PRODUCTION OF HYDROGEN-RICH GAS BY BIOMASS GASIFICATION
APPLICATION TO SMALL SCALE, FUEL CELL ELECTRICITY GENERATION IN RURAL AREAS

P.U. Foscolo

UNIVERSITY OF L'AQUILA

Contract JOR3-CT95-0037

PUBLISHABLE FINAL REPORT

January 1, 1996 to December 31, 1997

Research funded in part by
THE EUROPEAN COMMISSION
in the framework of the
Non Nuclear Energy Programme
JOULE III

Abstract

The research project is addressed to a preliminary technical and economic evaluation of a small/medium capacity biomass-to-energy system, based on gasification processes able to convert under proper conditions the energy of biomass directly to hydrogen, which is utilised for electricity and heat generation in fuel cell modular units. The siteability of the integrated system in rural areas is also investigated.

Two different gasification technologies are considered: the *entrained flow* gasifier, originally developed by NOELL Energie und Entsorgungstechnik GmbH for the conversion of residual and waste materials; the catalytic *dual interconnected fluidised bed* system, developed by University College London (UCL) on the base of experimental tests of fluidised bed biomass gasification previously performed at the University of L'Aquila (UNIVAQ). All *gas cleaning* operations have been identified and quantified in details. The results of the work carried out show that the integrated plant envisaged in the original proposal is technically feasible by means of both gasification systems, with considerable advantages linked to the high level of integration that can be obtained between the gasification and the electricity production sub-systems. Net electric efficiencies higher than 30 % are readily obtainable, with additional thermal power available for district heating or different utilities.

The catalyst characterisation and reactivity tests carried out at University Louis Pasteur of Strasbourg (ECPMS) have shown that trimetallic perovskite structures are able to assure high yield and selectivity for the conversion of tar and methane, with low levels of carbon build-up on the active surfaces and negligible sintering phenomena. A sample of such catalyst has been tested in a secondary fixed bed reactor downstream of a bench-scale *fluidised bed* gasifier, with very positive results: more than 2 Nm^3 of dry gas have been obtained per kg of biomass d.a.f., with a hydrogen content of about 60 % by volume and less than 0.3 g/Nm^3 of tar.

Hydrogen fed 850 kW phosphoric acid fuel cell (PAFC) modules are considered. They are studied by CLC s.r.l., based on the 200 kW natural gas units presently commercialised in Europe.

The data produced by ABIOTEC, the Emilia Romagna Agency for promotion of new agro-industrial systems, show that biomass sources can be identified, specifically from among the perennial crops (arundo donax, miscanthus), which are compatible with either the technical requirements of the integrated system (among these: moisture level, sulphur content, feedstock size range), and the considered local rural context; they allow a *round the year* utilisation of the electricity generation plant, with logistically and economically reasonable solutions for biomass storage and transportation.

Cost estimates have been performed, both for a small scale application based on a single PAFC module, and for a medium size plant based on 10 PAFC modules, which gives sensitivity to the system scaling-up. The analysis shows in general high investment and operation costs, which were expected as a result of joining new technologies (gasification and fuel cells), both at their first market entry. With a single 850 kW module system, revenues do not even balance overall running costs (investment, operation, maintenance, taxes and insurance). The larger plant with the *dual fluidised bed* gasifier hits the target of power production costs slightly lower than the selling price of the electric kWh obtained from renewable energy sources. These costs are obviously expected to reach more acceptable levels as new technologies come to the market and get beneficial effects from operation experience and increasing production volumes.

Partnership

UNIVAQ	Dipartimento di Chimica, Ingegneria Chimica e Materiali University of L'Aquila, Italy (Coordinating Institution) Prof. P.U. Foscolo - Email: foscolo@ing.univaq.it
ECPMS	Ecole de Chimie, Polymeres et Materiaux University of Strasbourg, France Prof. A. Kiennemann - Email: kiennemann@chimie.u-strasbg.fr
UCL	Department of Chemical and Biochemical Engineering University College London, United Kingdom Prof. J.G. Yates - Email: john.yates@ucl.ac.uk
ABIOTEC	Emilia Romagna Research Agency for Agriculture and Biotechnology Cervia, Italy Dr. A. Belletti - Email: abelletti@mail.asianet.it
CLC	CLC Srl, Ansaldo Group, Genova, Italy Dr. Ing. G. Caserza - Email: spadini@ansaldo.it
NOELL	NOELL-KRC Energie-und Umwelttechnik GmbH, Germany Dr. Ing. R. Warnecke - Email: WARNECKE.WU@NOELL.DE

1. Introduction

The development of small size, high efficient bio-electric generators, obtained by integrating Biomass Gasification (BG) with Fuel Cells (FC), is considered as an effective tool for introduction in rural areas of an innovative process, which is addressed to the implementation of major Community policies in the fields of environment, agriculture and energy production.

Systems resulting from the use of FC technology, which allows low pressure operation of the gasification process and a very simple arrangement of the overall process, would assure optimum siteability in rural areas, resulting in small size, easy to operate, modular, standard design units, with environmental impact lower than any other technology can give. This would make BG-PAFC systems very attractive for many small agricultural industries, thus opening the market to the relatively large volumes necessary to reduce the high investment costs which characterise new technologies at their market entry.

As an additional consideration, is worth stressing that bio-electric systems, such as the objective of this study, offer an opportunity for regional development, because they will contribute to the solution of the problem of electric power delivery to large areas of less developed regions, where biomass sources are abundant and electrification is poor.

2. The objectives of the RTD project

The main objective of this research project is the development of a biomass thermo-chemical conversion process to produce hydrogen-rich gas for fuel cell electricity generation, in a small scale unit (850 kWel.), located in rural areas of Emilia Romagna in Italy.

The activities involve a feasibility study of the coupling of a Biomass Gasification (BG) process with Phosphoric Acid Fuel Cells (PAFC), as well as laboratory investigations addressed to key issues of the fluidised bed gasification process (the catalytic conversion of tar and methane, the solid mixing and circulation in the *dual interconnected* gasifier).

The research project has been completed over 24 months, as it was originally planned. This Report covers the cooperative activities carried out, with reference to the technical development of the integrated system envisaged in the original proposal, as well as the characterisation of its siteability in the rural context.

3. Synthetic description of the integrated system for electricity generation

- **the phosphoric acid fuel cell module**

Phosphoric acid fuel cell (PAFC) technology was chosen because it is the only readily available fuel cell technology, with known proved characteristics derived from field operation. Its integration into a hydrogen producing biomass gasification system appears to be simple and advantageous, considering its low (practically ambient) operating pressure, tolerability to fuel pollutants (such as CO), easy operation with independent, not manned system control that makes it adequate for installation in the agricultural environment of small to medium size farms where the biomass can be easily found.

Natural gas phosphoric acid fuel cells plants are available at precommercial level in small cogeneration units for on-site application, while some MW size plants have been installed and are operating successfully. The operation experience of several installations all over the world guarantees their reliability, as well as their characteristics of quite long term, all automatic operation, and minimum environmental impact.

The hydrogen fed PAFC module considered for this project has a nominal power capacity of 850 kW(e), and is derived from the 200 kW PC25 packaged fuel cell power plant presently commercialised in Europe by CLC. Its new design is obtained using four PC25 stacks in a single module, with proper process arrangements for feeding it with hydrogen rich mixtures, and with a better interface with hydrogen producing processes.

For the BG-PAFC system, proper adaptations to specific operating conditions have been studied. The FC cogeneration system consists of the following functions:

- the FC Module (FCM), of standard and modular construction, which provides the conversion of the hydrogen coming from the biomass gasification system into electrical energy and heat. The FCM is arranged as a skid unit that provides the basement and housing for the four FC stacks, the process systems, the control system, and the electrical systems. The control system assures unmanned automatic operation, including the shut-down sequences in case of internal or external malfunction. FCM operating data and event logging are available for acquisition on an external remote centralised console.

- the Site Service Systems (SSS), which includes the auxiliaries necessary for the operation of the FCM connecting it physically and functionally to the external interfaces. While FCM is a standard unit, produced on a series basis, the SSS has to be designed for each specific installation, according to the local requirements.

The operation of the biomass gasification and gas conversion systems does not affect the FCM that bases its own operation on the availability/unavailability of the fuel, auxiliaries and heat/power loads with self adjustment of the operating parameters and auto monitoring of the operation safety.

The FCM requires minimal maintenance because of a very reduced number of movable parts. The routine maintenance of conventional equipment has to be performed according to the original manufacturer specifications. Nitrogen bottles and chemicals for the water clean-up system are the only auxiliary consumable needed. The major operating cost is related to the change of the FC stack, the nominal life of which is estimated to be five years; the criterion to determine the proper time for FC stack change is based on the evaluation of the residual performance.

The external connections of the PAFC system are all arranged through the SSS; the main process connections are related to the hydrogen supply and return lines, and hot water in and out lines. The auxiliary connections refer to the hydrogen supply line for fuel conduits washing during shutdown, instrument air, start-up steam, and make-up of demineralised water.

The electrical interfaces mainly consist of the power output line and the auxiliary power supply. The electrical interfaces characteristics will be defined according to the site requirements: it is possible to use the FCM as grid independent or connected system with values for frequency and voltage chosen according to the local utility.

FCM and SSS are both supplied as skid mounted units, preferably with standard ISO container size, to be positioned on concrete pads or plates at a suitable height to avoid flooding if any. Access ways are to be provided around the installation area for access by crane during the maintenance operation for the change of the stack.

The control system for fully automatic operation is provided with operator control interfaces connected to site plant control, and able to exchange information necessary for the correct operation in any operating conditions, including upset and failure operating conditions.

The main interface data and the requirements on the fuel composition (in terms of minimum hydrogen content and maximum concentrations allowed for the impurities), at nominal operating conditions, are known in details, referred to a single PAFC module.

- **input data for the biomass gasification system**

The development of two different biomass gasification processes has been considered, for the BG-PAFC integrated system: the *entrained flow* gasifier, operating at high temperature, and utilising pure oxygen for the necessary input of heat, and the *dual interconnected fluidised bed* steam gasifier. This choice follows from the research programme and involves the expertise of the Contractors in entrained flow and fluidised bed thermal conversion processes, respectively.

Biomass feedstock specifications have been also fixed, on the base of data concerning four different biomass types: *Sorghum bicolor, Mischantus sinensis, Arundo donax* and *Cynara cardunculus.* The raw chemical composition is not very sensitive to biomass type, therefore the following average figures (weight %) have been chosen as a reference for the material and energy balances:

- carbon (C): 36% (fixed 18 %)
- hydrogen (H): 4%
- oxygen (O): 33%
- nitrogen (N): 0.85%
- chlorine (Cl): 0.1%
- sulphur (S): 0.05%
- humidity (H_2O): 20%
- mineral ash: 6%
- lower calorific value: 17.5 MJ/kg d.a.f. (dry and ash free)

It has been assumed that the average size of the biomass available at the plant site is 30±10 mm. A biomass average density of 130 kg/m^3 has been also assumed, according to experimental data for materials arranged in rotobails.

One major point of investigation is related to the presence of sulphur, not only for the stringent requirements imposed by the PAFC specifications, but also because of the potential poisoning effect of this element on any catalytic conversion step. The data available in the literature on the sulphur content in biomass feedstocks are not very reliable and often contradictory. Therefore direct experimental evidence has been gathered on this point, by checking the sulphur content on samples of the 1996 harvest of annual and perennial energy crops in Emilia Romagna. In the biomass composition given above the sulphur content has been fixed equal to that found for *Mischantus* and *Arundo donax*.

- **the *entrained flow* gasification system**

The pressure gasification of pulverised solid fuels, based on the principle of partial oxidation in the entrained flow, was originally developed for gasification of coal and lignite, and further extended to the thermal treatment of solid and fluid wastes. The purpose here has been to study the applicability of *entrained flow* gasification as part of a system which produces electricity from biomass by fuel cells. Various treatment steps are involved:

- biomass pretreatment, including receipt, storage, shredding, grinding and dense flow feeding;
- pressure gasification, including oxygen production;
- quenching and scrubbing;
- desulphurisation;
- catalytic conversion of carbon monoxide to hydrogen and carbon dioxide;
- carbon dioxide scrubbing;
- electricity production by fuel cells.

The biomass is converted with technical oxygen by a flame reaction at about 1500 °C into a raw gas containing mainly carbon monoxide and hydrogen, and almost free of hydrocarbons as well as of chlorinated hydrocarbons. The mineral matter of the fuel is converted into a molten slag which leaves the gasifier downwards in parallel flow with the hot gas. Raw gas and slag are cooled by direct contact with water (quenching).

The gasifier reaction chamber is enclosed by a cooling tube screen that is refractory-lined with a SiC-based ramming mass. The liquid slag solidifies on the ramming mass and forms a layer which is an effective anticorrosive coat and ensures maintenance intervals of between 5 and 10 years.

After quenching the raw gas is cleaned and saturated with water in a washing process. The scrubber removes dust and acidic components, such as chloride and fluoride, almost completely.

In order to heat up the gas before it is supplied to the ZnO-reactor for desulphurisation, it has to pass through a heat exchanger. For gas preheating, waste heat of the gas stream leaving the first CO-shift reactor is used. The steam needed for the CO conversion is supplied by the waste heat from the second CO-shift reactor.

As it has been anticipated above, the CO-shift process consists of two reaction steps. The first step is performed at about 400 °C, the second at 250 °C. Both reactors are filled with commercially available catalysts. At the end of this process carbon monoxide is transformed to hydrogen and carbon dioxide by means of an exothermic reaction. Therefore, the major components of the reformed gas are carbon dioxide, hydrogen and water.

The gas now needs to be cooled down to 60 °C before it is taken into the carbon dioxide scrubber. The removal of carbon dioxide is performed in two steps, by using a water solution of potassium carbonate. Potassium-hydrogen carbonate is formed in the liquid phase, and the gas leaving the scrubber is almost free of carbon dioxide. When the adsorbent solution has been saturated, in order to reuse it, the liquid mixture is heated and potassium-hydrogen carbonated is transformed back again into carbon dioxide, water and potassium carbonate, with a complete regeneration process. Carbon dioxide is released into the atmosphere. Finally, the fuel gas is available for feeding the PAFC module.

The schematic flow sheet shown in Fig. 1 gives an overview of the overall process with the main streams. Starting with the different sub-systems, the tentative mass balance has been calculated for each of them and finally, the total system has been considered. The same procedure has been adopted for the energy balance.

- **the *dual interconnected fluidised bed* gasification system**

In this case the thermal conversion of biomass is accomplished at less severe operating conditions than those needed in the NOELL gasification process (temperature level of about 800 °C and pressure slightly above atmospheric); on the other hand, an additional catalytic conversion is necessary to reduce drastically tar components, under the very strict limits required by the fuel cell, and to produce more hydrogen from the methane obtained in the gasification process. The presence of steam helps the cracking and reforming processes of a substantial amount of the tar components formed as a result of the biomass particles devolatilisation.

The gasifier is a fluidised bed which is connected to a second fluid bed in which residual char from the first unit is combusted. Bed material is circulated between the two units so that the heat generated in the combustion section is used to provide the energy needed for the endothermic gasification. This arrangement has the additional advantage that all the char left in the gasifier (some of it deposited on the sand particles) can be easily transferred to the combustor together with the sand, and burnt there. The operating conditions for the gasifier have been fixed according to the results of the experiments carried out with a bench scale facility.

The sand circulation flux is a variable which can be used to optimise the process. The greater the flux the closer will be the temperature of gasifier and combustor. Calculations showed that for a temperature difference between the two units of 150 - 200 °C the sand circulation rate would be in the range 15000 - 20000 kg/hr. In the combustor both the char and the hydrogen unused by the fuel cell are burnt to provide the necessary energy for the gasification reactions.

Fig. 1. **Schematic flow sheet of the *entrained flow* gasification process.**

Fig. 2. **Flow sheet for the *dual interconnected fluidised bed* process.**

The downstream gas clean-up system consists essentially of a fixed-bed catalytic reactor for conversion of methane and higher hydrocarbons in the product stream and, as it has been already described above with reference to the *entrained flow* gasification system, of a water scrubbing unit, a desulphurisation unit, and a two stage water-gas shift reactor system for the conversion of carbon monoxide. There is no need in this case of the operation for carbon dioxide removal because the hydrogen concentration in the product gas is high enough to be compatible with the requirements of the fuel cell. A cyclone is positioned at the exit of the gas stream from the gasifier, to remove most of the particulate matter elutriated from the fluidised bed (mainly volatile ash).

The perovskite-based catalyst used in the fixed bed reactor for the conversion of methane and tar has been developed in the course of the research project; the working temperature of the catalyst is of the order of 800 °C.

The process flow sheet is shown in Fig. 2. Material and heat balances have been performed for a biomass feedstock with a moisture content of 20% by weight. The process electric efficiency (net kWel. produced/kWth. of biomass feedstock) is slightly above 30%. Thermal energy is also available for external uses (such as heating): the flue gases leave the plant at a temperature of 400-500 °C, the water shift reactor is exothermic and heat needs to be removed from that section of the plant, and finally the fuel cell module produces steam in excess of the requirements of the gasification process.

The combustion-gasification system has been dimensioned in details, and the pressure distribution around the solid circulation loop has been checked, by estimating the pressure drops due to weight of solid, frictional and acceleration losses.

4. Accompanying laboratory investigations

- **catalyst development and characterisation**

At the outlet of the fluidised bed gasifier, the gas is composed mainly by 40% of steam (on a volume base) and 60 % of permanent gases, including H_2 (45%), CO (20%), CO_2 (25%) and CH_4 (9%); hydrocarbures (saturated and aromatic ones) are also present (tar). The goal of the catalytic conversion step is to enhance the hydrogen content by reforming methane and tar components, utilising a catalyst having a good activity in the transformation of the outlet mixture (principally methane) and a good stability in time.

The literature shows that a catalyst allows to decrease significantly the reaction temperatures and that nickel deposited on a support is the best one compared to other metals. However Ni/Al_2O_3, the classical catalyst, loses rapidly its activity due to coke formation and poisoning of the nickel active sites. A different type of catalyst, Ni/CaO, loses activity because of the carbonatation of the calcium oxyde and the covering of the active sites.

Perovskite type catalysts containing Nickel and other elements of the periodic table, such as $LaNiO_3$, have a good activity for the steam reforming reaction and have a structure relatively stable with temperature, towards CO_2 and H_2O and under oxidative conditions. In this project, after several tests carried out with $BaNiO_3$ and $LaNiO_3$, the work has been addressed at the study of a series of mixed, trimetallic perovskites, in order to observe the effect of nickel content on syngas formation. In the structure the active element (Ni) is well dispersed and can be progressively reduced to give a system where the sintering of nickel particles is limited.

The catalysts prepared via a sol-gel method were characterised before and after tests by several procedures: by X-Ray Diffraction (XRD) to identify the different phases, by IR-Spectroscopy to individuate functional groups, by a dynamic method of nitrogen adsorption to determine their BET specific surface areas, by Temperature Programmed Reduction (TPR) to obtain information on the reduction of the structures, and by Temperature Programmed Desorption of CO_2 (TPD CO_2) to test the stability of the structures towards CO_2. Methane reforming tests were also performed to evaluate the reactivity of the catalysts.

The activity of the catalyst in the reforming reactions of methane depends on the temperature. The catalyst shows activity if some nickel sites are accessible to the gases, so at least part of the nickel should be reduced. However, this reduction occurs in situ during the oxyreforming and the dry reforming of methane, so the catalyst does not need to be previously reduced for these reactions. On the other hand, a previous reduction of the catalyst is necessary to observe activity in the case of the steam reforming reaction.

The first trials were made with **$BaNiO_3$** and the results obtained where rather disappointing. $BaNiO_3$ shows several disadvantages: its preparation is difficult, it has a weak activity and it is not stable under the reaction conditions. In a reductive atmosphere, the perovskite structure $BaNiO_3$ disappears at about 530 °C to form stable $BaCO_3$ and Ni metal. As soon as carbonates have been formed, $BaCO_3$ seems to cover nickel particles like a capsule and the metal is not accessible to the reactant any more. This could explain why the yield of CO in the oxyreforming of methane was very low. For all these reasons, a different catalyst, less sensitive to carbonates formation was chosen, by replacing the earth alkaline barium with the rare earth lanthanum.

No carbonate peak appeared on the IR-spectrum of **$LaNiO_3$** and the peaks corresponding to the perovskite structure were evident, for wavelengths equal to 400 and 700 cm^{-1}.The specific surface area of $LaNiO_3$ measured with nitrogen was equal to 5,45 m^2/g. This catalyst gave really good results in the catalysis of methane oxyreforming and less carbonates were formed in comparison to $BaNiO_3$; It gave also good results in the carbon dioxide reforming, but with a really short lifetime, because of sintering phenomena of Ni. Much less coke formation was observed in comparison with the commonly available nickel catalysts with acid support.

The subsequent step was to stabilise the perovskite structure by substituting part of the nickel by another metal, hoping that this one could form a more stable structure with lanthanum. Iron was chosen for this aim. The main advantages are an easy characterisation, a relatively high stability, a good dispersion of nickel within the structure, and very limited sintering phenomena of nickel particles. All these structures have a quite similar specific surface area, of about 5 m^2/g.

Very good results were obtained for the CO yield at 800°C in the oxyreforming of methane. Never was observed carbon formation. Similar favourable data for the conversion of methane were observed in the carbon dioxide reforming tests.

As far as steam reforming is concerned, the results obtained are equally very good, with reference to the CO yield and the carbon deposition, provided that the proper lanthanum/iron/nickel ratios are chosen for the catalyst structure. Two different values are considered for the steam/methane ratio, R; in the case of R = 3, hydrogen is also added to the reactant gas, in order to better simulate the product of the fluidised bed biomass steam gasifier. In such conditions, the data observed are indeed very promising. The catalyst reduction temperature was 600 °C. Ageing of this catalyst in the steam reforming of methane was also tested over a period of one month: almost no deactivation was observed, neither any negative trend in the CO yield.

So it has been found that the addition of a co-element, like iron, stabilises the lanthanum in the perovskite structure and produces active catalysts for the oxyreforming, the carbon dioxide reforming and the steam reforming of methane, with high H_2 and CO selectivities. These catalysts are quite stable, and the carbon deposition is almost negligible. The perovskite structure is easily regenerated after the catalytic tests, by an oxidative treatment of 24 hours at 750 °C. It is worthy to underline that the very good performance in terms of negligible carbon build-up and Ni sintering on the active surface is very promising for the utilisation of this catalyst with the gas produced in the biomass gasification process, where tar is present together with methane. One more advantage is related to the optimum temperature range for the catalytic conversion, which coincides with the operative temperature of the *fluidised bed* gasifier (about 800 °C).

- **optimisation of the fuel gas composition in the fluidised bed gasification process**

Experimental evidence was also gathered on the stability of the catalyst after utilisation in its *working environment*, that is in a bench scale gasification facility, a schematic diagram of which is shown in Fig. 3. The catalytic conversion is performed downstream of the gasifier, in a fixed bed reactor. The plant allows to carry out long-running, steady-state tests, at temperature levels up to 950°C, with inert gas or steam as fluidising medium. The biomass is continuously fed inside the bed at a constant flow rate.

The fluidised bed reactor, is made of a stainless steel cylindrical vessel, with internal diameter of 62 mm, with an allumina porous distributor plate, designed and fitted in the bed to allow a good gas distribution. The bed is located inside a cylindrical electric furnace connected to a temperature and heating rate control system. The fluidising gas is introduced from the bottom of the gasifier. Water for steam generation is introduced in an electrically heated boiler by means of a peristaltic pump, at a constant flow rate. The biomass feeding probe, having an internal diameter of 8 mm, cooled with air flowing in a jacket, is utilised to deliver the biomass well inside the bubbling bed. The catalytic fixed bed reactor, with internal diameter of 60 mm, has been inserted after the ceramic candle filter and is heated by a cylindrical electric furnace.

This facility offered the possibility to check the fluidisation quality when steam is utilised as the fluidising medium at high temperature, to study the reactivity of char in the gasifier, and to test alternative and complementary gas treatments, with the aim to gather experimental evidence about the optimum operating conditions.

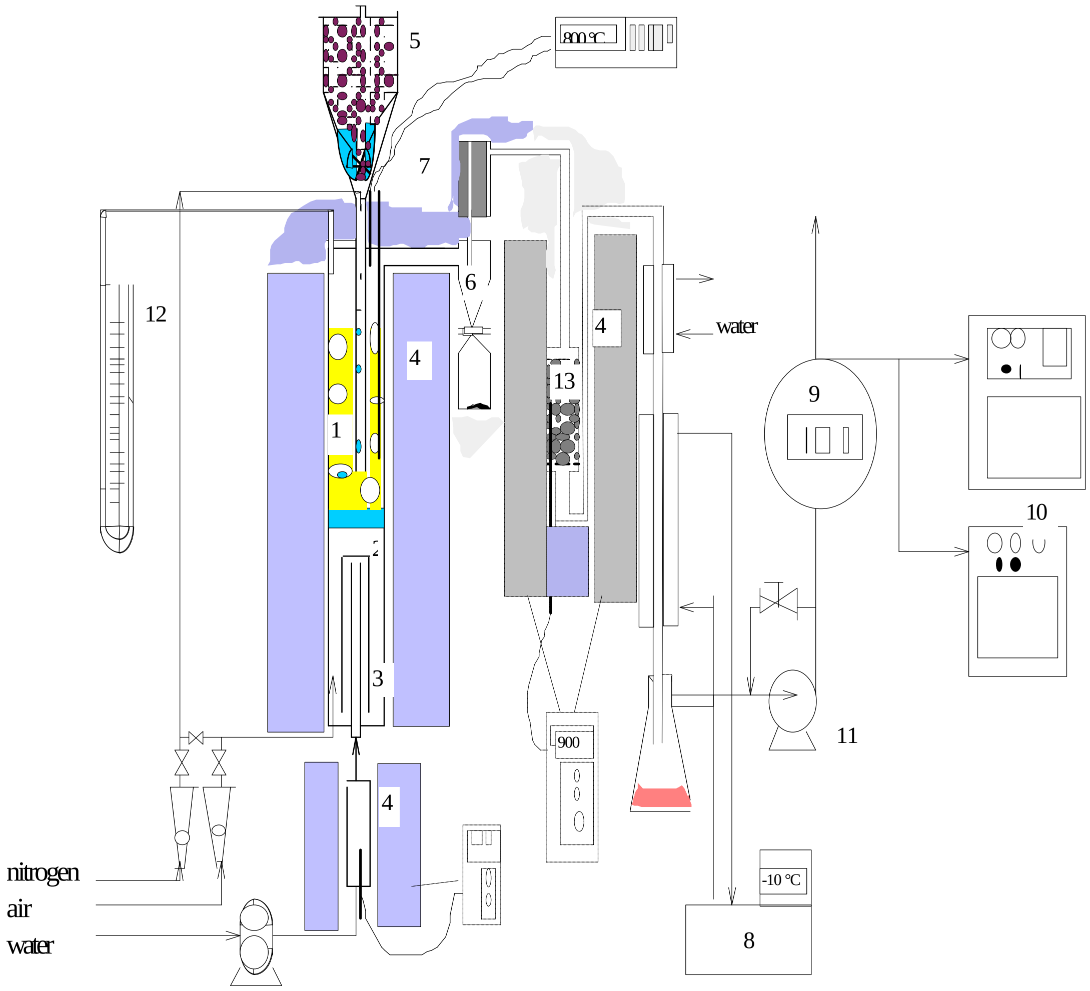


Fig. 3. The bench scale gasification plant

1- fluidised bed reactor, 2- gas distributor, 3- wind box, 4- electric furnaces, 5- biomass feeder, 6 cyclone, 7- ceramic filter, 8- cooling system, 9- gas flow-meter, 10- gas-chromatography, 11- pump, 12- water manometer, 13 catalytic fixed bed reactor.

Some preliminary tests were performed with either commercially available nickel catalysts for conventional processes of methane steam reforming, or mineral substances with catalytic activity (dolomite, olivine). As a result of them, the objective to produce a gas substantially clean from tar components and, at the same time, enriched in hydrogen was found to be feasible by putting olivine in the bed inventory of the gasifier (to convert most of the tar) and utilising the trimetallic perovskite catalyst in the secondary fixed bed reactor. The operating temperature in the catalytic reactor has been fixed at 800°C. The mean particle size of the catalyst sample (230 gr) was about 1 mm, in order to keep the pressure drop through the fixed bed at reasonable values. The gasifier conditions and its performance were those specified below:

• Bed inventory, olivine	d_p=410μm, ρ_p=2500 kg/m^3;
• Biomass, almond shells	d_p=1.1 mm, ρ_p=1200 kg/m^3, moisture 8.84%, ash 1.16%;
• Biomass composition (d.a.f.)	C 50.3%, H 6.1%, O 43.6% (by weight)
• Bed temperature,	770 °C;
• Biomass feed rate	0.3 kg/h;
• Steam/biomass feeding ratio	1;
• Total gas yield (dry gas)	1.69 Nm^3/kg of biomass d.a.f.;
• Gas composition (dry gas)	H_2 52.2%, CO 23.0%, CH_4 7.9%, CO_2 16.9%;
• Tar yield	4.2 g/kg of biomass;
• Char yield	60 g/kg of biomass.

For the catalytic fixed bed reactor, the gas hourly space velocity (GHSV) is defined as the ratio between the gas flow rate at the exit of the reactor and the bulk volume of the catalyst, whereas the weight hourly space velocity (WHSV) is given by the mass flow rate of biomass fed to the gasifier, divided by the mass of catalyst in the reactor.

Table 1 shows typical values obtained for gas yield and composition, whereas the tar content in the gas product downstream of the catalytic treatment is shown in Fig. 4.

In the characterisation "after test", no carbon deposition on the catalyst itself was detected. This important result is indirectly confirmed by the very high gas yield obtained, superior to that found with fresh commercial nickel catalysts.

The experimental data of the reactivity tests performed at the process operating conditions clearly indicate that the perovskite catalyst developed in this project hits the target of a gaseous fuel product clean and rich in hydrogen, able to match the requirements of the fuel cell (provided that the downstream treatments included in the complete process flow-sheet are performed). As far as methane and tar conversion is concerned, its performance appears slightly lower than that exhibited by fresh commercial nickel catalysts. However, the main advantage of the perovskite catalyst is represented by the negligible coke deposition on its surface, which allows continuous operating conditions and process feasibility at industrial level.

Table 1. **Gas yield and composition obtained with catalyst $LaNi_{0.3}Fe_{0.7}O_3$.**

Temperature of the catalytic fixed bed, °C	800
WHSV, h^{-1}	1.30
GHSV, h^{-1}	18230
Gas yield, normal m^3 per kg of daf biomass	2.1
Gas composition, in % by volume: H_2	60.5
CO	25.3
CO_2	10.3
CH_4	3.9

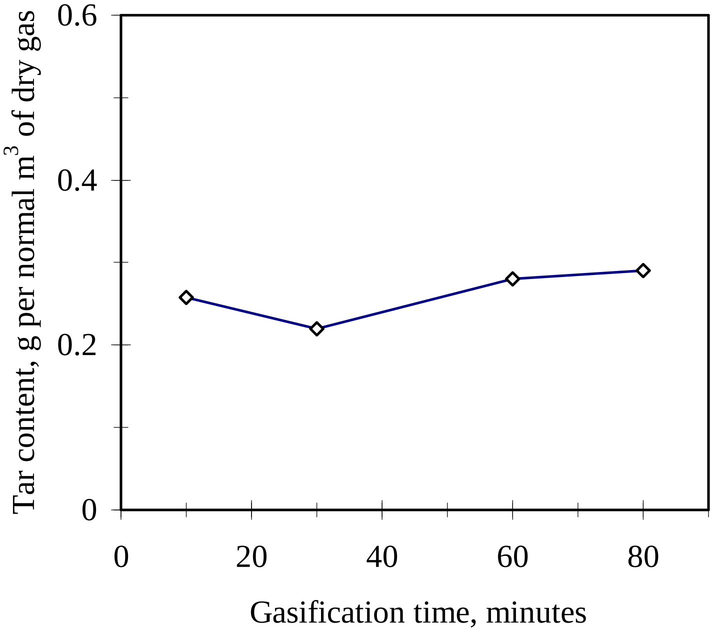


Fig. 4. **Tar content in the product gas resulting from the catalytic treatment**

- **gas cross-flow and solid circulation in the *dual fluidised bed* system**

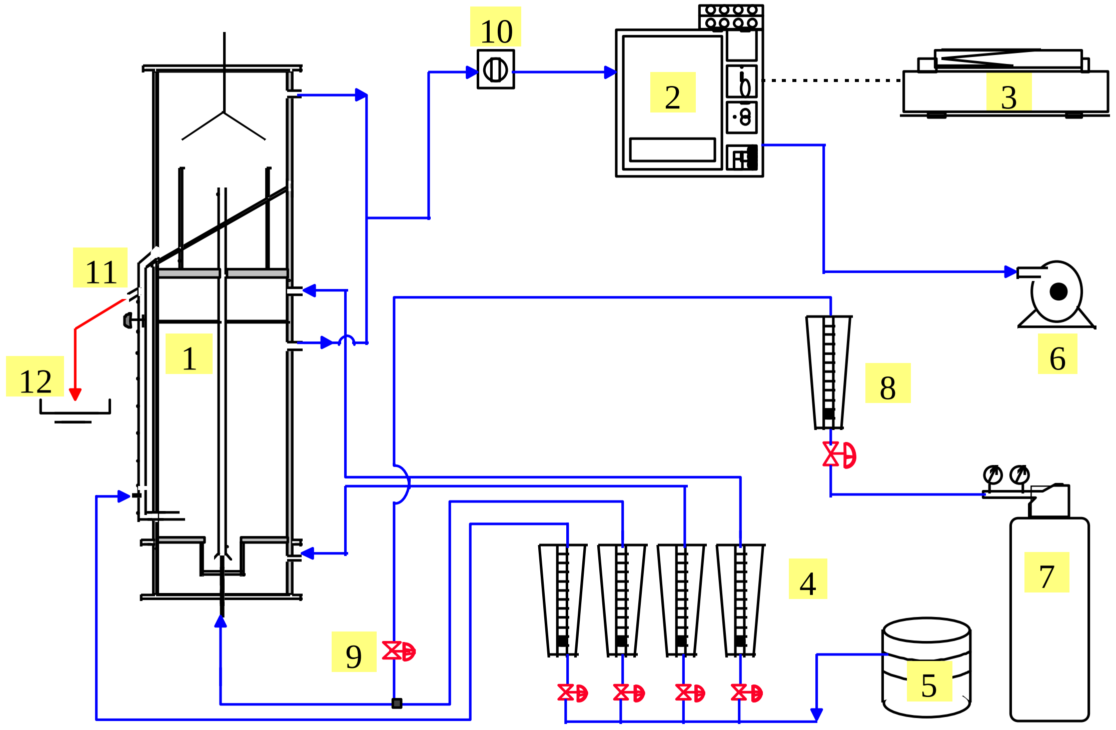
Experiments were performed to study the principles supporting the design of the *dual interconnected fluidised bed* system. A Plexiglas rig has been built, operating at ambient conditions, according to the schematic diagram shown in Fig. 5. The bed material is pneumatically transported by an air jet from the first bed (combustor, 0.2 m I.D. and 0.6 m high) to the second (gasifier, 0.17 m I.D. and 1.2 m high) via a centrally placed riser. The riser inlet mouth being below the distributor plate in order to minimise gas mixing. The solids flow over from the second bed and are collected and returned to the first bed via a standpipe fitted with an ‘L’ valve. While high solid circulation rates are required, gas mixing between the two units must be minimised or eliminated.

The experiments have been performed over a wide range of operating conditions to study the degree of solid mixing, gas cross-flow (using carbon dioxide as a tracer gas and an on-line gas chromatography), and solid circulation. Moreover, pressure measurements were conducted around the loop of the circulating system, in order to gain information on the components of the pressure balance. Fig. 6 shows the results of solid circulation flux (the results are given per unit cross sectional area of the riser for comparative purposes) as a function of the gas velocity in the riser, U_r. It can be seen clearly that solid circulation can be increased by either increasing the gas rate to the riser or to the main beds. Continuous and controllable solid circulation rates of up to 100 kg/m^2s can be attained between the beds.

Fig. 7 shows the gas cross-flow rate from the combustor (the lower bed) to the gasifier (the results are given as a percentage of the total gas flow rate supplied to the combusting section). Here, the tracer gas was injected into the combustor via the bottom windbox, and gas samples were continuously withdrawn just below the exit of the riser in the gasifier for analysis. Increasing the gas velocity in the riser increases the quantity of gas cross-flow (flue gas) from the combustor to the gasifier, leading to a certain level of contamination of the product gas. However, even at the highest solid circulation rate the gas cross-flow is less than 8% at low fluidisation velocity in the main beds, and decreases to about 5% with an increase in gas rate to the main beds up to values comparable with those of interest in practical applications.

On the other hand, injecting the gas tracer in the upper bed (gasifier) makes the gas cross-flow via the L-valve and the downcomer completely negligible over the whole range of gas rates explored. Therefore, there is no loss of product gas to the combustor.

Schematics of the Experimental Set-up



1 - Combustor-Gasifier
2 - Gas Chromatograph
3 - Integrator
4 - Mass Flow Meters
5 - Compressed air
6 - Vacuum pump
7 - Tracer gas cylinder
8 - Tracer flow rotameter
9 - Valve
10 - Gas sampling valve
11 - Solids sampling port
12 - Balance

Fig. 5.

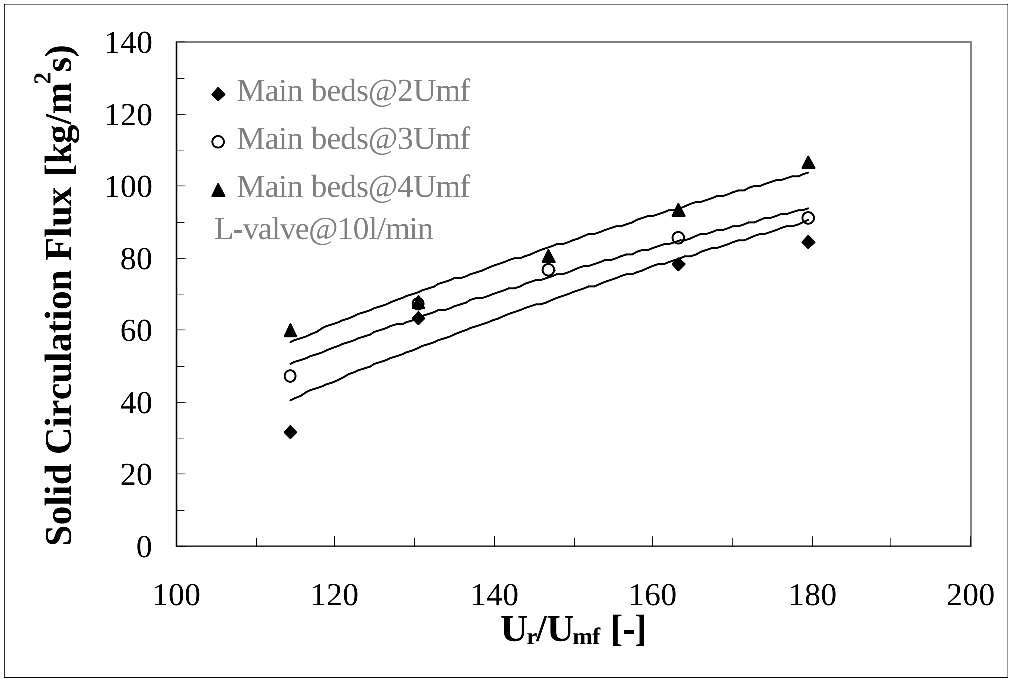


Fig. 6. **Solid circulation flux as a function of the gas rate in the riser and in the main beds**

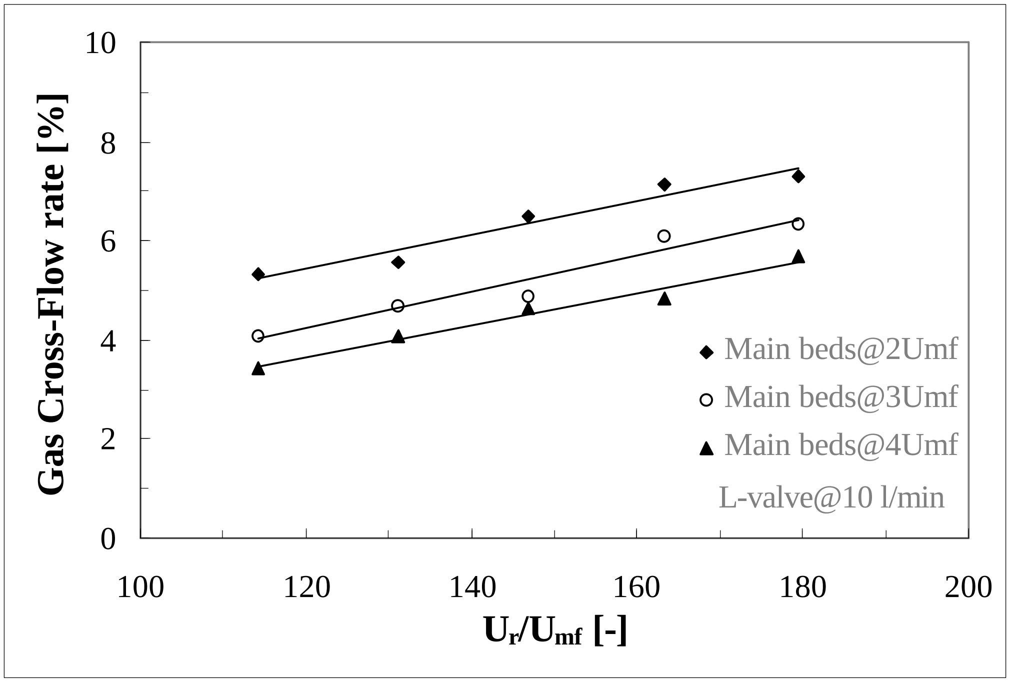


Fig. 7. **Percentage of flue gas cross-flow as a function of gas rate in the riser and in the main beds**

5. Plant siteability in the rural context

Starting from the first year of application (1993) of the EU directive 1765/92, the acceptance of this new agricultural policy among the farmers of Emilia Romagna region resulted quite significant, above the national average. In spite of the traditional diffidence of the agricultural world for the set-aside practice, and of the shortage of clear and opportune information on the modalities of the reform, a considerable and increasing land surface has been withdrawn from the food production (rotation practice) and a substantial part of it has been assigned to non food crops. Such a response allows to consider realistic the development in the near future of extensive energy crops cultivation at regional level, provided that incomes are made available for the farmers comparable with the costs reported in the previous Tables.

In this framework, it is possible to envisage a continuous, round the year utilisation of the *biomass gasification - fuel cell* plant (8000 running hours per year). As far as scale-up prospects are concerned, it is reasonable to assume 2000 - 2500 ha (hectares) of cultivated land available for the production of the biomass needed by the integrated electricity production system. This represents less than 8% of the whole land cultivated just in one province of Emilia Romagna (Ravenna), and therefore appears to be compatible with regional agronomic constraints. Assuming an annual production rate of 20 - 25 ton/ha of dry matter (well inside the range of values found in the cultivation trials - it takes into account also the possible loss of dry matter during the storage period), up to 8 ton/h of dry biomass feedstock are available for the gasification plant, and with the values obtained in this study for the conversion efficiencies, up to 10 MW of electric power can be produced, more than ten times the capacity of the modular PAFC unit assumed as a reference in the design project.

Within these throughput limits, the transportation costs have been estimated to be less than 10 ECU/ton, because the production sites do not exceed the distance of 30 - 50 km from the gasification plant. Moreover, no special problems should arise for biomass storage throughout the year: after harvesting the crop can be left to dry on the land, to reduce the humidity content down to about 20%, then the product is assembled in rotobails to be stored and delivered at the proper time. In this way no major alteration processes are expected during the storage period, because of the relatively low humidity content and the absence of sugars, which prevents fermentation.

The choice to arrange the biomass storage close to the cultivation areas is dictated both, by the presence of sheds and curtains spread around the whole region and available for such purpose, and by the possibility of even lower transport costs (than those mentioned above) when the biomass delivery to the plant is programmed throughout the year, because these are linked to the demand which reaches its peak during the harvesting season. In addition, the problem of providing big storage silos at the plant premises is also avoided.

A reliable evaluation of the cost of the biomass feedstock has been obtained, with reference to the choice of perennial herbaceous crops, the most convenient, as it results from the agronomic and technical analyses ofthis study. Considering a gasification plant life of 15 years implies that the planting should take place 1.5 - 2 times over the all period, according to the cultivation trials performed in Emilia Romagna. It follows that a safe estimate of the production costs for Arundo donax is 40 ECU/ton. Adding the transport costs makes the overall estimate for the biomass cost at the plant site to be 50 ECU/ton.

6. Industrialisation of the biomass gasification - fuel cell (BG - FC) plant

- **technical considerations and results**

The aim of this study is to design two different processes for biomass gasification coupled with fuel cell electricity generation, and to evaluate their costs. They differ in the kind of gasification reactors: one process uses a newly developed fluidised bed reactor, the other requires a proven entrained flow technology. For both the combination with a fuel cell is a completely new field of application. Therefore both need a rather complex gas cleaning system, to reach the extraordinary high requirements for the fuel cell. The most restrictive limitations are imposed by the chemical specifications of the fuel cell; above all, the reduction of sulphur, tar and CO represent costly limitations. To be able to compare the two processes, it was tried to use nearly the same components for the gas cleaning and an identical fuel cell.

It has been assumed that the **biomass** will be supplied continuously, and that the provision of a big storage at the plant site is not necessary; the biomass can be stored close to the rural areas of cultivation and delivered to the plant throughout the year. The storage facilities at the plant are limited to a feed dosing hopper and a silo with the capacity of 200 cubic meters (correspondent to a plant running time of the order of one day).

The **fluidised bed process** contains the feeding system and the reactor including a cyclone. The gas cleaning system is build up by a catalytic reactor for methane and tar reforming, a scrubber, a desulphurisation unit and a two-step CO-shift. The electricity production is performed by the phosphoric acid fuel cell (PAFC).

The **entrained flow process** contains the shredder mill including water vaporisation (from 20% to 10% water content), the feeding system, the reactor with internal quench and a cyclone. The gas cleaning includes a scrubber, a desulphurisation unit, the first CO-shift, a CO_2-separator with regenerator, the second CO-shift and a safety filter. The phosphoric acid fuel cell is identically the same as in the fluidised bed process.

In the following the **differences** between the two processes are summarised.

The entrained flow reactor needs a highly sophisticated pretreatment. The particle size has to be reduced to less than 500 µm. A special mill can perform this. Additionally, the water content is reduced in the same process.

The lower temperatures and larger particle sizes lead to a significant tar content in the product gas of the fluidised bed process. Therefore downstream tar reduction is essential. Two parallel reactors with a perovskite catalyst have to provide this task.

The solid residues leave the process in different ways. The entrained flow reactor melts all ash and changes it into a inert slag, that can be deposited without any danger. From the fluidised bed reactor the solid components will be taken out with the combustion flue gas and separated in a cyclone. If the quality standards are reachable, it can be used as a fertiliser.

The fluidised bed process produces more hydrogen than the entrained flow reactor referring to the same amount of biomass, because of the steam gasification (fluidised bed) instead of the oxygen gasification (entrained flow). So the fluidised bed needs less biomass.

Moreover, with its higher hydrogen content in the product gas, the fluidised bed reactor needs lower efforts in gas treatment. The CO_2-separator is not necessary in the fluidised bed process. For preventing the fuel cell from critical components, in the entrained flow process there is added an adsorption filter in front of the PAFC.

In the entrained flow process there is a large amount of heat in form of steam and hot water available. It is assumed that this heat can be sold to nearby users.

Finally, for estimating the reliability of the two plants, it should be mentioned, that the entrained flow process in its main components is a tested unit, whereas the fluidised bed reactor and the perovskite catalyst are in an early stage of development.

- **economic considerations and results**

The technical optimisation of the process configuration and the dimensioning calculations of the major plant components allowed a reliable evaluation of costs, with reference to present market prices. However, before discussing financial figures, it is worth mentioning that in the case of a completely new industrial application, such as that of a PAFC hydrogen module coupled with a biomass gasification process, the attention should be focused on future prospects of expanding the market potentialities, thereby drastically reducing unit costs. This study has shown the technical feasibility of the BGFC integrated plant, by means of direct experimental evidence in key areas, and original conceptual developments, so it will certainly contribute to a cost reduction strategy in this field, with the attendant benefits.

A computer programme has been developed, able to perform the basic calculations for a reasonable estimate of the investment and operating costs of the whole system. The calculations were performed for a throughput of about 1 Mg/h. To show the „advantage of scale-up“ there were also made calculations for a factor of 10 in throughput. Table 2 summarises the main results.

Table 2 Results of the investment and operating costs calculation

	Low throughput		**High thoughput**	
	Fluidised bed	**Entrained flow**	**Fluidised bed**	**Entrained flow**
Investment in M ECU	6.6	9.7	30.6	45.1
Costs balance in ECU/ton	- 111	- 113	+ 1	- 37
Biomass throughput in ton/h	0.732	1.008	7.32	10.08
Costs balance per year, in k ECU/year	- 650	- 911	+ 59	- 2,984

The *fluidised bed* option with a high throughput (7.32 ton/h) is able to hit the market price of a ton of biomass to be treated. All other constellations lead to negative financial balances, with costs between 650,000 and 2,984,000 ECU/year. The high throughput version of the fluidised bed leads to revenues of 59,000 ECU/year. It is worth noticing that the figures reported in table 2 include also the running capital costs.

Both processes have a number of risks for being available for 8.000 h/year. A period of time for test phases or trial run will be necessary. The *dual fluidised bed* gasification process certainly needs further verifications for a continuous operation; however, the electrical power supply will be much more effective in this case.

When the low throughput application is considered, the costs calculated with both gasification options are rather high in comparison to today electricity production devices. A rise in size (for example ten times the developed processes) leads to better prospects for the financial evaluations. In this framework, it should be also taken into account the expected reduction in the cost of the PAFC module, based on further technological progresses and on expected large production volumes, which allow full economy of scale to be obtained.

The risks usually related to the availability of any new technology are of course to be considered, although they can not be accounted for in terms of precise cost estimates. In order to reduce these risks, and to practically test the plant configuration which appears as the most promising one, it is recommended to build and run a small pilot plant arranged according to the fluidised bed steam gasification technology studied and developed in this Project, with a throughput of the order of 100 kg/h of biomass.