HYDROGEN-RICH GAS FROM BIOMASS STEAM GASIFICATION

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Contract JOR3CT970196

Publishable Final Report

Start of the project: 02.03.98
Duration of the project: 33 months

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

Vienna, 31st March 2001

1 Abstract

The aim of this project was the development of a fluidised bed gasification process for the production of a hydrogen rich gas from biomass.

To achieve this aim, a 500kW$_{th}$ pilot plant was build and tested, a catalyst for fluidised beds was developed and fundamental research on the fluid dynamics was done.

The pilot plant consists of a feeding system, the gasifier, a flue gas treatment and a product gas treatment system and a fuel cell with an extra gas upgrading system.

The gasification reactor consists of two zones, a gasification and a combustion zone. The circulating bed material serves as heat carrier from the combustion to the gasification zone. Steam is used as gasification agent and a catalyst is used as bed material to increase the amount of hydrogen and reduce the amount of tar in the product gas.

The erection of the pilot plant was finished in July 2000 and then the first tests started. During start up of the pilot plant the following problems occurred:

- Damaging of PTFE bags;
- Tar condensation on the plant in particular on the product gas blower and stainless steel bag;
- Long heating up time.

These problems were solved, but it was not possible to do the whole experimental program, which was defined in the contract (tests of catalyst in the pilot plant, tests of fuel cell together with gasifier).

The experiments done till the end of the project, showed, that the nitrogen content in the product gas is below 5% and that the necessary circulation rate can be reached easily.

On the cold flow model at UCL the circulation rate, the gas cross flow and the behaviour of the biomass was investigated. The results, showed, that the pilot plant was designed well and will operate as provided. Additional a new scaling parameter was introduced, which enables to calculate the circulation rate in dependency of the total amount of bed material inside the gasifier.

The work of ECPMS and UNIVAQ aimed at the development of a catalytic system. Two catalysts were developed during the project. One is based on a LaNiFe perovskite catalyst, which has shown very good activity in tar destruction and methane reforming in a separated fixed bed reactor, but is not resistant to a fluidised bed. The catalytic system NiO/olivine used a new concept to integrated NiO in the olivine structure. It was characterized and tested in dry and steam reforming of methane and presented no deactivation and no coke formation. After these results, it was synthesized in a large amount (135 kg). Its activity was confirmed in the fluidised bed (2 kg) reactor of UNIVAQ and in the fluidised bed (35 kg) reactor of TUV. The results have confirmed its remarkable activity with an increase of H_2 concentration of 8% and a decrease of CH_4 concentration of 3% in the dry gas mixture. Moreover, tar content is divided by 6 or 7 with regard to the tar content without catalyst, and no additional small particles has been formed by attrition. So, this catalyst meets the requirement of attrition resistance, hydrogen production and tar destruction in the effective operating conditions encountered in biomass gasification.

General the results of this project are:

- A pilot plant with a thermal power of 500kW was build and the first experiments were done. These tests showed, that the circulation rate can be reached easily and that the nitrogen content in the product gas is below 5%.
- At the work on the cold flow model a new scaling parameter was introduced.
- A new catalyst for fluidised beds was developed and tested. This catalyst showed good activity in reduction of tars and increase of hydrogen.

2 Partnership of the project

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3 Objectives of the project

The objective of the project is the development of a fluidized bed gasification process for the production of a hydrogen rich gas from biomass. The gasification process is based on an Internally Circulating Fluidized Bed (ICFB) configuration with a gasification and a combustion zone. In order to achieve the necessary high hydrogen yield, steam has been chosen as the gasification agent and suitable catalysts will be included in the bed inventory. With this gasification process it is possible to produce a gas with 40-60 % hydrogen, nitrogen content below 5 %, calorific values above 11 MJ/Nm^3, and low tar content (<0,6 g/Nm^3). The project demonstrates one powerful application of the product gas, producing electric energy in a fuel cell, which will be integrated in the process.

The work content of this project can be divided into group tasks shown in the following table. This enables responsibilities and milestones to be defined so as to assist in the progress of the overall project.

TASK	DESCRIPTION OF WORK
A	Overall system requirements.
B	Design and manufacture of gasifier; specification of ancillary units.
C	Balance of Plant (BOP) design.
D	Equipment procurement, assembly of the pilot plant and related instrumentation, including the fuel cell.
E	Accompanying laboratory research: cold modelling fluid-dynamic studies (E1); optimisation and manufacture of catalyst (E2).
F	Specification of plant tests and analysis of the results.
G	Operation of the pilot plant: gasification and BOP related tests.

4 Scientific and technical description of the project

The work content of this project is divided into tasks, as mentioned before. An overview of the technical progress is given in the following chapters.

4.1 Overview on the Technical Progress

4.1.1 Task A

The objective of Task A is to define the general requirements of the pilot plant, and its instrumentation; to carry out the heat and material balances; to specify the sub-systems boundaries and interface requirements (gasifier, gas clean-up system, fuel cell)

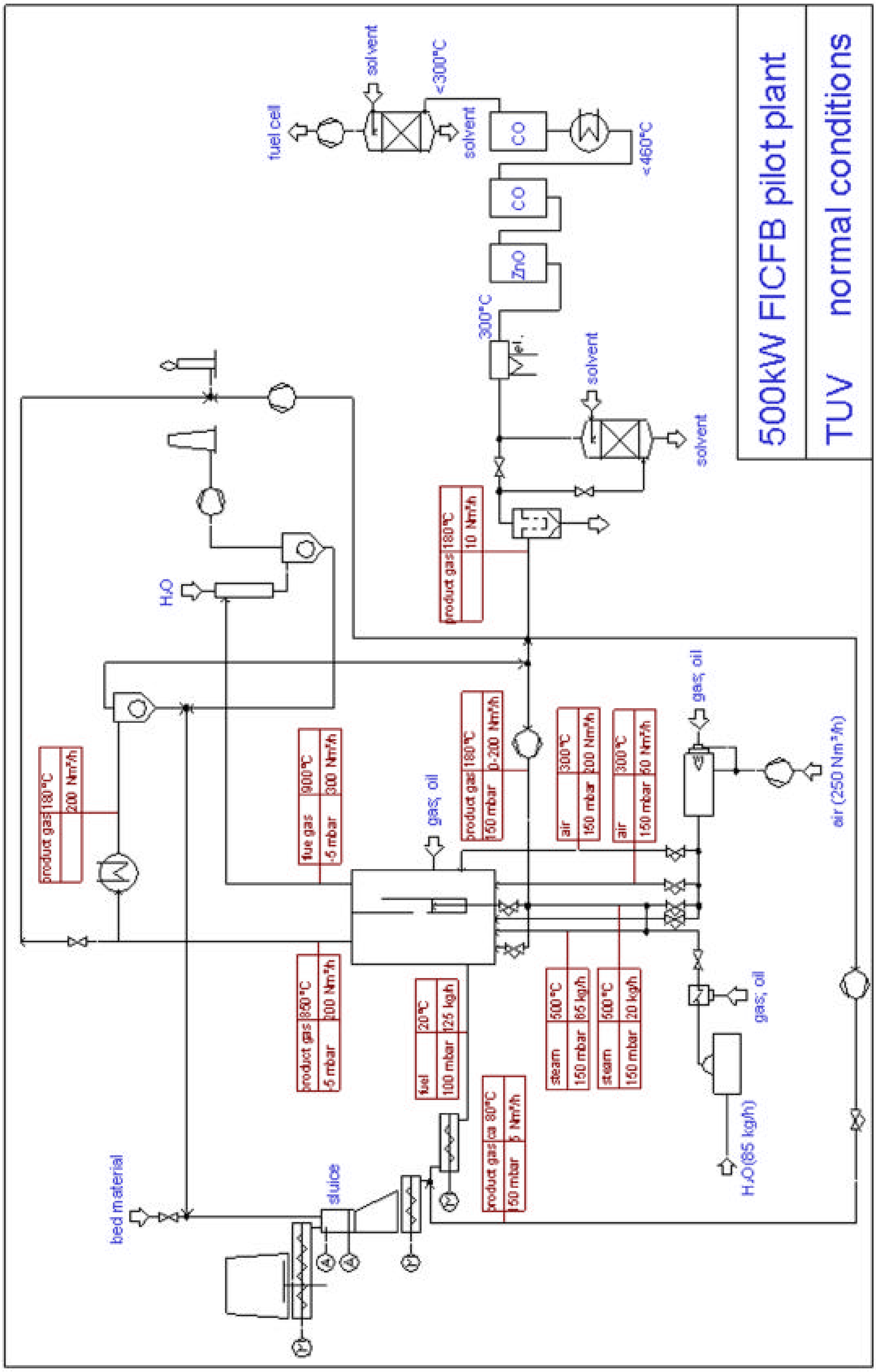
4.1.1.1 Basic design of the pilot plant

The following figure shows the flow chart of the gasification system including the mass flows, temperatures and pressures.

The gasification reactor consists of two zones, a gasification and a combustion zone. The circulating bed material serves as heat carrier from the combustion to the gasification zone. Steam is used as gasification agent which is produced by an industrial steam generator unit and is overheated up to 500°C. There is also the possibility to mix the steam with recycled product gas to vary the steam-fuel ratio. Air used as fluidisation gas in the combustion zone is supplied by a compressor and heated up to 300°C.

The flue gas treatment consists of a cooler, a filter, a fan and at last a chimney. The product gas treatment consists primarily of a heat exchanger, a filter, a fan and a flare, where the main part of the gas is burned. An amount up to 200 Nm³/h can be mixed with the steam and recycled to the gasification zone as mentioned above. A small amount (about 25 Nm³/h) is led to the fuel cell.

Before feeding the gas into the fuel cell a gas treatment is necessary. First the rest of particulates and tars is removed by a dust filter, then the H_2S and NH_3 is removed by two steps of scrubbers. The rest of H_2S is removed by a zinc oxide catalyst. To increase the amount of hydrogen a two step shift reactor converts CO with steam to H_2 and CO_2. After this treatment the gas is ready to be used in the fuel cell.


500kW FICFB pilot plant
TUV normal conditions
fuel cell
solvent
<300°C
solvent
CO
CO
ZnO
<460°C
300°C
el.
solvent
solvent
H₂O
product gas 180°C 10 Nm³/h
product gas 180°C 200 Nm³/h
flue gas -5 mbar 900°C 300 Nm³/h
product gas 150 mbar 180°C 0-200 Nm³/h
gas; oil
air 150 mbar 300°C 200 Nm³/h
air 150 mbar 300°C 50 Nm³/h
gas; oil
air (250 Nm³/h)
product gas -5 mbar 850°C 200 Nm³/h
fuel 100 mbar 20°C 125 kg/h
steam 150 mbar 500°C 65 kg/h
steam 150 mbar 500°C 20 kg/h
gas; oil
product gas 150 mbar ca 80°C 5 Nm³/h
bed material
sluice
H₂O(85 kg/h)

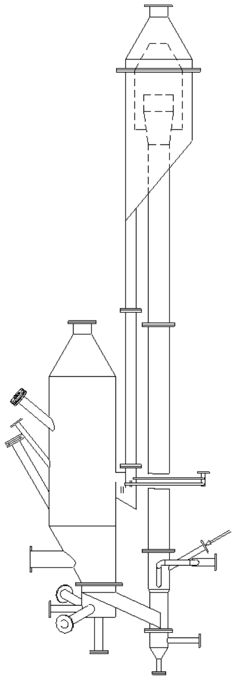
Flow Chart

4.1.2 Task B

The objective of task B is to perform the detailed design and construction of a 500 kW_{th} ICFB gasifier, on the base of the previous experience of TUV and AE&E from a laboratory test rig (100 kW_{th}). Further on, to provide the design and mechanical specifications of ancillary units of the gasification section of the pilot plant.

The following ancillary units are necessary to operate the gasifier:

- Fuel feeding system
- Bed material feeding system
- Steam production unit
- Air supplement
- Product gas treatment
- Flue gas treatment



The 500kW gasifier

The following table shows the main dimensions of the gasifier:

dimensions of the gasification zone		
diameter inlet	400	mm
diameter freeboard	800	mm
height of fluidized bed	850-1500	mm
height of freeboard	2000	mm
dimensions of the combustion zone		
diameter	250	mm
height	6770	mm

4.1.3 Task C

The objective of this task is to produce the detailed process design of the BOP system (design specifications, P&ID instrumentation lists, equipment and instrumentation data sheets, control requirements, system layout). Further on, to provide the design and mechanical specifications of ancillary units of the gas treatment section and PAFC-section.

4.1.3.1 Design specifications for fuel cell simulation and gas analysis

CLC's objective within task C was to produce the detailed process design of the experimental gas clean-up system, necessary to treat the gas from the gasifier up to the specification required to feed the phosphoric acid fuel cell unit.

A preliminary analysis performed within task A gave following main requirements:

- Maximum flexibility of operation: the gas clean-up system would permit easy testing of different operation units in different operating conditions and arrangements, with the purpose of finding during the tests the most efficient and possibly cheap system configuration.
- Total gas clean-up flowrate of 1/10 of the gasifier product flowrate, as a compromise between reason of low cost and flexibility of operation, and the necessity of having meaningful results for scaling up to full size.
- Restriction of equipment to the more promising technologies in terms of efficiency and low cost.
- Easy to transport skid mounted unit.

From the analysis performed, the system configuration was defined, based on unit operation given below.

- Venturi scrubber
- Sand filter
- Packing scrubber with alcaline treatment
- Activated carbon filter
- Packing scrubber with acidic treatment
- Sulphur removal on zinc oxide bed
- Two stages of CO shift reaction

The work done within Task C was completed, and the design of the gas clean-up system was synthesised.
The intermediate results of system design have been discussed with TUV for compliance with overall plant design and interfaces, and with ENEA for compliance with cost targets.

Deliverable documents were sent to ENEA for the subsequent phase of equipment procurement and plant assembly within Task D.

4.1.4 Task D

This task involves the site-mounting of the gasifier and the purchased equipment; assembly of the overall pilot plant (piping, electrical connections, connections with the utilities available at the site); operability tests with all plant components.
The construction of the pilot plant was much more difficult and expensive, than expected. ENEA spent 70kEuro more than it was foreseen in the contract for purchasing and assembling the ancillary units.
The pilot plant was finished in July 2000.

The following photos show the pilot plant

4.1.5 Task E

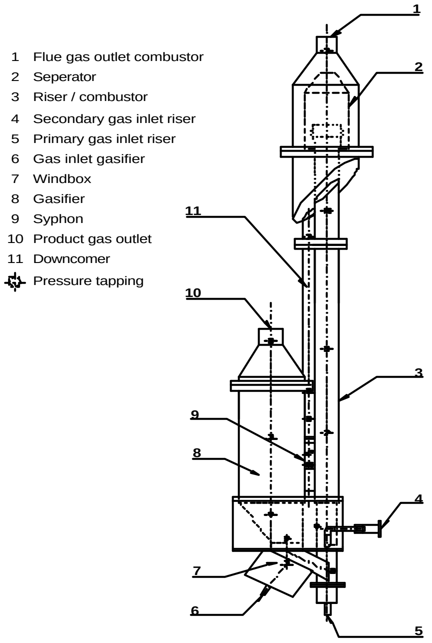
In this task all accompanying fundamental research in laboratories are done. This is: cold modelling fluid-dynamic studies (Task E1); manufacture and characterisation of catalyst (Task E2).

4.1.5.1 Task E1: Cold Model and Fluid-Dynamic Investigations

At University College London (UCL) the following points were investigated during Task E1:

1. Scaling of a cold model of the pilot plant based on existing scaling guidelines.
2. Fluid-dynamic investigations including measuring the:
    a) solid circulation rate (SCR),
    b) gas cross flow from combustion into the gasification section
    c) pressure drop and pressure fluctuations,
    d) biomass circulation.
3. Determination of the operating parameters in the pilot plant.
4. Comparison of the scaled model with results obtained with the cold model in Vienna.
5. Verification of the applicability of the existing scaling guidelines.

Scaling of a cold flow model of the pilot plant based on existing scaling rules



A cold laboratory model was built in order to study the fluid dynamic behaviour of the 500 kW pilot plant. To ensure similar fluid dynamic behaviour between the cold laboratory model and the pilot plant, existing scaling rules were used. On the base of the full set of scaling parameters derived by Glicksman et al. a 5th scale cold model was designed at UCL. As circulating bed material, bronze particles (d_s=180 µm, ρ_s=8900 kg/m^3) were chosen; the riser was fluidised with ambient air while the gasifier was fluidised using a gas mixture of 55:45 % helium:air. On the base of the assumed operating parameters in the pilot plant, the ratios of the scaling parameters in the pilot plant (pp) and the model (mod) were calculated.

Fluid-dynamic investigations

a) The SCR was measured by switching off the flowrate into the syphon which caused a gradually filling of the downcomer.

As a result of these experiments it was shown that the SCR depends only on the superficial velocity in the riser, u_0, and the total mass load in the system. A new scaling parameter was introduced which enables to calculate the dimensionless mass turnover defined as:

$$M = \frac{m^*}{m} \cdot \frac{D_{comb}}{u_t} \tag{1}$$

for a wide range of particles, mass loads and velocities investigated using:

$$M = \frac{-w}{1+\left(\frac{U-x}{y}\right)^z} + w \tag{2}$$

with

$$w = 0.0013, x = 0.68, y = 0.74, z = 3.54 \tag{3}$$

Furthermore, experiments were carried out in order to investigate the influence of the PSD on the SCR. Therefore, sand particles with different PSDs were used. It can be seen that the SCR is decreasing if the bed material contains a higher fraction of big particles.

b) As conclusion from the gas cross flow from combustion into the gasification section measurements can be said that all gas leaking into the gasifier results from the primary gas inlet into the combustor. Decreasing the volumetric flowrate in the primary inlet the gas leakage can be reduced. Consequently, in order to maintain the circulation rate required, the flowrate in the secondary inlet has to be increased. Thus, the gas leakage can be decreased even further. By increasing the flowrate in the gasifier, the leaking gas becomes more diluted, however, the total amount of leaking gas will be increased.

c) The pressure drop of the model and the pressure fluctuations were measured. Pressure fluctuation measurements revealed that a bubble is generated in the gasifier every 2 to 3 Hz depending on the solid mass load, m, in the system.

d) Experiments concerning the scaled gasified biomass revealed that bigger biomass particles are not circulating into the combustion section at all, but they are well mixed with the bed material in the gasifier. Only small biomass particles are transported together with the bed material to the combustion zone.

Determination of the operating parameters in the pilot plant

For the operation of the pilot plant the operation parameters were determined based on the results obtained with the cold model and are listed in the table below.

Using the flow conditions, the nitrogen content of the product gas was estimated to be 2.8%.

Operating Parameters for the Pilot Plant

Parameter (pilot plant)	**Value for the pilot plant**
m^*	5000 kg/h
m	550 kg
$u_{0,comb}$	4.73 m/s
V^*_{comb}	908 m^3/h
V^*_{prim}	49 m^3/h
V^*_{sec}	859 m^3/h
V^*_{gasi}	391 m^3/h
V^*_{cross}	13 m^3/h

Difference between the cold model at TUV and the new designed cold model at UCL

The solid circulation of the model in Vienna and in London were compared. The mass flux in the Austrian unit is much less compared to the newly designed pilot plant. Furthermore, a minimum gas cross flow of 5 % of the total flowrate in the riser was stated while in the unit in London the gas cross flow is only 1.5 %. From this comparison it can be seen, that these two cold flow models are completely different.

Conclusion

Except "Verification of the applicability of the existing scaling guidelines" of the work at UCL all task were carried out and gave useful and promising results for the operation of the pilot plant. Further work has to be carried out in order for better understanding of the behaviour of the biomass in the system. In addition, the results obtained with the pilot plant will reveal if the proposed scaling parameters will give similarity between a model and a cold laboratory unit.

4.1.5.2 Task E2: Manufacture and characterisation of catalyst

The objectives of the Task E2 performed at ECPM and UNIVAQ were the development of a catalyst in an important quantity to be used to enhance the hydrogen production by biomass gasification in a fluidised bed.

This catalyst had to meet the requirements of a triple objective:

- to reform methane with CO_2 and H_2O,
- to decrease the tar quantity,
- to resist to attrition.

For that, two catalyst families have been developed.

Part I: Development of the catalyst

Introduction

The perovskite catalysts $LaNi_xFe_{1-x}O_3$ met the first and the second requirement when they were used in a fixed bed reactor. This perovskite catalyst did not resist to the attrition phenomena during the tests made in a fluidised bed reactor at l'Aquila and the catalyst becomes inactive after a short time.

The second catalyst family was directly derived from the olivine with an insertion of nickel in the initial structure. Natural olivine comes from an Austrian mine. It mean formula can be calculated with the data, given in the table below, obtained by atomic adsorption. It is close to $(Mg_{0.92}Fe_{0.08})_2SiO_4$ with an iron excess (0.7wt-%) in the form of free iron oxide. It already contains small amount of nickel as well as of Ca, Al or Cr. Its specific surface area is very small ($< 1m^2/g$).

Element	Mg	Si	Fe	Ni	Ca	Al	Cr
wt-%	30.5	19.6	7.1	0.19	0.20	0.07	0.08

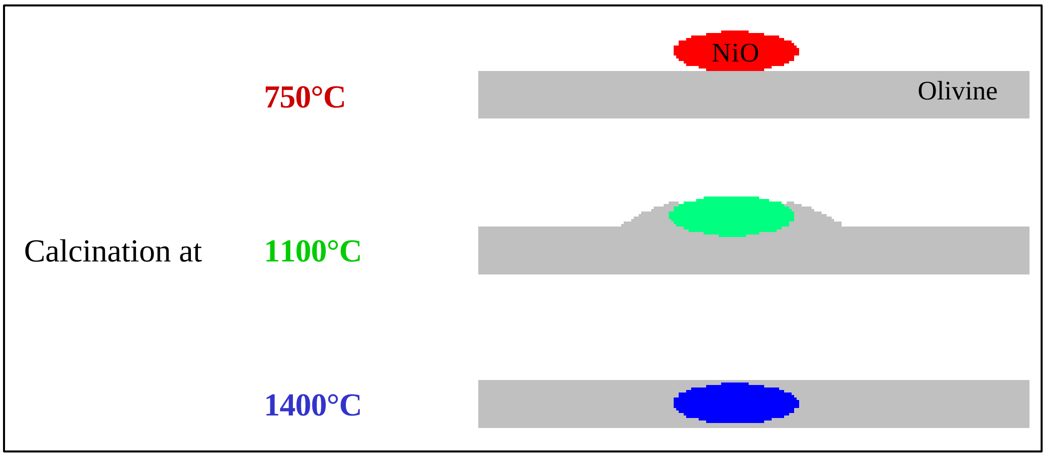
Preparation and characterisation of the catalysts

Natural olivine granulometry was chosen between 250 and 600µm. Then it was impregnated by an aqueous solution of $Ni(NO_3)_2$, $6H_2O$ in excess to obtain a 2.8wt-% of Ni content on olivine (measured by atomic adsorption). After the evaporation of the excess water, the samples have been calcined at various temperatures (400°C, 750°C, 1100°C or 1400°C) for four hours in order to form NiO particles and to integrate them into the olivine structure.

In conclusion, 2.8wt-% of Ni on olivine and calcined at 1100°C is the most appropriated catalyst for methane reforming and for it use in fluidised bed gasifier. In fact, calcination at a lower temperature did not permit to insert all the nickel. The part of nickel (free nickel), which is not inserted in the olivine, is inclined to sinter on the surface during the gasification. This sintering will strongly decrease the catalyst efficiency in methane reforming and tar reduction and increase the carbon formation on the catalyst surface.

Calcination at a higher temperature (1400°C) will integrate the nickel totally in the support structure. However, the nickel-structure is then very strong and the nickel reduction becomes impossible below 900°C, temperature used for gasification. The catalytic system will be also inactive.

The state of the nickel in the samples calcined at various temperatures is schematised in the figure below.



Catalytic reactivity of the samples

In order to determine the catalytic activity and stability of the various catalysts in the conditions of biomass gasification, the reactions of dry and steam reforming of methane has been studied.

As a conclusion of the results and also from other experiments, it could be affirmed that ageing of the NiO/olivine calcined at 1100°C is very good in dry and steam reforming and that this catalyst could be tested in fluidised bed.

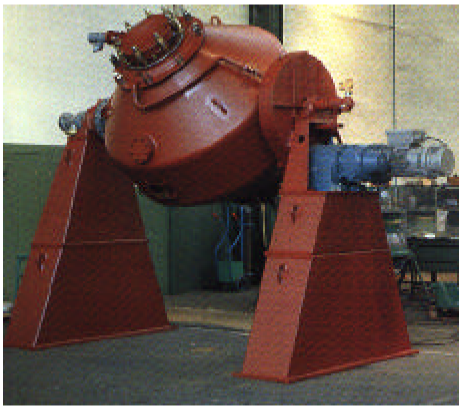
Characterisations of the NiO/olivine samples after catalytic tests

The scanning electron micrographs of the sample calcined at 1100°C confirm that the size of nickel containing particles remained constant during catalytic tests (dry and steam reforming). In fact, these particles are better linked and grafted to the olivine surface, which seems to be smoother. So, no nickel containing particle migration and no sintering is observed.

The samples present very low carbon contents (always lower than 1wt-%). Less coke is formed in dry reforming and after steam reforming with hydrogen, carbon content tends to increase versus water concentration in the inlet gas mixture.

The state of surface and the low carbon formation explain the good ageing behaviour of this catalyst.

Preparation of a large amount of NiO on olivine catalyst



Strasbourg's group prepared 135 kg of NiO/olivine. The natural olivine (400 and 600 µm) is from Magnolithe GmbH in Austria. A cover glass lined steel rotary dryer as described in the photo beside is used for the preparation. The total amount of catalyst is prepared in five portions due to the capacity of the reactor (60 L). Nitrate nickel $Ni(NO_3)_2,6H_2O$ was dissolved in water into the reactor. Natural olivine was added after the nitrate dissolving. The sample was mixed by the rotation of the reactor and then heated at 100°C. After evaporation of the water, the catalyst was take off. The sample was dried one night in an oven at 120°C and calcined at 1100°C during four hours after a temperature increase slope of 3°C min^{-1}. The sample was collected after cooling. The percentage of Ni was equal to 2.8wt-%. The results of characterisation are in good agreement with those obtained for catalysts prepared in fewer amounts.

Conclusion of this study

In conclusion, the catalyst containing 2.8wt-% of Ni and calcined at 1100°C for 4 hours has met the requirements of activity and yield in syngas and of stability with time of stream (> 260 hours). In dry reforming with $CO_2/CH_4 = 1$, methane conversion reached 95% and hydrogen yield were 80% at 750°C. In steam reforming with $H_2O/CH_4 = 1$, methane conversion and hydrogen yield was respectively higher than 88% and 75% at 750°C. In steam reforming with $H_2O/CH_4 = 3$ and $H_2/CH_4 = 2$ ratios, methane conversion was close to 70% and hydrogen yield close to 55% at 850°C.

Moreover, 135 kg of NiO/olivine catalyst was prepared with success. High homogeneity and high NiO–olivine interaction are obtained. The preparation of this system in large amount shows the ability of the Strasbourg's laboratory to have a good control of the evolution from laboratory scale to industrial scale for this type of catalyst.

Part II: Tests in the effective operating conditions

Introduction

The activities have been directed at the acquisition of the knowledge and experience needed to operate the pilot plant assembled at ENEA premises, where the catalyst will be placed directly in the gasifier. Therefore, they have been focussed to check the capability of the catalyst to stand the particle attrition problems typical for fluidised bed inventories, and the cyclic exposure to chemically reductive and oxidative atmospheres (induced by the circulation between the gasification and combustion zones of the gasifier itself) without substantial loss of activity. Moreover, the influence of changes in the operating conditions on the yield and quality of the fuel gas product has been also investigated.

As a whole, the work performed can be divided in the following “sub-tasks”:

- Verification of the performance of perovskite catalyst samples ($\mathbf{LaNi_{0.3}Fe_{0.7}O_3}$) placed in a fixed bed reactor downstream of the gasifier, in terms of gas yield and composition, its tar content, and carbon deposition on the active surface of the catalyst particles; influence of the reduction procedures and of alternate exposure to gasification and combustion products.
- Utilisation of the above catalyst supported on olivine particles in the fluidised bed inventory of the gasifier; check of catalytic activity and mechanical resistance to attrition phenomena.
- Process sensitivity to changes in major operating parameters (the gasification temperature and the steam/biomass ratio).
- Utilisation of a new generation of Ni-olivine catalysts (developed by ECPMS as a result of the previous findings) and check on its performance either in steady-state conditions and in cyclic tests, with intermittent air injection.

The starting point in these activities has been offered by the results and the conclusions of a previous EU Contract (JOR3-CT95-0037), where the development of a catalyst suitable for biomass gasification was deeply investigated both, at ECPMS and UNIVAQ. Those studies ended up with the preparation and testing of the perovskite catalyst mentioned above, which showed very good activity for tar destruction and methane reforming at the operating conditions of the gasification process, and, at the same time, a remarkable capability of its chemical structure to keep the Nickel particles well dispersed, so avoiding the phenomenon of coke deposition almost completely. However, the catalyst developed under the previous Contract could not be used in a fluidised bed (the particles are rather soft) unless impregnated on a suitable support.

Experimental

The process configurations examined are, respectively, a *two-step* system in which a catalytic reactor is placed downstream of the gasifier, and a *one-step* gasification and catalytic conversion system in which the catalyst is introduced directly in the fluidised bed of the gasifier.

The bench-scale equipment consists essentially of the following units: a bubbling fluidised bed gasifier with a continuous biomass feeding facility and a steam generator; a gas cleaning section with a cyclone, a ceramic candle filter, and a cooling system to separate condensable components; measurement devices for the continuous monitoring during the gasification tests of flow rates, temperatures, pressures, and product gas composition. When the secondary catalytic reactor is utilised (*two-step* configuration), it is positioned downstream of the gas filter.

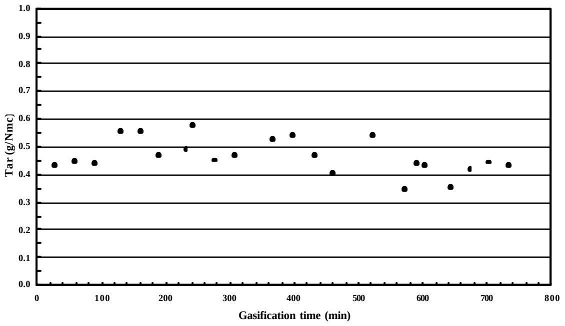
Ni-olivine catalyst resistant to fluidized bed attrition and to cyclic exposure to oxidation/reduction environments

The evaluation of the Ni-olivine catalyst’s mechanical strength at the temperature levels encountered in the fluidised bed gasification process has been performed by means of vigorous fluidisation tests, each lasting 5 hours, at 800°C and relatively high fluidisation velocity (U = 0.3 m/s, about six times the minimum fluidisation velocity). The catalyst sample was weighted before and after each test to obtain the percentage of bed inventory elutriated (fine particles produced by fragmentation). The size distribution “after test”, obtained by sieving the catalyst sample, was also checked and compared with that obtained before, to detect any shift towards smaller particle diameters.

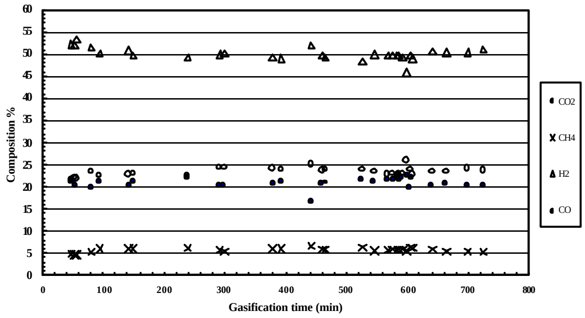
The results obtained show that the bed loss never exceeded 3% of the whole particle bed weight, and that the size distribution curve, remains practically unchanged.

A fresh sample of the catalyst has been utilised for biomass gasification runs lasting altogether more than 12 hours. No sign of activity loss is detectable from the experimental results obtained. In fact, as a steady state gasification test progresses, an increase in the gas yield is noticed, probably as a result of improving the reduction state of the Nickel by the hydrogen present in the gaseous product itself.

The gas production rate is stable with time of operation, always in the range 1.8 – 2.2 Nm^3/kg of daf biomass. The tar content in the gas is between 0.4 – 0.5 g/Nm^3 of dry gas, and the hydrogen volumetric fraction in the dry gas is as high as 50%. It is also worth noticing that the water conversion level is in the range 40% - 50%, which, as mentioned above, indicates a remarkable catalytic activity.



Tar content in the gaseous product, expressed as $C_{10}H_8$



Dry gas composition

Final conclusion

This part of the contract aimed the development of a catalytic system. This one is based on a LaNiFe perovskite catalyst, which has shown very good activity in tar destruction and methane reforming in separated fixed bed reactor.

The catalytic system NiO/olivine used a new concept to integrate NiO in the olivine structure. It was characterized and tested in dry and steam reforming of methane and presented no deactivation and no coke formation. After these results, it was synthesized in a large amount (135 kg). Its activity was confirmed in the fluidized bed (2 kg) reactor of UNIVAQ and in the fluidized bed (35 kg) reactor of TUV. The results have confirmed its remarkable activity with an increase of H_2 concentration of 8% and a decrease of CH_4 concentration of 3% in the dry gas mixture. Moreover, tar content over time is divided by 6 or 7 with regard to the tar content without catalyst and no additional small particles has been formed by attrition.

So, this catalyst meets the requirement of attrition resistance, hydrogen production and tar destruction in the effective operating conditions encountered in biomass gasification.

4.1.6 Task F

The objective of task F is to design the experimental tests at the pilot plant; to define the sequence of experimental activities, in order to evaluate the plant performance.

4.1.6.1 Specification of plant tests

The sequence of the experimental activities to be performed with the pilot plant includes three major steps:

- The first tests were addressed to find the standard operation parameters.
- Parameter tests, lasting 5 - 10 hours, should then be carried out to investigate the influence of major process parameters on the performance of the gasifier.
- Finally, long term tests, lasting some days, should be carried out to check the overall performance of the integrated system and its reliability.

The first tests are addressed to find the standard operation parameters. These should be:

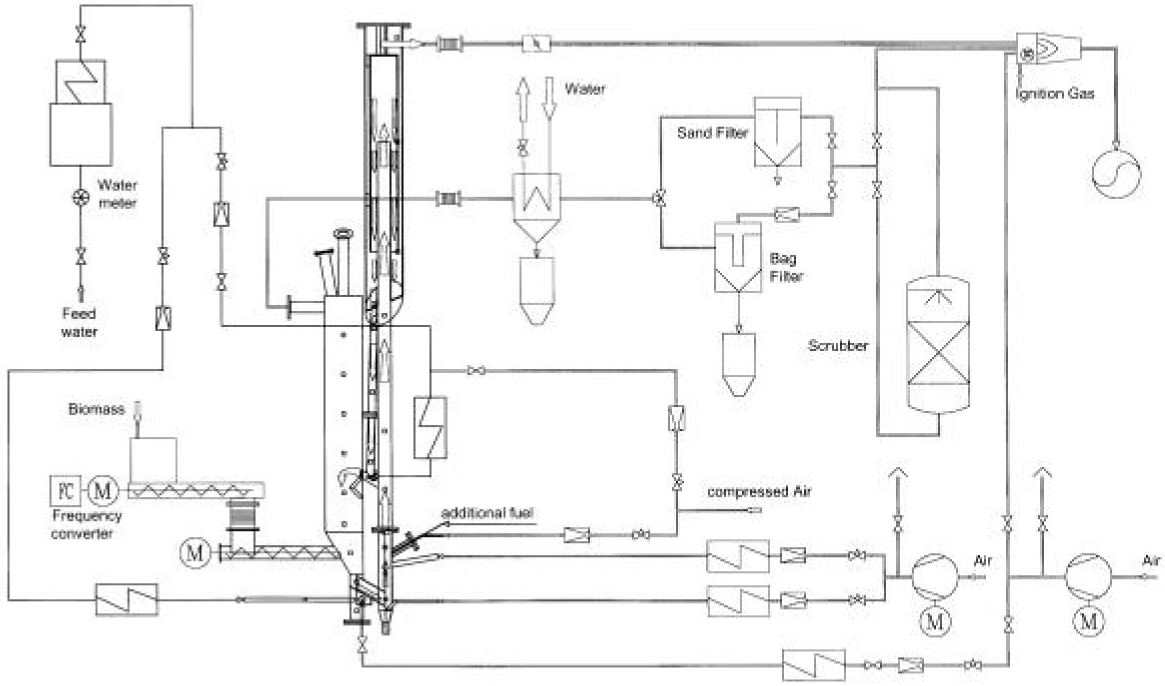
feedstock: wood chips
water content of feedstock: 15%
gasification agent: steam
gasification temperature: 800°C
load: 100% (500kW_{th})
bed material: olivine

Due to the delay in the plant construction as well as problems during the experimental practices, the consortium decided to do some experiments at the 100kW_{th} gasifier at TUV, which has the same design as the pilot plant. These results are included into this report.

4.1.6.2 Analysis of the results

Experiments at TUV

In November 1999 a new 100kW_{th} gasifier was installed at TUV. This gasifier has a similar design as the pilot plant in Trisaia. So it was possible to do some experiments with the catalyst at TUV in March 2000. ECPMS produced 35kg of catalyst for these experiments. The catalyst was mixed with natural olivine and used for the experiment. The catalyst was not reduced before the tests.

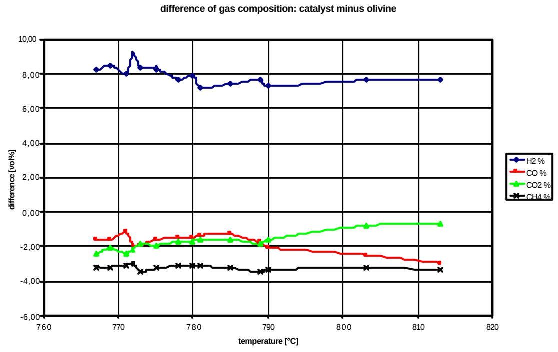


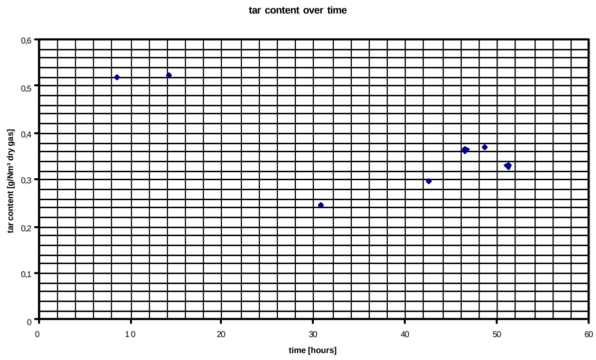
flow chart of the $100kW_{th}$ gasifier at TUV

The following parameters were used for the experiment:

fuel	wood pellets
fuel flow	25 kg/h (wet)
steam fuel ratio	0.5
gasification temperature	770-830°C
bed material	44% NiO/olivine-catalyst in Olivine

The main results of these experiments are shown in the diagrams below.


difference of gas composition: catalyst minus olivine


tar content over time

In the diagram above “difference of gas composition: catalyst minus olivine“ the influence of the catalyst on the gas composition is shown. Zero is the gas composition when only olivine is used as bed material. It can be seen clearly that the hydrogen content increases and the content of carbon monoxide, carbon dioxide and methane decreases.

In the diagram “tar content over time” the tar content of the product gas is shown. At the beginning the tar content is about 500 mg/Nm³. When the catalyst is reduced by the hydrogen, which is produced by the gasification reactions, the tar content goes down to about 300 mg/Nm³. It can be clearly seen, that the catalyst has no loss of activity for the experimental time of 50 hours.

The main results of the experiments at TUV are:

tar content of the product gas:	<500 mg/Nm³
hydrogen content:	>40 vol%
nitrogen content:	<5 vol%
attrition of the bed material:	~0,3 m%/h

Experiments at the pilot plant

In the 500kWth pilot plant at ENEA one gasification experiment was done. The description of the experiment is described in task G and the results are described below.

Results of the gasification experiment:

Product gas composition:

A number of samples for the analysis of the gas were collected at the exit of the product gas blower. The gas conditioning system comprises of a condenser, filter and the suction pump. The gas analyser is a Gas-Chromatograph. The analysis time is around 20 min, whereas the sampling time was from 1:40 to 2:00.

Gas dry	Sample 01
Components	%
CO_2	30.96
C_2H_6	1.97
H_2	22.29
N_2	5.14
CH_4	3.16
CO	36.49

Gas dry	Sample 02
Components	%
CO_2	20,54
C_2H_6	1,29
H_2	17,43
N_2	29,92
CH_4	2,47
CO	28,35

<u>Product gas analysis</u>

Gas_{dry} density:	1.2 kg/Nm³
Medium molecular weight gas_{dry}:	26.8
LHV:	7838 kJ/kg_{dry}
Steam content:	0.508 kg_{steam}/kg_{tot}
Tar content:	8.9 g/Nm^3_{dry}, 7.42 g/kg_{dry}, 3.65 g/kg_{tot}

The significant difference from the two samples can be attributed to the product gas filter cleaning system. The samples were collected during the period when the cleaning system was in operation, so there was a nitrogen pulse.

Also the gas composition of the product gas is much different from the estimated values. This can be explained by the low gasification temperature and the not steady state of the gasifier.

Analysis of Tar

The point for the tar sampling is in the top of gasifier. The sampling system comprises of an inox steel heated line, glass fiber filter, battery bottles and vapour traps before the suction pump. The tar is collected by condensation in 4 bottles containing Dichloromethane. Two bottles were at 0°C, and two at –17°C. The dichloromethane solution and the aqueous solution have been separated. The solutions have been measured and analysed.

Volume of gas collected: 0.080 Nm^3
Tar content with evaporation at 80°C ⇒ 6.1 g/Nm^3 (dry)
Tar content with evaporation at 35 °C ⇒ 8.9 g/Nm^3 (dry)

The dichloromethane solution has been analysed with a GC-MS. The tar contains various mono and policylic aromatic hydrocarbons, the main are, BTX, Naphthalene, Fluoranthene and Pyrene. The mixture of tar can be assumed to be Naphthalene $C_{10}H_8$ so: MW 128.17, T_b 218.2 °C, LHV 40200 kJ/kg.

Water Solution

The water solution has a pH value of 7.5 as well as traces of phenol and Naphthalene. The water content in the product gas is 1236 g/Nm^3 (dry).

Materials Flow and Process Conditions.

The main data were obtained from the data acquisition system. Other value were determined from energy balance or from calibration diagram. It has however to be noted that due to short working time as well as few values effected by errors, certainly the present tests cannot be representative of the gasification process.

	Name	**Flowrate** [kg/h]	**T [°C]**	**P [mbar_g]**	**Power [kW]**
In gasifier					
	Steam	71	290	100	60,2
	Product gas	0	100	150	0
	Bed materials	0	10	0	0
	Biomass	80	10	0	375,5
In siphone					
	Steam	34	290	150	28,8
	Product gas	0	100	150	0
In combustor					
	Air 1°	47	400	150	5,3
	Air 2°	210	400	150	23,6
	Air	20,6	35	150	0,2
	Gasoil	12,8	10	150	151,8
Total in		475,4	**Total in**		645,4
Out gasifier					
	Product gas	188	760	-5	347
Out combustor					
	Flue gas	286	770	-5	78,9
Total out		474	**Total out**		425,9
Difference In-out		1.4			219.5

In-Out Reactor energy and mass

Total carbon in the product gas	2.58 kmol/h.
Total hydrogen in the product gas	1.19 kmol/h
Esteemed carbon in the biomass	$C_6H_{8.39}O_{3.54}N_{0.1}$ PM 138.4 =3.16 kmol/h.
Esteemed hydrogen in the biomass	$C_6H_{8.39}O_{3.54}N_{0.1}$ PM 138.4 =2.20 kmol/h.
Total water in gasifier	77-111.4 kg/h
Water in the product gas	96 kg/h
Real steam biomass ratio	1.05

Moreover, due to short testing time, mass and energy balances could not be completed, i.e.

- was not possible to have a real biomass flow rate from weighted storage bin,
- pilot plant was not in steady state.

Moreover, there was a problem with biomass feeding. The high difference in the energy balance can be attributed to the incorrect biomass flow rate, product gas and flue gas combustible particles, product gas and flue gas non-combustible particles, imperfect gas oil combustion (CO in the flue gas) and energy loss through the insulation, etc.

Considering the fact that plant's working period was not long enough to permit a stabilization of the reactor and the ancillary units, the results presented here are preliminary. In addition the problems listed below were also encountered during present experimental test campaign, i.e.

- the torch flame was not continuous.
- the product gas filter where the pressure drop increased at very fast rate,

For these reasons the operation was stopped .

The flame was not stable essentially because the pellets feeding was not continuous. It was because of pellets humidification and its breaking in biomass powders, so the screw conveyor didn't work correct. For the same reason the biomass flow rate obtained from the calibration of the screw was not correct.

The pressure drop of the product gas filter increased at very fast rate. When the filter was opened, it was observed that some bags were collapsed internally.

The bags were collapsed because some material (fly coke and fly ash) deposited on the bag surface. During the previous tests, as in the period before the gasification operation, the filter has been worked correctly.

Some materials have been collected from the bags and the bin below the filter. They have been analysed. The results showed that the materials were different, essentially for the organic phase. In fact, after the extraction with dichloromethane, only 1% of the material of the bin went in solution, while for the bag filter 22% went in solution.

	Inorganic residue	Organic residue	DCM Extraction
Bag deposist	56,70	43,30	22% of total
Bin deposist	48,15	51,85	1% of total

The solution extracted from bag materials were analysed in the GC-MS to search its main components. The main components of the solutions were polycyclic aromatic hydrocarbon, at three, four or five cycle.

The boiling point of these constituents of tar was in the range 300-500°C. The temperature of the gas at the exit of product gas heat exchanger was around 220-240°C. Policyclic aromatic hydrocarbons condensed thus creating a mist with charcoal. The mist deposit on the bag surface as glue. In the middle of the bag perhaps there was the condensation of hydrocarbons with low cycle number because the nitrogen pulse had a temperature around 90-100°C. The interval of cleaning pulses is 1/min, so the bags are also cooled by the nitrogen. In this way some bags didn't work, the pressure drop increased and reached the critical value where mechanical resistance was exceeded.

4.1.7 Task G

The objective of task G is to carry out the experimental tests with the pilot plant; and to implement hardware modifications, when necessary. Parameter tests (5-10 hours) to investigate the influence of various parameters on the performance of the gasifier and long term tests (some days) to study the overall performance of the integrated system should have been done. On the basis of these tests the pilot plant had to be improved.

In September the first tests with the pilot plant were done. For the first tests it was decided to use almond shells as fuel. The size and the shape of this fuel should not cause any problems in the fuel feeding system. As bed material Olivine was used.

Different problems occurred during the start up of the pilot plant. While some of these problems could normally happen on any general machine and are not critical and could be solved easily, other associated with product gas filtration line and heating up system were quite serious and thus important. In principle the main problems were:

- Damaging of PTFE bags;
- Tar condensation on the plant in particular on the product gas blower and stainless steel bag;
- Long heating up time.

During the experimental campaign, several modifications related both to the pilot plant and plant procedures were adopted and implemented.

Safety filter of the blower

Damaged bag filter

In January the first gasification experiments were done.
The gasification test started with biomass feed (wood pellets) at the below conditions:

- Combustor temperature 870°C
- Gasifier temperature 780°C.
- Steam temperature 290°C
- Steam siphone flowrate 22 kg/h
- Steam gasifier flowrate 69 kg/h
- Combustor primary air 40 Nm³/h
- Combustor secondary air 180 Nm³/h

The feeder screw conveyor started with a programmed flow rate of nearly 80 kg/h. The following problems were encountered during the tests:

- pressure drop increased very fast in the product gas filter
- the siphon was blocked,
- after ½ hour, the torch flame was not continuous.

At this stage the operation was stopped because pressure drop at the product gas filter increased and the torch flame was not stable. During this time the gas was collected for analysis. Recorded data during the gasification time is shown in the figures below.

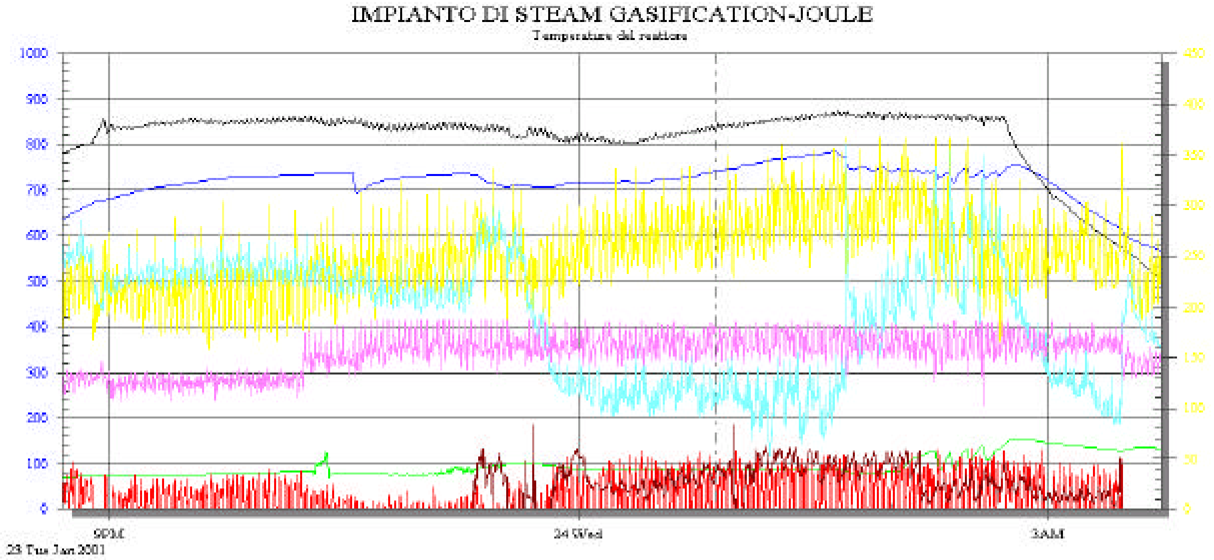


diagram of the test on 23th January 2001

5 Results and Conclusion

The aim of this project was the development of a fluidised bed gasification process for the production of a hydrogen rich gas from biomass.
To achieve this aim a 500kW$_{th}$ pilot plant was build and tested, a catalyst for fluidised beds was developed and fundamental research on the fluid dynamics were done.
The gasification reactor consists of two zones, a gasification and a combustion zone. The circulating bed material serves as heat carrier from the combustion to the gasification zone. Steam is used as gasification agent and a catalyst is used as bed material to increase the amount of hydrogen and reduce the amount of tar in the product gas. Heat and material balances were calculated and the amount of catalyst was defined.

During start up of the pilot plant problems of different nature related to both the components and sections of the plant. While some of these problems that could normally be encountered on any general machine, were not critical and could be solved easily, other associated with product gas filtration line and heating up system were quite serious and thus important. In principle following were the main problems:

- Damaging of PTFE bags;
- Tar condensation on the plant in particular on the product gas blower and stainless steel bag;
- Long heating up time.

These problems were solved, but it was not possible to do the whole experimental program, which was defined in the contract (testing the catalyst as bed material, using the fuel cell together with the gasifier).
The results obtained from the steam biomass gasification during the short time test are quite clear. Here, the plant was in transient phase. Moreover, the gasification started near the low temperature limits so the tar production was high. Generally it was demonstrated, that the gasifier produces a gas with a nitrogen content of about 5% and that the necessary circulation rate of bed material was reached.
On the cold flow model at UCL the circulation rate, the gas cross flow and the behaviour of the biomass was investigated. The results, showed, that the pilot plant was designed well and will operate as provided. Additional a new scaling parameter was introduced, which enables to calculate the circulation rate in dependency of the total amount of bed material inside the gasifier.
The work of ECPMS and UNIVAQ aimed at the development of a catalytic system. Two catalysts were developed during the project. One is based on a LaNiFe perovskite catalyst, which has shown very good activity in tar destruction and methane reforming in a separated fixed bed reactor, but is not resistant to a fluidised bed. The catalytic system NiO/olivine used a new concept to integrated NiO in the olivine structure. It was characterized and tested in dry and steam reforming of methane and presented no deactivation and no coke formation. After these results, it was synthesized in a large amount (135 kg). Its activity was confirmed in the fluidised bed (2 kg) reactor of UNIVAQ and in the fluidised bed (35 kg) reactor of TUV. The results have confirmed its remarkable activity with an increase of H_2 concentration of 8% and a decrease of CH_4 concentration of 3% in the dry gas mixture. Moreover, tar content is divided by 6 or 7 with regard to the tar content without catalyst and no additional small particles has been formed by attrition. So, this catalyst meets the requirement of attrition resistance, hydrogen production and tar destruction in the effective operating conditions encountered in biomass gasification.

General the results of this project are:

- A pilot plant with a thermal power of 500kW was build and the first experiments were done. These tests showed, that the circulation rate can be reached easily and that the nitrogen content in the product gas is below 5%.
- At the work on the cold flow model a new scaling parameter was introduced.
- A new catalyst for fluidised beds was developed and tested. This catalyst showed good activity in reduction of tars and increase of hydrogen.

6 Exploitation plans and anticipating benefits

The research groups involved in the project include academic and industrial partners. The two industrial partners (AE&E and CLC Ansaldo) are primarily interested in the commercial exploitation of the systems to be developed through the R&D and Demonstration Phases of the project (gasifier, fuel cell).

There are mainly 3 parts of the project which will be commercially exploited:
- The gasifier, which produces a medium calorific gas with a high hydrogen content
- The integration of the fuel cell into the process, including product gas treatment to reach fuel cell gas quality requirements, for clean power and heat generation
- A catalyst for gasification in fluidised beds, which increases the amount of hydrogen and decreases the amount of tars.

AE&E interests

AE&E provides complete solutions in the field of power systems and environmental technology, and has much experience in building fluidised bed combustors. AE&E did in their whole history much research in different fields.
At the moment Austria is one of the leading countries in using bioenergy. The most common utilisation of biomass for energy is combustion for heating applications. In Austria a law named ELWOG declares, that till 2007 the electricity from renewable energy has to be increased to 4%. For this job AE&E is developing the biomass power station, which utilises the dual fluidised bed gasification system to achieve high efficiency. At the moment there is a demonstration plant under construction. It will have $8MW_{th}$ and will be situated in Güssing, Burgenland. In this plant a gas engine will be used to produce electricity from the gas. The plant will go in operation in September 2001. For this scaling up step the results of the $500kW_{th}$ gasifier in this project were very important.

Ansaldo interests

Concerning the group, research on both fuel cells and gas clean-up systems, the two subjects of present project, are still actively performed. Particularly Ansaldo Ricerche, the group research company, is working since early eighties on fuel cells, as well on gas combustion and gas clean-up technologies, and is now developing one of the most promising European molten carbonate fuel cell technology (the MOLCARE Project, financed by the EC), while now entering the specific field of the gasification product gas clean-up.
The potential of the technology investigated within this project is therefore well considered in the Ansaldo Group, and proper actions will be taken in a suitable way, not only to fulfill present CLC contract obligations, but also to take such technology to the market, obviously if considered suitable for a real commercial application.
Fuel cell coupling with a biomass gasifier gives the best potential for low environmental impact and high conversion efficiency. The dual bed steam gasifier technology investigated in this project is the most suitable one to give the high hydrogen yields and product gas purity required by fuel cells.
One of the targets of this project was therefore to demonstrate that such gasifier can generate product gas characteristics sufficiently good for feeding a fuel cell.

The size of the pilot plant is suitable for a Molten Carbonate Fuel Cell, which is at the moment under development. The MCFC is a technology more suitable to be coupled with a gasifier, since it operates at temperature closer to the gasifier ones, and uses CO directly instead of requiring CO shift as PAFC does, even less mature and therefore more expensive at present.

catalyst

ECPMS and UNIVAQ got a patent of the catalyst. This catalyst is a new invention, which was devoloped during this project. It decreases the content of tar and increases the content of hydrogen in the product gas. The novelty of this catalyst is, that it can be used direct in the fluidised bed and no secondary reactor is necessary. This is a important improvement for the area of gasification, because the secondary cracker will not be necessary anymore, if this catalyst will be used.

Clean Energy from Biomass

Most partners of the consortium of this project are in the following project "Clean Energy from Biomass" (ENK5-CT2000-00314). The objective of the project is Biomass-Gasification and Fuel-Cell coupling via high-temperature gas clean-up for decentralised electricity generation with improved efficiency.
The project is aimed at studying the integration between biomass gasification and fuel cell; this is relevant for the development of biomass conversion technologies and efficient, reliable and cost effective fuel cell systems, which are both listed among the priorities under the Key Action 5 of the EU 5th Framework Programme (Cleaner Energy Systems, Renewable Energy Sources).
To prove the technical feasibility of this integration, the existing pilot plant will be modified, which includes catalytic biomass steam-gasification, hot gas clean-up, and coupled with a 125 kW_{el} molten carbonate fuel cell. Ancillary research activities will be focussed on key areas of direct relevance to the optimisation of the plant scheme and performance.