of 14 compounds in PG was compared with theoretical concentration that would result if the tar had not been destroyed. For all tar compounds, except phenol, the theoretical increase in concentration is much higher than the experimentally measured one. It follows that almost 70–90% of the recycled tar is destroyed. The author asserts that tar destruction can be ascribed to oxidizing conditions; the tar is expected to evaporate and oxidize before pellets pyrolysis starts.

Indirectly those tests by ECN validate the decision made at the beginning of this review about not to interfere with the existent reactor. The choice of adding a secondary reactor for tar recycling was in order to leave unchanged the plant as much as possible. The author reports variations in gasifier operating conditions during tar recycling: moisture content of the fuel increasing from 12% to 30% generates a series of side effects which force to modify system parameters (Temperature, ER).

Conclusions

The analysis of data allows asserting that the addition of a secondary reactor for gasification of recycled tar is a potential alternative way to conventional tar disposal techniques. The improvement of the overall efficiency of plant would be combined to smaller flow of waste products, with consequent reduction of operating costs.

However, a small scale fixed-bed solution with air as a gasification agent is unprecedented, since analogue arrangements have not been ascertained from ad hoc review implemented.

The literature review has been useful in addressing specific issues to be explored and evaluated in detail. The first is formation of carbon deposits in nozzles or other parts of reactor that could cause corrosion and obstructions. The second is about yield and quality assessment of the PG from additional reactor; limits have to be set in order to avoid major alterations of the primary stream.

7.2 Experimental analysis on tar upgrading

The case study: tar features

Aim of the work has been to measure and evaluate chemical-physical compatibility of recycled tar as a fuel in primary motors. The mixture comprehends tar, char and water and derives from gas cleaning system of a biomass gasifier. The cleaning system of the plant consists of Venturi scrubber and ESP.

In Table 7-4 data of 3 samples from different site plants are reported. A significant presence of oxygen is visible, primarily due high water content in the mixture. Kinematic viscosity and Conradson Carbon Residue (CCR) are very high, while density, flash point and calorific value are similar to pyrolysis oils features.

Table 7-4: Chemical and physical parameters of the for samples A, B and C

	Unit	Technical specification	Sample A	Sample B	Sample C
Water content	% wt.	ISO 3733:1999	33,0	15,8	0,36[12]
Oxygen		ASTM D 5291-09	32,3		
Density (15°C)	kg/dm3	UNI EN ISO 12185:1999	1,2	1,20	1,09
Kinematic viscosity (40°C)	cSt	UNI EN ISO 3104:2000	-	-	6169
Flash point	°C	UNI EN ISO 2719:2005	-	98	> 85
CCR	% wt.	UNI EN ISO 10370:1998	33,6	32,00	31,6
LHV	MJ/kg	ASTM D 240-09	23,9	-	23,85

Mixing tests

Tar solubility with four potential blending fuels has been observed: Gasoline, Diesel fuel, Biodiesel and Ethanol. Tests were carried out at 40 °C because fluidity and homogeneity at ambient temperature posed practical barriers in test execution.

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[12] After centrifugation process

The mixing was performed at 4:1 ratio by volume (tar:fuel) for a total tar quantity of 100mL. After first results a test at 1:4 ratio has been carried out. Tests showed:

- Petrol and Diesel: these traditional fuels do not mix spontaneously with tar and even after shaking tend to separate quickly in two phases
- Biodiesel: forced mixing is necessary but after agitation no phase separation has been recorded
- Ethanol: good spontaneous mixing. After forced mixing homogenization seems complete and persistent over time

Figure 7-2: Tar mixing test with (in order from left to right) Biodiesel, Diesel fuel, Ethanol and gasoline

Tar is poorly miscible with gasoline and diesel fuel due to different chemical composition. In particular traditional fuels contain aliphatic hydrocarbons poorly miscible with water. Difference in density is an additional barrier to miscibility among tar and hydrocarbons.

Esters in Biodiesel, on the other hand, contain oxygen and thus are sufficiently miscible with Tar after mixture is stirred. Presence of nonpolar and hydrophobic hydrocarbon chains can explain the non-spontaneous mixing.

Polarity and hydrophilicity of Ethanol, despite the difference in density, lead to persistent homogeneity over time.

Tar upgrading

As from Table 7-5, tar has a density superior to other fuels, a lower calorific value and a considerable amount of water. Kinematic viscosity at 40 °C is extremely high compared to other fuels. The value of CCR and oxygen content are both very high. Furthermore, pH of tar could lead to corrosive effects (4.86 is the smaller value detected in samples).

Table 7-5: Comparison among main chemical-physical properties of tar mixture and other liquid fuels

	Tar Mixture	**Pyrolysis**	**Diesel**	**Gasoline**	**Biodiesel**	**Ethanol**
Reference	RE-CORD Laboratory	[96] [97]	UNI EN 590	UNI 20156	EN 14214	(pure)
Density [kg/dm^3]	1,2	1,10-1,30	0,820-0,845	0,720-0,775	0,860-0,900	0,789
LHV [MJ/kg]	23,9	13 - 18	42,9	44	37	21
H2O [% wt.]	33,0	20 - 30	< 0,02	trace	< 0,05	absent
Kinetic viscosity [cSt @40°C]	6168	15 - 35	2,0 – 4,5	negligible	3,5 – 5,0	negligible
Flash Point [°C]	98	40 - 110	> 55	> - 40	> 101	12
CCR [% m/m]	33,6	17-23	< 0,35	negligible	< 0,30	negligible
Oxygen [% wt.]	32,3	40-50	0	< 2,7	11	34,7

Evaluating the properties of biodiesel and those of the Tar what can be expected in the event of an upgrade of the Tar adding Biodiesel are the following changes:

- decrease in the density
- Raising the net calorific value (LHV)
- a decrease in viscosity
- reduction of the CCR
- decrease in the percentage of oxygen

However, those advantages may require significant percentages of Biodiesel. As an example, assuming for simplicity a linear variation of the parameters, Table 7-6 shows expected change in the value of LHV and CCR with 20% Biodiesel blending: parameters would still far from those of conventional fuels.

Table 7-6: Prediction of change in mixture parameters

	LHV [MJ/kg]	CCR [% m/m]
Tar (as determined)	23,9	33,6
Tar : Biodiesel (4:1)	25,9	28,5

As a conclusion, although upgrading may lead to an improvement of various chemical-physical parameters, values remain distant from those of reference fuels. Furthermore, from an economic point of view the process could be too expensive and other valorisation apart from primary motors could be recommended.

Conclusions

The work has been made possible by two distinct research **projects** on agro residue valorisation by means of small scale gasification. The first one, named AGROGAS, was focused exclusively on the conversion technology. Partners of AGROGAS were UniFi, IISc and ENEA and project was funded by Italian ICE (National Institute for Foreign Commerce) and Indian MNRE (Ministry of New and Renewable Energy). The second one, named VISPO, was focused on the upstream agro-chain and just partly on energy conversion. VISPO is an on-going project funded by Region Tuscany.

A **70kWe** gasification system for power production with innovative reactor developed by IISc has been successfully adapted and installed in Italy. Test run for plant optimization and experimental campaign has been implemented with different type of biomass and extensive analysis of data. Campaigns focused on reactor, in order to explore behaviours of the innovative design on the tar formation and cracking mechanism, namely primary measure for tar removal.

Among biomass selected, **agricultural and forestry residues** have been of particular interest since the fuel flexibility is one of major achievements of reactor developed. In order to ensure full sustainability of the whole process, upstream-side activities has been monitored including agro-residues collecting, logistic and treatment with purpose of overall energy analysis of process.

Results show a very appreciable operational stability of the system in relation to parameters adopted; many and various system configurations ended up with very good engine performance. Among process parameters, the superficial gas velocity turned out as the key issue to explain most of the phenomenon observed. Minimization of particulate and tar concentration in the PG has been the key drive of the study, influencing continuously activity of design, modelling, experimental data acquisition and literature review. Plant efficiency showed up a close to 19% net electrical efficiency, a widely acceptable value in small scale applications. This is the demonstration of a good balance between the different (and sometimes conflicted) upshots of reliability and efficiency.

Drawbacks of such an approach set for a very high quality PG production are few. A complementary activity to minimize side effects of this method is the author’s main suggestion for future works, first of all the size and weight of reactor (specific to kWth) since can be a barrier for diffusion of commercial plants derived from the case study.

Regarding EU **commercialization,** significant steps in this direction have already been done during this work, first of all the complete system CE marking. Still to be improved two important issues reflecting the Indian imprinting of the plant, that is an abundant use of water and low automation.

Agro-residues demonstrated to be fit to the reactor features but the upstream process has to be better managed in order to search for less burdensome procedures, especially regarding indispensable compaction of agricultural residues. Nevertheless the energy effectiveness of the whole “**pruning-to-electricity**” tested activity demonstrated to be energetically worth, and showed some interesting net energy gain values.

Appendix A – Pictures

Figure A-1: Sawmill waste for test

Figure A-2: Vineyard pruning residues discharge on May 2012

Figure A-3: Vine stock piled open air

Figure A-4: Vineyard A (left) and B (right) at Grassi Farm

Figure A-5: Olive grove for VISPO project test

Figure A-6: Area equipped with biomass pre-treatment machinery

Figure A-7: Manual chipping machine with detail of disk and blades (right)

Figure A-8: Mobile use of JENZ HEM 561 chipping machine

Figure A-9: Briquettes of chipped (left) and milled (right) forestry residues. Is visible the size in cm.

Figure A-10: Cummins G855 70kWe Genset

Figure A-11: Pressure gauge in PG line between first and second scrubber

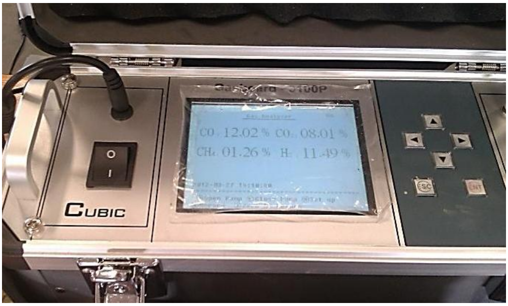

Figure A-12: Gas analyser during IISc tests in India, it is visible the percentage concentration of CO, CO_2, CH_4, H_2

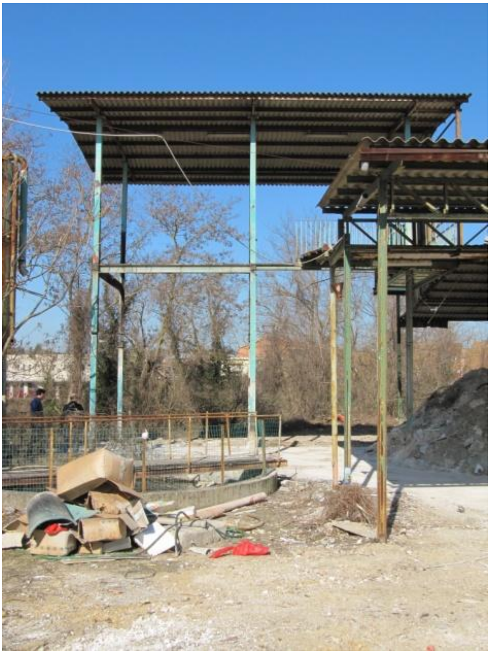

Figure A-13: Shed before system installation

Figure A-14: µGC Thermo Scientific c2V – 200.

Figure A-15: Sampling unit during test, ice bath on the left and volume flow meter on the right

Figure A-16: Engine control panel during full load operation

Figure A-17: Solid particle filtration (Left) and Rotavapor (Right) for Isopropanol evaporation.

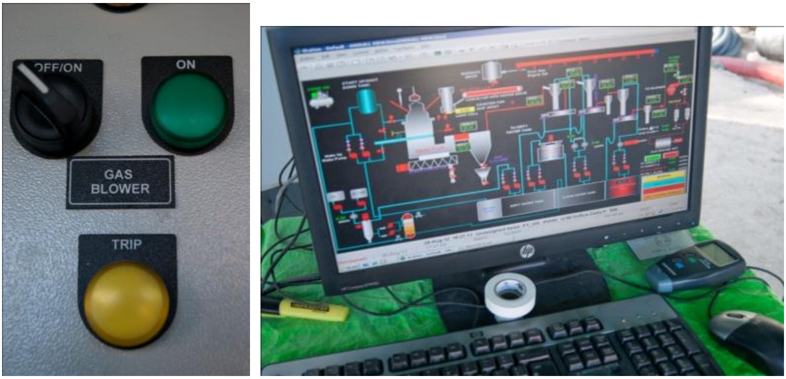

Figure A-18: The gasification plant can be operated manually (left) or through PLC connected software (right).

Appendix B – Laboratory analysis

Table B-1: Sample OM1-A data

BIOMASS PROPERTIES	UNIT	VALUE
Moisture content (ad[13])	wt.% , w.b.	9,1
Ash content (ad)	wt.%	3,9
C (ad)	wt.%	43,60
H (ad)	wt.%	6,40
N (ad)	wt.%	0,36
S (ad)	wt.%	0,46
O (ad, diff.)	wt.%	45,28
HHV (ad)	MJ/kg	17,5
LHV (ad)	MJ/kg	16,2
LHV (dry)	MJ/kg	18,0

Table B-2: Sample OM1-B data

BIOMASS PROPERTIES	UNIT	VALUE
Moisture content (ad)	wt.% , w.b.	19,2
Ash content (ad)	wt.%	3,1
C (ad)	wt.%	39,37
H (ad)	wt.%	6,65
N (ad)	wt.%	0,19
S (ad)	wt.%	0,47
O (ad, diff.)	wt.%	50,21

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[13] As Determined

HHV (ad)	MJ/kg	15,5
LHV (ad)	MJ/kg	14,2
LHV (dry)	MJ/kg	18,1

Table B-3: Sample OM1-C data

BIOMASS PROPERTIES	UNIT	VALUE
Moisture content (ad)	wt.%, w.b.	27,86
Ash content (ad)	wt.%	2,38
C (ad)	wt.%	35,17
H (ad)	wt.%	7,17
N (ad)	wt.%	0,16
S (ad)	wt.%	0,05
O (ad, diff.)	wt.%	55,07
HHV (ad)	MJ/kg	13,9
LHV (ad)	MJ/kg	12,5
LHV (dry)	MJ/kg	18,2

Table B-4: Sample OM1-D data

BIOMASS PROPERTIES	UNIT	VALUE
Moisture content (ad)	wt.% , w.b.	40,755
Ash content (ad)	wt.%	2,495
C (ad)	wt.%	28,70
H (ad)	wt.%	7,88
N (ad)	wt.%	0,35
S (ad)	wt.%	0,05
O (ad, diff.)	wt.%	60,53
HHV (ad)	MJ/kg	11,4
LHV (ad)	MJ/kg	9,8

LHV (dry)	MJ/kg	18,1

Table B-5: Sample OM1-E data

BIOMASS PROPERTIES	UNIT	VALUE
Moisture content (ad)	wt.% , w.b.	16,66
Ash content (ad)	wt.%	2,29
C (ad)	wt.%	40,73
H (ad)	wt.%	6,70
N (ad)	wt.%	0,21
S (ad)	wt.%	0,04
O (ad, diff.)	wt.%	50,03
HHV (ad)	MJ/kg	16,0
LHV (ad)	MJ/kg	14,7
LHV (dry)	MJ/kg	18,1

Table B-6: Sample OM1-F data

BIOMASS PROPERTIES	UNIT	VALUE
Moisture content (ad)	wt.% , w.b.	37,88
Ash content (ad)	wt.%	2,55
C (ad)	wt.%	31,80
H (ad)	wt.%	7,88
N (ad)	wt.%	0,04
S (ad)	wt.%	0,04
O (ad, diff.)	wt.%	57,69
HHV (ad)	MJ/kg	119
LHV (ad)	MJ/kg	10,3
LHV (dry)	MJ/kg	17,9

Table B-7: Sample OM1-G data

BIOMASS PROPERTIES	UNIT	VALUE
Moisture content (ad)	wt.% , w.b.	9,83
Ash content (ad)	wt.%	4,34
C (ad)	wt.%	43,17
H (ad)	wt.%	6,37
N (ad)	wt.%	0,45
S (ad)	wt.%	0,08
O (ad, diff.)	wt.%	45,60
HHV (ad)	MJ/kg	17,4
LHV (ad)	MJ/kg	16,1
LHV (dry)	MJ/kg	18,1

Table B-8: Sample OM2-A data

BIOMASS PROPERTIES	UNIT	VALUE
Moisture content (ad)	wt.% , w.b.	15,62
Ash content (ad)	wt.%	1,71
C (ad)	wt.%	40,50
H (ad)	wt.%	6,80
N (ad)	wt.%	0,02
S (ad)	wt.%	0,04
O (ad, diff.)	wt.%	50,93
HHV (ad)	MJ/kg	16,0
LHV (ad)	MJ/kg	14,6
LHV (dry)	MJ/kg	17,7

Table B-9: Sample VM1-A data

BIOMASS PROPERTIES	UNIT	VALUE

Moisture content (ad)	wt.% , w.b.	12,50
Ash content (ad)	wt.%	6,50
C (ad)	wt.%	41,77
H (ad)	wt.%	6,31
N (ad)	wt.%	0,26
S (ad)	wt.%	0,46
O (ad, diff.)	wt.%	44,71
HHV (ad)	MJ/kg	16,0
LHV (ad)	MJ/kg	14,7
LHV (dry)	MJ/kg	17,1

Table B-10: Sample VM1-B data

BIOMASS PROPERTIES	UNIT	VALUE
Moisture content (ad)	wt.% , w.b.	29,00
Ash content (ad)	wt.%	4,80
C (ad)	wt.%	33,33
H (ad)	wt.%	6,99
N (ad)	wt.%	0,18
S (ad)	wt.%	0,52
O (ad, diff.)	wt.%	54,18
HHV (ad)	MJ/kg	13,2
LHV (ad)	MJ/kg	11,8
LHV (dry)	MJ/kg	17,5

Table B-11: Sample VM1-C data

BIOMASS PROPERTIES	UNIT	VALUE
Moisture content (ad)	wt.%, w.b.	16,28
Ash content (ad)	wt.%	6,44

C (ad)	wt.%	38,80
H (ad)	wt.%	6,19
N (ad)	wt.%	0,20
S (ad)	wt.%	0,06
O (ad, diff.)	wt.%	48,31
HHV (ad)	MJ/kg	15,5
LHV (ad)	MJ/kg	14,2
LHV (dry)	MJ/kg	17,4

Table B-12: Sample VM1-D data

BIOMASS PROPERTIES	UNIT	VALUE
Moisture content (ad)	wt.% , w.b.	32,19
Ash content (ad)	wt.%	13,72
C (ad)	wt.%	27,90
H (ad)	wt.%	6,72
N (ad)	wt.%	0,18
S (ad)	wt.%	0,07
O (ad, diff.)	wt.%	51,41
HHV (ad)	MJ/kg	10,8
LHV (ad)	MJ/kg	9,5
LHV (dry)	MJ/kg	15,0

Table B-13: Sample VM1-E data

BIOMASS PROPERTIES	UNIT	VALUE
Moisture content (ad)	wt.% , w.b.	15,61
Ash content (ad)	wt.%	1,70
C (ad)	wt.%	41,30
H (ad)	wt.%	6,44

N (ad)	wt.%	0,09
S (ad)	wt.%	0,05
O (ad, diff.)	wt.%	50,42
HHV (ad)	MJ/kg	16,3
LHV (ad)	MJ/kg	14,9
LHV (dry)	MJ/kg	18,1

Table B-14: Sample VM1-F data

BIOMASS PROPERTIES	UNIT	VALUE
Moisture content (ad)	wt.% , w.b.	30,44
Ash content (ad)	wt.%	2,35
C (ad)	wt.%	34,00
H (ad)	wt.%	7,12
N (ad)	wt.%	0,08
S (ad)	wt.%	0,04
O (ad, diff.)	wt.%	56,41
HHV (ad)	MJ/kg	13,4
LHV (ad)	MJ/kg	12,0
LHV (dry)	MJ/kg	18,2

Table B-15: Sample VG1-A data

BIOMASS PROPERTIES	UNIT	VALUE
Moisture content (ad)	wt.% , w.b.	31,30
Ash content (ad)	wt.%	5,00
C (ad)	wt.%	33,60
H (ad)	wt.%	7,09
N (ad)	wt.%	0,25
S (ad)	wt.%	0,49

O (ad, diff.)	wt.%	53,57
HHV (ad)	MJ/kg	13,0
LHV (ad)	MJ/kg	11,5
LHV (dry)	MJ/kg	17,8

Table B-16: Sample VG1-B data

BIOMASS PROPERTIES	UNIT	VALUE
Moisture content (ad)	wt.% , w.b.	19,46
Ash content (ad)	wt.%	2,76
C (ad)	wt.%	39,20
H (ad)	wt.%	6,59
N (ad)	wt.%	0,14
S (ad)	wt.%	0,05
O (ad, diff.)	wt.%	51,26
HHV (ad)	MJ/kg	15,5
LHV (ad)	MJ/kg	14,1
LHV (dry)	MJ/kg	18,1

Table B-17: Sample VG1-C data

BIOMASS PROPERTIES	UNIT	VALUE
Moisture content (ad)	wt.% , w.b.	21,43
Ash content (ad)	wt.%	3,31
C (ad)	wt.%	38,47
H (ad)	wt.%	6,67
N (ad)	wt.%	0,29
S (ad)	wt.%	0,06
O (ad, diff.)	wt.%	51,20

HHV (ad)	MJ/kg	15,2
LHV (ad)	MJ/kg	13,8
LHV (dry)	MJ/kg	18,2

Table B-18: Sample VM2-A data

BIOMASS PROPERTIES	UNIT	VALUE
Moisture content (ad)	wt.% , w.b.	16,33
Ash content (ad)	wt.%	3,35
C (ad)	wt.%	42,45
H (ad)	wt.%	6,66
N (ad)	wt.%	0,51
S (ad)	wt.%	0,06
O (ad, diff.)	wt.%	46,98
HHV (ad)	MJ/kg	16,5
LHV (ad)	MJ/kg	15,1
LHV (dry)	MJ/kg	18,5

Table B-19: Sample VM3-A data

BIOMASS PROPERTIES	UNIT	VALUE
Moisture content (ad)	wt.% , w.b.	33,40
Ash content (ad)	wt.%	3,80
C (ad)	wt.%	49,20
H (ad)	wt.%	6,00
N (ad)	wt.%	0,10
S (ad)	wt.%	0,60
O (ad, diff.)	wt.%	40,30
HHV (ad)	MJ/kg	19,2

LHV (ad)	MJ/kg	18,0
LHV (dry)	MJ/kg	28,1

Table B-20: Data of briquette made by sawdust of forestry residue

BIOMASS PROPERTIES	UNIT	VALUE
Moisture content (ad)	wt.% , w.b.	10,16
Ash content (ad)	wt.%	3,34
Density	Kg/m^3	830
C (ad)	wt.%	44,57
H (ad)	wt.%	6,38
N (ad)	wt.%	0,38
S (ad)	wt.%	0,60
O (ad, diff.)	wt.%	44,73
HHV (ad)	MJ/kg	17,3
LHV (ad)	MJ/kg	16,0
LHV (dry)	MJ/kg	18,1

Table B-21: Data of briquette made by sawmill factory waste

BIOMASS PROPERTIES	UNIT	VALUE
Moisture content (ad)	wt.% , w.b.	10,92
Ash content (ad)	wt.%	0,59
Density	Kg/m^3	888
C (ad)	wt.%	45,77
H (ad)	wt.%	6,66
N (ad)	wt.%	0,31
S (ad)	wt.%	0,60
O (ad, diff.)	wt.%	46,08

HHV (ad)	MJ/kg	18,0
LHV (ad)	MJ/kg	16,7
LHV (dry)	MJ/kg	19,0

Table B-22: Data of briquette from mixing of chipped Durmast Oak and waste sawdust

BIOMASS PROPERTIES	UNIT	VALUE
Moisture content (ad)	wt.% , w.b.	9,72
Ash content (ad)	wt.%	0,16
Density	Kg/m^3	906
C (ad)	wt.%	45,47
H (ad)	wt.%	6,47
N (ad)	wt.%	0,23
S (ad)	wt.%	0,60
O (ad, diff.)	wt.%	47,09
HHV (ad)	MJ/kg	17,6
LHV (ad)	MJ/kg	16,2
LHV (dry)	MJ/kg	18,2

Appendix C – Gasification models review

Reference article	*Comments*
3.1	*No tars included in the analysis. Two separated and finally compared models included. Bed length of reduction zone included, CRF (char reactivity factor)linear behaviour in the reduction zone.*
3.2	*No tars included in the analysis (pyrolysis products completely cracked), but an error coefficient is defined. Interesting definition of char reactivity factor (kept constant in reduction zone). Only reduction numerical modelling.*
3.3	*Most interesting feature is the partial load inclusion in modelling.*
3.4	*In the model are present correlations from biomass and coal gasification*
3.5	*Based on model 54 with modifications on CRF variation along the bed kept constant basing on new assumption on the outlet Temperature. Coupling of K and TE model types.*
3.6	*The model is not exhaustively explained, it is coupled with experimental data from gasifier for tea drying (hot air is the purpose). Coupling of K and TE model types.*
3.7	*Basing on modelling of 41 this work adds a CRF variable along the char bed length.*
3.8	*Very detailed chemical reactions are present, including tar cracking phenomenon. Tars are modelled as hydrocarbons* $CH_{1.522}O_{0.0228}$ *with molecular weight equal to 95 and combustion is included. Fluid dynamics and heat and mass transport included.*
3.9	*Interesting the referring to SV*
3.10	*Very accurate model in the pyrolysis temperature area, no proximate analysis requested as input, no tar present. Coupling of K and TE model types. Not experimentally validated.*
3.11	*Clear description of any single chemical reaction included. Irrespective of design of reactor.*
3.12	*The model is an update based on coal gasification models. Irrespective of design of reactor.*
3.13	*The model is coupled with output from the computer program Cycle-tempo. Interesting the validation on an open top reactor. The model is not described in this paper but the computational details can be found in* [98]
3.14	*Based on experimental data from a PCFB. The model type is TE but is "kinetically modified to estimate carbon conversion" by mean of a* β *coefficient evaluated through a correlation.*
3.15	*Innovative feature of this model are not interesting for the purpose of this investigation*
3.16	*The equilibrium model was developed considering the concept of carbon boundary point (CBP). The CBP is obtained when exactly enough gasifying medium is added to avoid carbon formation and achieve complete gasification. The second part of the model is addresses in re-elaborate data at T different from CBP. Exergy analysis addressed in* η *maximization.*
3.17	*Corrective coefficient for mole fraction of* CH_4, *and CO adjusting because no tar formation is considered.*
3.18	*Corrective coefficient K1 e K2 addressing equilibrium constant. Very clear description including the algorithm flowchart. Interesting report of differences in waste composition in developed and developing countries.*
3.19	*Detailed explanation of mode of spouted bed gasifier. Analysis on the effects of including or not including the carbon conversion efficiency.*
3.20	*The usual methodology of T modification by means of corrective coefficient is here addressed with an inherit mechanism well explained in the text (picture 5). Same gasifier as 51. Carbon and methane conversion are input only for the modified model.*
3.21	*Model coupled with interesting data from pyro/gasification batch reactor. Temperature may be not covering all case study reactor zones.*

3.22	*The model start with a full equilibrium computational methodology and then changing in Homogeneous equilibrium. The change is dictated to avoid char mass value <0*
3.23	*No model implemented, the text has been added because it explain very well and studies SV, a very interesting parameter that will come up useful for next chapters of this work.*
3.24	*Physical parameters like velocity and pressure are included in this model validated on an IISc gasifier of 20 kWe.*
3.25	*Very complex kinetic model, with a high number of outputs. Interesting the implementation of chemical reactions of tars reforming*
3.26	*SV is included in the model but is not the focus, neither analysis on SV are implemented. Interesting because it couples two kinetics models respectively on pyrolysis and gasification.*
3.27	*Not a model, just an experimental analysis. It has been considered and catalogues because of the strong focus on SV and tar cracking mechanisms.*
3.28	*Focused on pressure drop along parts of reactor and the influence of those on SV.*
3.29	*Flame propagation front velocity study, both relative to descending biomass through reactor than absolute velocity. Interesting the inclusion of air flow distribution among model inputs because tuyeres with mass flow controllers are present.*

Table C-1: Notes for each model catalogued

Appendix D – List of directives for CE Marking of gasifier power system

- Directive (2006/42/EC) Machinery safety. Essential health and safety requirements relating to the design and construction of machinery
- Directive (2006/95/EC) the Low voltage Directive.
- Directive (2004/108/EC) Regulating the electromagnetic compatibility of equipment
- Directive (97/23/EC) Pressure equipment directive.
- Directive (94/9/EC)
    - Applies to equipment and protective systems intended for use in potentially explosive atmospheres
    - Safety devices, controlling devices and regulating devices intended to use outside, potentially explosive atmospheres, but required for contributing to the safe functioning of equipment and protective system with respect to the risks for explosion.
- EN 60204-1: 2006 -Safety of machinery electrical equipment general requirements.
- BS EN ISO 14121: 2007- Safety of machinery. Risk assessment. Principles.
- BS EN 982- Safety of machinery. Safety requirements for fluid power systems and their components. Hydraulics.
- BS EN 60034-1:1998 - Rotating electrical machines. Rating and performance
- EN 287-1: 2004- Welders, Fusion welding, Arc welding, Welding, Steels, Approval testing, Acceptance (approval), Examination (education), Quality assurance systems, Test specimens, Testing conditions, Position, Welded joints, Certification (approval), Designations, Records
- EN ISO 15614-1:2004 - Specification and qualification of welding procedures for metallic materials. Welding procedure test. Arc and gas welding of steels and arc welding of nickel and nickel alloys
- ISO 7000:2004- Graphical Symbol for use on equipment-Index & synopsis
- ISO 9001:2008- Quality Management system

Appendix E – Gasification of tar-like compounds

Table below reports the complete list of 47 articles reviewed for analysis on re-gasification presented in section 7.1. Articles are grouped by specific argument.

TITLE	AUTHORS	JOURNAL	ISSUE	DATE
Gasification of heavy refinery residues				
Shall deep thermal conversion	AAVV	/	/	
Operation of ISAB energy and SARLUX IGCC projects	G. Collodi	Gasification technologies conference, San Francisco	/	2000
Black liquor gasification				
Performance of black liquor gasifier/gas turbine combined cycle cogeneration in the kraft and paper industry	E. D. Larson, S. Consonni	Making a Business from Biomass		1997
Pyrolysis and steam gasification processes of black liquor	A. Demirbas	Energy Conversion and Management	43	2002
A gasification-based biorefinery for the pulp and paper industry	S. Consonni, R.E. Katofsky, E.D. Larson	Chemical Engineering Research and Design	87	2009
CHP in the pulp industry using black liquor gasification: thermodynamic analysis	N. Berglin, T. Berntsson	Applied Thermal Engineering	18	1998
CHEMREC's atmospheric & pressurized BLG technology	M. Lindblom, I. Landälv	/	/	2007
Sewage sludge gasification				
Low-temperature pyrolysis of sewage sludge and putrescible garbage for oil production	L. Shen, D. Zhang	Fuel	84	2005
Gasification property of drect coal liquefation residue with steam	X. Chu, B. Li, H. Chen	Process Safety and Environmental Protection	84	2006
Utilization of sewage sludge in EU application of old and new methods—A review	D. Fytili, A. Zabaniotou	Renewable and Sustainable Energy Reviews	12	2008
Sewage sludge combustion	J. Werthera, T. Ogada	Progress in	25	1999

		Energy and Combustion Science		
High temperature steam gasification of wastewater sludge	N. Nipattummakul, I. Ahmed, S. Kerdsuwan, A.K. Gupta	Applied Energy	87	2010
Energy recovery from secondary pulp/paper-mill sludge and sewage sludge with suoercritical water tratment	L. Zhang, C. Xu, P. Champagne	Bioresource Technology	101	2010
Effect of moisture content in sewage sludge on air gasification	L. Xie, L. Tao, J. Gao, X. Gao, X. Wu, Y. Jiang	Journal of Fuel Chemistry and Technology	38	2010
Devolatilization and ash comminution of two different sewage sludges under fluidized bed combustion conditions	R. Solimene, M. Urciuolo, A. Cammarota, R. Chirone, P. Salatino, G. Damonte, C. Donati, G. Puglisi	Experimental Thermal and Fluid Science	34	2010
Three-dimensional modeling of a circulating fluidized bed gasifier for sewage sludge	I. Petersen, J. Werther	Chemical Engineering Science	60	2005
Combustion characteristics of sewage sludge in an incineration plant for energy recovery	T.Murakami, Y. Suzuki, H. Nagasawa, T. Yamamoto, T. Koseki, H. Hirose, S. Okamoto	Fuel Processing Technology	90	2009
The characterisation of tars produced during the gasification of sewage sludge in a spouted bed reactor	A. Adegoroye, N. Paterson, X. Li, T. Morgan, A.A. Herod, D.R. Dugwell, R. Kandiyoti	Fuel	83	2004
Combustible gas production from sewage sludge with a downdraft gasifier	"A. Midillia, M. Dogru, C.R. Howarth, M.J. Ling			
Teoman Ayhana"	Resources, Conservation and Recycling		2001	
Production of bio-fuels by high temperature pyrolysis of sewage sludge using conventional and microwave heating	A. Domınguez, J.A. Menendez , M. Inguanzo, J.J. Pıs	Bioresource Technology	97	2006

A review of methods for the thermal utilization of sewage sludge: The Polish perspective	S. Werle, R. K. Wilk	Renewable Energy	35	2010
Air-steam gasification of sewage sludge in a bubbling bed reactor: Effect of alumina as a primary catalyst	J.M. de Andrés, A. Narros, M.E. Rodríguez	Fuel Processing Technology	92	2011
Tar removal				
Connecting a steam fluidized bed to a high temperature gas reactor to reduce the methane and tar content of biomass syngas	S. Valin, S.Ravel, P. Castelli, E. Masson, A. Dufour, F. Defoort	17th European Biomass Conference and Exhibition	/	2009
DALHAM - OLGA Tar Removal Technology	AAVV	Technical Information Paper		2010
Resources, properties and utilization of tar	C. Li, K. Suzuki	Resources, Conservation and Recycling	54	2010
Syngas production through gasification and cleanup for downstream applications — Recent developments	P. Mondal, G.S. Dang, M.O. Garg	Fuel Processing Technology		2011
Tar reduction in biomass producer gas via mechanical, catalytic and thermal methods: A review	S. Anis, Z. A. Zainal	Renewable and Sustainable Energy Reviews	15	2011
OLGA Tar removal	J.W. Könemann, R. Zwart	Gasification Technology Conference, San Francisco	/	2007
Effect of reformer conditions on catalytic reforming of biomass-gasification tars	C.M. Kinoshita, Y. Wang, Jiachun Zhou	Ind. Eng. Chem. Res.	34	1995
The reduction and control technology of tar during biomass gasification/pyrolysis: An overview	J. Han, H. Kim	Renewable and Sustainable Energy Reviews	12	2008
Biomass tar recycling and destruction in a CFB gasifier	L.P.L.M. Rabou	Fuel	84	2005
Product and process innovation in the energy	F. Gulli	Energy Policy	23	1995

industry: The development of integrated tar gasification				
Bio oil gasification				
Steam gasification reactivity of char from rapid pyrolysis of bio-oil/char slurry	M. Sakaguchi, A.P. Watkinson, N. Ellis	Fuel	89	2010
Steam gasification of bio-oil and bio-oil/char slurry in a fluidized bed reactor	M. Sakaguchi, A.P. Watkinson, N. Ellis	Energy Fuels	24	2010
Production of synthesis gas by partial oxidation and steam reforming of biomass pyrolysis oils	D. Rennard, R. French, S. Czernik, T. Josephson, L. Schmidt	International Journal of Hydrogen Energy		2010
Challenges in the production of sustainable fuels from pyrolysis oil – Design of efficient catalysts for gasification of char	B.M. Güell, G. van Rossum, W.P.M. van Swaaij, S.R.A. Kersten, L. Lefferts, K. Seshan	Applied Catalysis B: Environmental	101	2011
Gasification of bio-oil and bio-oil/char slurry	M. Sakaguchi	PHD Thesis	/	2010
Catalytic and non catalytic gasification of pyrolyisis oil	Guu. van Rossum, S. Kersten, W. van swaaij	Ind. Eng. Chem. Res.		2007
Production of synthesis gas/high-btu gaseous fuel from pyrolysis of biomass-derived oil	S. Panigrahi, S.T. Chaudhari, N.N. Bakhshi, A.K. Dalai	Energy & Fuels	16	2002
Energy potential of producer gas				
Small industrial-scale producer gas units	A. Bliek, W.P.M. van Swaaij, K.R. Westerterp	Prog. Energy Combust. Sci.	10	1984
Banana biomass as potential renewable energy resource: A Malaysian case study	J.Y. Tock, C.L. Lai, K.T. Lee, K.T. Tan, S. Bhatia	Renewable and Sustainable Energy Reviews	14	2010
Thermochemical production of liquid fuels from biomass: Thermo-economic modeling, process design and process integration analysis	L. Tock, M. Gassner, F. Maréchal	Biomass and Bioenergy		2010
Thermochemical conversion of biomass to second generation biofuels through integrated process design—A	T. Damartzis, A. Zabaniotou	Renewable and Sustainable Energy Reviews	15	2011

review				
Contemporary issues in thermal gasification of biomass and its application to electricity and fuel production	L. Wanga, C.L. Weller, D.D. Jones, M.A. Hanna	Biomass and bioenergy	32	2008
Other				
Sulfur transfers from pyrolysis and gasification of direct liquefaction residue of Shenhua coal	X. Chu, W. Li, B. Li, H. Chen	Fuel	87	2008
Sustainable route to hydrogen – Design of stable catalysts for the steam gasification of biomass related oxygenates	B.M. Guëll, I.M. Torres da Silva, K. Seshan, L. Lefferts	Environmental	88	2009

Bibliography

[1] IEA, ""World Energy Outlook 2010"," International Energy Agency, Paris, 2010.

[2] Vaclav Smil, *Energy Transitions: History, Requirements, Prospects.*: Praeger, 2010.

[3] Jo Dewulf and Herman Van Langenhove, *Renewables-Based Technology*., 2006.

[4] Interceptor (Mad Max), 1979.

[5] R. Janssen D. Rutz, *Biofuel Technology Handbook*., 2008.

[6] Timothy F. Smith, Robert B. Mangoyana, "Decentralised bioenergy systems: A review of opportunities and threats," *Energy Policy,* pp. Pages 1286-1295, 2011.

[7] S. Cotana, G. Cavalaglio, "Recovery of vineyards pruning residues in an agro-energetic chain, ," in *15th European Biomass Conference & Exhibition*, 2007.

[8] I. Bernetti, "A methodology to analyse the potential development of biomass energy sector: an application in Tuscany," *Forest Policy and Economics*, pp. 415-432, 2004.

[9] Gaius Plinius Secundus, *Natural History (Naturalis Historia)*., AD 77–79.

[10] Maurizio Maggiani, "L'ulivo," *L'Unità*, November 1987.

[11] Armando Boccone. (2012, September) Risorse economia ed ambiente. [Online]. http://aspoitalia.wordpress.com/2012/09/30/le-radici-di-una-vecchia-fornace/

[12] Juan J. Hernández, Amparo Pazo, Julio López Magín Lapuerta, "Gasification and co-gasification of biomass wastes: Effect of the biomass origin and the gasifier operating conditions," *Fuel Processing Technology*, vol. 89, no. 9, pp. 828–837, September 2008.

[13] Leen Kuiper en Jan Oldenburger, "The harvest of forest residues in Europe," Probos , D15a, February, 2006.

[14] B., L. Kuiper, G. J. Nabuurs Meuleman, *EU forest for renewable energy to mitigate climat*. Utrecht: Ecofys, 2005.

[15] C.T. Wright, K.L. Kenney, J.R. Hess, "Cellulosic biomass feedstocks and logistics for ethanol production," *Biofuels, Bioprod. Bioref.*, pp. 1:181–190, 2007.

[16] P. Venturi, R.E.H. Sims, "All-year-round harvesting of short rotation coppice eucalyptus compared with the delivered costs of biomass from more conventional short season, harvesting systems," *Biomass and Bioenergy*, pp. 27–37, 2004.

[17] T. Kåberger, K. McCormick, "Key barriers for bioenergy in Europe: economic conditions, know-how and institutional capacity, and supply chain co-ordination," *Biomass and Bioenergy*, pp. pp. 443-452, 2007.

[18] Stefan Seuring Stefan Gold, "Supply chain and logistics issues of bio-energy production).," *Journal of Cleaner Production*, pp. pp. 32-42, 2011.

[19] Gianluca Cavalaglio, Stefano Cotana, Marbanera Marco, and Giraldi Daniele, "Valorizzazione energetica degli scarti di potatura dei vigneti,".

[20] Enrico Cini and Lucia Recchia, "Energia da Biomassa: un'opportunità per le aziende agricole," 2008.

[21] K. Aruga, T. Nitami, H. Kobayashi, H. Sakai, T. Yoshioka, "Energy and carbon dioxide (CO2) balance of logging residues as alternative energy resources: system analysis based on the method of a life cycle inventory (LCI) analysis)," *Journal of Forest Research*, vol. Vol. 10, no. No. 2 , pp. pp. 125-134, 2005.

[22] Mario Palumbo, Pacifico M. Pelagagge, Federica Scacchia Antonio C. Caputo, "Economics of biomass energy utilization in combustion and gasification plants: effects of logistic variables," *Biomass and Bioenergy,* vol. Volume 28 , no. Issue 1, pp. Pages 35–51, January 2005,.

[23] (2012, December) Wikipedia. [Online]. http://en.wikipedia.org/wiki/EROEI#cite_note-mh2010-1

[24] "Designing a regional forest fuel supply network," *Biomass and Bioenergy*, vol. 31, no. 6, pp. 393–402, June 2007.

[25] Martin Schneider John A. Jacobs III. (2009, May) Cogeneration application considerations - GE Energy. [Online]. http://site.ge-energy.com/prod_serv/products/tech_docs/en/downloads/GER3430G.pdf

[26] Joel Puncochar. (2008) Evaluating cogeneration for your facility. [Online]. http://www.cumminspower.com/www/literature/technicalpapers/PT-7018-EvaluatingCogen-en.pdf

[27] Sergio Martínez, Miquel Rigola, Joan Rieradevall, Assumpció Anton, Juan Carrasco, Pilar Ciria, Xavier Gabarrell Carles M. Gasol, "Feasibility assessment of poplar bioenergy systems in the Southern Europe," *Renewable and Sustainable Energy Reviews*, vol. 13, no. 4, pp. 801–812, May 2009.

[28] A. Kumar, D.D. Jones, and M.A Hanna, "Thermochemical Biomass Gasification: A Review of the Current Status of the Technology," *Energies* , vol. 2, , no. 556-581., 2009.

[29] Klass D.L., *Biomass for renewable energy, fuels, and chemicals.*. San Diego: Academic Press, 1998.

[30] Jian Chang, Yanjun Guan, Honggang Chen, Yongping Yang, Jianchun Jiang Kai Zhang, "Lignocellulosic biomass gasification technology in China," *Renewable Energy,* , vol. Volume 49, no. Pages 175–184, 2013.

[31] Prabir Basu, *Biomass Gasification and Pyrolysis : Practical Design and Theory*.: Elsevier, 2010.

[32] S. Dasappa and H.S. Mukunda, *Biomass to Energy*. Bangalore: Aditya Printers, 2003.

[33] CGPL @ Glance . [Online]. http://cgpl.iisc.ernet.in/site/Default.aspx

[34] Roberto Mussi, David Chiaramonti, Francesco Martelli, and S. Dasappa, "Installation of an open top twin fire biomass gasifier in Tuscany.," in *Atti del 66° Congresso Nazionale ATI (Associazione Termotecnica Italiana),* Cosenza, 2011.

---

[35] D. N. Subbukrishna, K. C.Suresh, P. J. Paul, G. S. Prabhu S. Dasappa, "Operational experience on a grid connected 100 kWe biomass gasification power plant in Karnataka, India.," *Energy for sustainable development*, 2011.

[36] H. S., Dasappa, S., Paul, P. J., Rajan, N. K. S. and Shrinivasa, U. Mukunda, "Gasifiers and combustors for biomass–technology and field studies.," , 1994, pp. 27–38.

[37] P.J. Paul, S. Dasappa, U. Shrinivasa, H. Sharan, R. Buehler, P. Hasler, H. Kaufmann H.S. Mukunda, "Results of an Indo-Swiss programme for qualification and testing of a 300-kW IISc-Dasag gasifier," *Energy for Sustainable Development*, vol. 1, no. 4, pp. 46–49, 1994.

[38] M Jayamurthy, S Dasappa, G Sridhar, H V Sridhar, H S Mukunda, P J Paul, ""Tar characterisation in new generation agro-residue gasifier-cyclone and downdraft open top twin air entry systems"," in *Biomass Gasification and Pyrolysis: State of the Art and Future prospects*. U.K.: CPL Press, 1997.

[39] P. J. Paul, H. S. Mukunda, N. K.S. Rajan, H. V. Sridhar S. Dasappa, "Biomass gasification technology – a route to meet energy needs.," *Current Science*, vol. Vol 87, no. No.7, 2004.

[40] S. Chopra and A. Jain., "“A Review of Fixed Bed Gasification Systems for Biomass”.," *Agricultural Engineering International: the CIGR Ejournal.*, vol. Vol. IX., no. No. 5, 2007.

[41] H V Sridhar, S Dasappa, P J Paul, N K S Rajan and H. S. Mukunda G Sridhar, "Development of producer gas engines," in *Proceedings of the Institution of Mechanical Engineers, Part D: Journal of Automobile Engineering*, 2005, pp. 423-438.

[42] AspenTech. Aspen Plus®. [Online]. http://www.aspentech.com/products/aspen-plus.aspx

[43] TU Delft (Delft University of Technology). Cycle-Tempo. [Online]. http://www.cycle-tempo.nl/

[44] Evans RJ, Abatzoglou N Milne TA, "Biomass gasifier "Tars": their nature, formation and conversione," NREL, Golden, NREL/TP-570-25357, 1998.

[45] ECN-Biomass. (2009, June) Thersites: the ECN tar dew point site. [Online]. http://www.thersites.nl/classification.aspx

[46] Kenzi Suzuki Chunshan Li, "Resources, properties and utilization of tar," *Resources, Conservation and Recycling*, vol. 54, no. 11, pp. 905–915, 2010.

[47] Jun Han and Heejoon Kim, "The reduction and control technology of tar during biomass gasification/pyrolysis: An overview," *Renewable and Sustainable Energy Reviews*, pp. 397–416, 2008.

[48] T. Hanaoka, S. Inoue, S Uno, T. Ogi, and T. Minowa, "Effect of woody biomass components on air- steam gasification. ," *Biomass Bioenergy*, vol. 28, pp. 69–76, 2005.

[49] M.P. Domínguez, M. Hernández, F. Sanz-Pérez G. San Miguel, "Characterization and potential applications of solid particles produced at a biomass gasification plant," *Biomass and Bioenergy*, vol. 47, pp. 134–144, December 2012.

[50] Rondo Cameron and Larry Neal, *Storia economica del mondo - Dalla preistoria al XVII secolo*.: Oxford press, 1989.

[51] David Sutton, Brian Kelleher, and Julian R.H. Ross, "Review of literature on catalysts for biomass gasification," *Fuel Processing Technology 73*, pp. 155-173, 2001.

[52] R.W.R. Zwart B.J. Vreugdenhil, "Tar formation in pyrolysis and gasification ," ECN - Energy research Centre of the Netherlands , Petten, ECN-E--08-087, June 2009.

[53] Ziad Abu El-Rub, *Experimental Comparison of Biomass Char with other Catalysts for Tar Reduction*., 2008.

[54] Kalkunte S. Seshadri and Abolghasem Shamsi, "Effects of Temperature, Pressure, and Carrier Gas on the Cracking of Coal Tar over a Char-Dolomite Mixture and Calcined Dolomite in a Fixed-Bed Reactor," *Ind. Eng. Chem. Res.*, pp. 3830-3837, 1998.

[55] P. Gilbert, C. Ryu, V. Sharifi, and J. Swithenbank, "Tar reduction in pyrolysis vapours from biomass over a hot char bed," *Bioresource Technology*, pp. 6045–6051, 2009.

[56] Peder Brandt, Elfinn Larsen, and Ulrik Henriksen, "High Tar Reduction in a Two-Stage Gasifier," *Energy & Fuels*, pp. 816-819, 2000.

[57] Sou Hosokai et al., "Mechanism of decomposition of aromatics over charcoal and necessary condition for maintaining its activity," *Fuel*, pp. 2914–2922, 2008.

[58] Tae-Young Mun, Jin-O Kim, Jin-Won Kim, and Joo-Sik Kim, "Influence of operation conditions and additives on the development of producer gas and tar reduction in air gasification of construction woody wastes using a two-stage gasifier," *Bioresource Technology*, 2011.

[59] Z. Abu El-Rub, E. A. Bramer, and G. Brem, "Review of Catalysts for Tar Elimination in Biomass Gasification processes," *Ind. Eng. Chem. Res.*, pp. 6911-6919, 2004.

[60] Duo Wang, Wenqiao Yuan, and Wei Ji, "Char and char-supported nickel catalysts for secondary syngas cleanup and conditioning," *Applied Energy*, pp. 1656–1663, 2011.

[61] M. J. Castaldi N. Klinghoffer, "Deactivation and energy analysis of char catalysts in biomass gasification systems," in *Proceedings of the 20th Annual North American Waste-to-Energy Conference*, Portland, Maine, USA, 2012, pp. NAWTEC20-7036.

[62] V. Sivaramakrishnan, R. Nalini, T. Sekar, M. Premalatha, P. Subramanian V. Kirubakaran, "A review on gasification of biomass," *Renewable and Sustainable Energy Reviews*, vol. 13, pp. 179-186, 2009.

[63] Jie Chang , Tiejun Wang , Yan Fu , Yong Chen Pengmei Lv, "Hydrogen-rich gas production from biomass catalytic gasification," *Energy Fuels* , vol. 18, no. 1, pp. 228–233, 2004.

[64] Ajmal Latif Sergio Rapagnà, "Steam gasification of almond shells in a fluidised bed reactor: the influence of temperature and particle size on product yield and distribution," *Biomass and Bioenergy*, vol. 12, no. 4, pp. 281–288, 1997.

[65] G. Koufodimos, Z. Samaras and A. Zabaniotou V. Skoulou, "Low temperature gasification of olive kernels in a 5 kW fluidized bed reactor for H2-rich producer gas," *International Journal of Hydrogen Energy*, vol. 33, pp. 6515 - 6524, 2008.

[66] Prabir Basu, *Biomass gasification and pyrolysis - Practical design and theory*.: Elsevier Inc, 2010.

[67] A. Orio, M. P. Aznar, J. Corella I. Narvaez, "Biomass gasification with air in an atmospheric bubbling fluidized bed. Effect of six operational variables on the quality of the producer raw gas," *Industrial & Engineering Chemistry Resaerch*, vol. 35, pp. 2110-2120, 1996.

[68] Walt R, Ellis S, Das A, Deutch S Reed TB, "Superficial velocity - The key to downdraft gasification," in *4th Biomass Conference of the Americas*, Oakland, CA, 1999.

[69] H Kozu, S Yamagata, N Murao, S Ohta, S Shiya,T Ohba T Yamazaki, "Effect of Superficial Velocity on Tar from Downdraft Gasification of Biomass," *Energy & Fuels*, vol. 19, pp. 1186-1191, 2005.

[70] Y. Wang, J. Zhou C.M. Kinoshita, "Tar formation under different biomass gasification conditions," *Journal of Analytical and Applied Pyrolysis*, vol. 29, no. 2, pp. 169–181, August 1994.

[71] Claes Brage, Guanxing Chen, Krister Sjöström Qizhuang Yu, "Temperature impact on the formation of tar from biomass pyrolysis in a free-fall reactor," *Journal of Analytical and Applied Pyrolysis*, vol. 40–41, pp. 481–489, Mat 1997.

[72] Ramesh Sharma, Mohammad Hajaligol Thomas McGrath, "An experimental investigation into the formation of polycyclic-aromatic hydrocarbons (PAH) from pyrolysis of biomass materials," *Fuel*, vol. 80, no. 12, pp. 1787–1797, October 2001.

[73] M.C. Juárez, M.P. Morales, P. Muñoz, M.A. Mendívil J.A. Ruiz, "Biomass gasification for electricity generation: Review of current technology barriers," *Renewable and Sustainable Energy Reviews*, vol. 18, pp. 174–183, February 2013.

[74] A. Datta, N. Chakraborty Prokash C. Roy, "Modelling of a downdraft biomass gasifier with finite rate kinetics in the reduction zone," *International Journal of Energy Research*, vol. 33, pp. 833-851, 2009.

[75] Yimeng Zhang, Qisheng Zhang, Yongbiao Qu, Jianbin Zhou, Hengfei Qin Zhongqing Ma, "Design and experimental investigation of a 190 kWe biomass fixed bed gasification and polygeneration pilot plant using a double air stage downdraft approach," *Energy*, vol. 46, no. 1, pp. 140–147, October 2012.

[76] T. B. Reed, R. Walt, S. Ellis, A. Das, and S. Deutch, "Proceedings of the 4th Biomass Conference of the Americas," , Oakland, California, 1999, pp. 1001-1007.

[77] T. B. Reed and S. Gaur,. Golden, CO: ERL and BEF, Inc., 2001.

[78] Electo Eduardo Silva Lora, Rubenildo Viera Andrade, René Lesme Jaén Juan Daniel Martínez, "Experimental study on biomass gasification in a double air stage downdraft reactor," *Biomass and Bioenergy*, vol. 35, no. 8, pp. 3465–3480, August 2011.

[79] A. Das T.B. Reed, "Handbook of biomass downdraft gasifier engine systems," Solar Energy Research Institute, Golden, ISBN 1-890607-00-2, 1988.

[80] Roberto Mussi. (2013, January) Electricity from forestry and agricultural residues. [Online]. http://energyunforeseen.blogspot.it/2013/01/electricity-from-forestry-and.html

[81] S.V.B. Kiel, J.H.A. Paasen, "Tar formation in a fluidised-bed gasifier," ECN, March, 2004.

[82] P. Hasler, "Producer gas quality from fixed bed gasifiers before and after gas cleaning," Zurich, Proceedings of the IEA Thermal Gasification. Seminar – IEA Bioenergy and Swiss Federal Office of Energy, 1997.

[83] K. Suzuki C. Li, "Resources, properties and utilizations of tar," *Conservation and Recycling*, vol. 54, pp. 905-915, 2010.

[84] CONCAWE's Petroleum Products and Health Management Groups, "Heavy fuel oils," Brussels, Product dossier no. 98/109, 1998.

[85] G. Que B. Shi, "Chemical structure change of re cycling vacuum bottom residue from slurry-bed hydrocracking of Karamay atmospheric residue in the pilot plant," in *The 226th ACS National Meeting, New York, NY, September 7-11, 2003*, New York, 2003.

[86] M.S. Rana, E. Furimsky J. Ancheyta, "Hydroprocessing of heavy petroleum feeds: Tutorial," *Catalysis Today*, vol. 109, pp. 3-15, 2005.

[87] E. Furimsky, "Gasification in Petroleum Refinery of 21st Century," *Oil & Gas Science and*

Technology, vol. 54, no. 5, pp. 597-618.

[88] A.V. Bridgwater, "Review of fast pyrolysis of biomass and product upgrading," *Biomass and bioenergy*, vol. 38, pp. 68-94, 2011.

[89] A.V. Bridgwater S. Czernik, "Overview of Applications of Biomass Fast Pyrolysis Oil," *Energy & Fuels*, vol. 18, pp. 590-598, 2004.

[90] S.R.A. Kersten, W.P.M. van Swaaij G. van Rossum, "Catalytic and noncatalytic gasification of pyrolysis oil," *Industrial and Engineering Chemistry Research*, vol. 46, no. 12, pp. 3939-3967, 2007.

[91] E. Warsaw Henrich, "The status of the FZK concept of biomass gasification.," in *2nd European Summer School On Renewable Motor Fuels.*, 2007.

[92] Masakazu Sakaguchi, Gasification of bio-oil and bio-oil/char slurry, tesi di dottorato in Chemical and Biological Engineering, University of British Columbia, Aprile 2002.

[93] S.T. Chaudari, N.N. Bakhshi, A.K. Dalai S. Panigrahi, "Production of Synthesis Gas/High-Btu Gaseous Fuels from Pyrolysis of Biomass-Derived Oil," *energy & Fuels*, vol. 16, pp. 1392-1397, 2002.

[94] Kevin Whitty, "Black Liquor Gasification: Development and Commercialization Update," in *2005 ACERC Conference*, 2005.

[95] Luc Robou, "Biomass tar recycling and destruction in a CFB gasifier," *Fuel*, vol. 84, pp. 577-581, 2005.

[96] Anja Oasmaa and Cordner Peacocke, "A guide to physical property characterisation of biomass-derived fast pyrolysis liquids.," VTT Energy., 2011.

[97] Anja Oasmaa, D.C. Elliott, and S. & Müller, "Quality Control in Fast Pyrolysis Bio-Oil Production and Use. ," *Environmental Progress & Sustainable Energy*, vol. 28, no. 3, pp. 404 – 409, 2009.

[98] Mirandola A, Altafini CR, "A chemical equilibrium model of the coal gasification process based on the minimization of the Gibbs free energy, in: , , Italy, ," in *Proceedings of Flowers'97*, Florence, 1997, pp. pp. 419–427.