

A NOVEL APPROACH FOR THE INTEGRATION OF BIOMASS PYROLYTIC CONVERSION PROCESSES IN EXISTING MARKETS OF LIQUID FUELS AND CHEMICALS

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Abstract

A bench scale biomass flash pyrolysis reactor has been developed in co-operation by AUA and CRES during previous EC projects. The major novelty concept of this reactor configuration, virtually a Circulating Fluidized Bed (CFB), is the recirculation of pyrolysis by-product char in the lower portion of the CFB, where it is combusted, providing thus the energy requirements to carry out the biomass devolatilisation process. The main objective of the current project was to carry out further improvements as far as the CFB reactor stability, performance, product consistency, product characteristics and scale-up are concerned.

More specifically work was performed and results are reported on the following:

- Characterisation of biomass feedstock properties,
- Pyrolysis experiments in the CFB reactor,
- Modifications in the liquid and solids recovery equipment of the CFB reactor,
- Experimentation on a laboratory scale plasma reactor and parametric studies on the pyrolysis liquids upgrading,
- Design and construction of three cold flow models for the derivation of the scale-up rules,
- Compilation of technoeconomic, environmental, and safety analysis for the pyrolytic process.

The main conclusions of the project are summarized below:

- Ready-to-feed feedstock availability is a crucial requirement for the successful outcome of any biomass-to-energy project.
- The liquids yields achieved varied from 38 % wt maf feedstock for wheat straw at riser temperature 670 $^{\circ}$ C, to 63.4 % wt maf feedstock for hardwood, at riser temperature 450 $^{\circ}$ C.
- Though fully upgraded pyrolysis oil with the new technique was not produced, the improvement of the oil characteristics cannot be overseen: An essential rise in the energy input leads to a clearly visible increase in pH value, water content and H/C value of the BCO. From the results of single compounds analysis it is assumed that the most significant effect is the destruction of acetic acid by the electrical discharge.
- For further evaluation of the scaling criteria and validation of cold flow model results exploitation and operation of a CFB pyrolyzer pilot plant with approximately 100 kg/h biomass flow rate would be desirable.
- Even though, most of the standard methods for the analysis of petroleum products can be used for BCO, it is crucial to modify existing standard methods or to develop new analytical methods.
- The overall cost (including feedstock costs) of converting biomass to BCO with the current process is calculated to 45-56 ECU per GJ of delivered energy for a 1 ton/h plant, using pine as feedstock. Economies of scale will reduce these costs to 30-40 ECU for a 15 tons/h plant. In comparison heavy oil with a sulphur content of 3.5% costs range from 2 up to 4 1990 ECU per GJ of delivered energy.

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1 Economic/Industrial objectives and strategic aspects

The overall objective of the project is to carry out further improvements as far as the circulating fluidized bed (CFB) reactor stability, performance, product consistency, product characteristics and scale-up are concerned. Primary objectives include:

- pyrolysis of alternative feedstocks, such as straw, arundo donax, hardwood (eucalyptus species) as well as miscanthus,
- evaluation of physical and chemical characteristics of qualified feedstocks (ultimate and proximate analysis and calorific value),
- optimisation of flash pyrolysis as well as char combustion processes to increase liquid yields and improve liquids quality,
- close-coupling of existing CFB reactor, post treatment (product stream dedusting and pyrolysis vapour quenching) and upgrading (plasma reactor) processes,
- derivation of precise scale-up rules for larger, up to 1 maf (moisture-and-ash-free) tonne/h, flash pyrolysis plants,
- setting-up of requirements for thorough risk analysis of integrated advanced pyrolysis systems including detailed study on techno-economics for either heat or power applications, and
- identification and proposals for the removal of barriers to introduce pyrolysis liquids to niche markets, such as to existing refinery infrastructure.

As a result of the present project, it is expected that a series of technical uncertainties (solids removal from pyrolysis liquids, upgrading issues, scale-up guidelines) will be assessed and resolved, while the applied risk analysis and techno-economics assessment will constitute a valuable tool for further industrial exploitation.

The environmental impact of this project is anticipated to be positive, because the pyrolysis of biomass feedstocks has a neutral CO₂ balance and therefore it addresses the issue of global warming.

The project is not anticipated to have any direct social impact. However, the introduction of new norms and standards for the widespread use of energy from renewable sources, will have a very positive impact for the European society in the long run.

2 Technical description

This project focused on research topics related to the development of an innovative reactor for the flash pyrolysis of biomass in order to maximise the pyrolysis liquids production. The work programme combined the scientific efforts aiming to exploit persistent, unresolved technical uncertainties concerning reactor operability, stability and optimisation of performance with the introduction of new concepts, such as the on-line upgrading of pyrolysis liquids and provision of scale-up principles. The results of the applied research were further integrated in terms of risk and environmental analysis as well as technoeconomic assessment dealing the penetration of pyrolysis liquids to existing (heat and/or power) and future (refinery chemicals) markets. More specifically, the work programme followed to achieve the project objectives was divided into 6 work packages (in addition to project coordination) which are presented in detail below:

Work Package 0: Project Coordination

Agricultural University of Athens/Laboratory of Farm Structures was the responsible organisation to carry out project co-ordination. 6 project meetings were conducted during the 2 years of the project in order to ensure interaction and collaboration among the participants and the integration of the project into the general RTD framework Community programme.

Work Package 1: Feedstock logistics and biomass pretreatment

The feedstock species that were studied within this project, included those of interest both in Southern and Northern Europe, namely: miscanthus, hardwood and softwood species (forest/pine residues), arundo donax, and agricultural residues such as straw. All feedstocks were characterised in terms of:

- calorific value (ASTM D3286),
- proximate analysis (ASTM D3172/75),
- elemental analysis.

Moreover, logistics data concerning the contribution of those feedstocks to the technoeconomic analysis of the entire process were collected.

Work Package 2: Pyrolysis experiments in the Bench Scale Unit (BSU) flash pyrolyzer

During the experimental programme in the Bench Scale Unit (BSU) three variables were closely tested and controlled, namely:

- biomass feedstock,
- temperature,
- vapor residence time.

The influence of these factors were worked out in order to obtain the necessary data on mass and energy balances for the pyrolytic conversion. In addition, a solids recovery system for complete dedusting was designed and constructed (hot gas filtration-HGF), while a direct vapour product recovery train, based on direct vapour quenching (DVQ) was designed and tested.

Work Package 3: On-line improvement and upgrading of pyrolysis vapors

In the framework of this work package, the upgrading of liquid pyrolysis vapors was investigated using a high frequency dielectric barrier discharge (plasma) reactor. The plasma reactor was tested using a lab scale pyrolyzer and its prompt operation verified.

Work Package 4: Derivation of scale-up guidelines for the CFB pyrolyzer

The main objective of this work package was to derive scale-up guidelines for the Circulating Fluidized Bed (CFB) pyrolyzer. The investigation focused mainly on the fluid mechanics of the CFB reactor. For scale up reasons 3 cold flow models with different scale were constructed and tested (10, 200, 1000 kg/h). The following data were measured in all 3 units:

- solids circulation rates (SCR),
- pressure distribution along the CFB circulation loop,
- fuel particle distribution,
- gas mixing.

The influence on CFB performance of the following parameters was studied:

- variation of gas flows
- variation of bed inventory
- variation mean diameter (and kind) of the bed material
- variation of geometrical details.

Work Package 5: Pyrolysis liquids incorporation to niche markets

Physical and chemical analysis and characterisation of the pyrolysis liquid was carried out by CRES and UnS. In addition the possibilities for the use of the pyrolysis liquid, either untreated or treated, as component of fuels or for the production of chemicals were examined.

Work Package 6: Safety and environmental risk analysis including technoeconomic analysis

The integrated safety, environmental risk and technoeconomic analysis included:

- Identification of potential hazard sources, resulting both from the inherent physical characteristics, as well as from the envisaged scale-up from the laboratory scale to applications of industrial relevance
- definition of credible accident scenarios that may lead to inadvertent release of hazardous to man and/or the environment material and energy
- estimation of the resulting risk (i.e. the product between the accident consequences times the probability of its occurrence) to man and the natural environment from the technology scale-up to industrial dimensions
- integration of the results of the analyses described above to the design of industrial-level pyrolysis plants by proposing engineering solutions leading to enhanced passive and inherent safety characteristics of the system.
- contribution to the overall system techno-economic and environmental/safety optimization by coupling the safety and environmental features of the integrated pyrolysis system with the relevant economic considerations.

3 Results and conclusions

Work Package 1: Feedstock logistics and biomass pretreatment

Feedstock characterization

Based on the H/C ratio, the potential of the examined feedstocks for pyrolysis liquid production, is classified in the following order: Miscanthus > Eucalyptus > Arundo Donax > Wheat straw. But based on the H/O ratio, the potential of the examined feedstocks for pyrolysis liquid production, is: Wheat straw > Miscanthus > Eucalyptus > Arundo Donax.

Feedstock requirements prior to feeding

- Ready-to-feed feedstock availability is a crucial requirement for the successful outcome of any biomass-to-energy project.
- Feedstock handling and pretreatment is a labour intensive procedure which involves dust, noise, and mechanical health hazards. Highly automated pretreatment and feeding systems are therefore required for a cost effective feedstock preparation step prior to feeding.
- Size reduction to the 1-2 mm particle size range of Miscanthus and Arundo Donax is difficult due to the tendency of those feedstocks to form fibers.

Work Package 2: Pyrolysis experiments in the bench scale unit flash pyrolyzer

Pyrolysis vapors recovery system modifications and results

- The pyrolysis vapors collection and recovery system was extensively modified. The two major modifications included: a direct liquid-vapor quenching system and an Electrostatic Precipitator (ESP). The ESP was sized, constructed and initially tested, but short-circuiting was observed. After certain modifications in the ESP's DC current supplier, the problem of bridging between the ESP's electrodes causing the short-circuiting was solved. This way the ESP performed more effectively.
- The modified pyrolysis vapors collection and recovery system, replaced the previously installed indirect pyrolysis vapors cooling system, comprising of a shell-and-tube heat exchanger and a cotton wool filter, resulting in:
 - improved liquids collection efficiency (from 38 % wt maf feedstock to 63.4 % wt maf feedstock),
 - improved quality of the pyrolysis liquids collected,
 - prolonged pyrolysis plant operation,
 - significantly simpler cleaning and maintenance procedures,
 - better process integration.

Solids recovery system modifications

In order to improve solids collection efficiency and therefore minimize sand and ash ending in the pyrolysis liquids, a hot gas filtration system was designed and constructed.

Experimental runs

In the current contract nine experimental runs were conducted and three different feedstocks were tested as fuels. In particular 2 runs with wheat straw, 2 runs with mixed softwood, and 5 runs with mixed hardwood were performed.

The range of the vapor residence time used in the experiments was 360-557 ms.

The total liquids yields achieved varied from 38 % wt maf feedstock for wheat straw, at riser temperature 670 °C and the indirect pyrolysis vapors cooling system, to 63.4 % wt maf feedstock for mixed hardwood, at riser temperature 450°C and the modified pyrolysis vapors collection and recovery system.

The operability of the bench scale unit was prolonged and the operation at steady-state reached approximately 1 h.

Pyrolysis liquids composition

Regarding the pyrolysis liquids composition, it should be mentioned that the increase in the riser temperature leads to the increase of the Hydroxyacetaldehyde concentration and at the same time to the decrease of the Levoglucosan concentration in the pyrolysis liquids.

Work Package 3: On-line improvement and upgrading of pyrolysis liquids

The results, obtained from the parametric studies of pyrolysis liquids, show that the physical and chemical alterations in the BCO caused by the electronic upgrading process are running in the right direction - the pH value as well as the H/C value are rising.

The higher water content in the upgraded oil should cause a lower viscosity, which is desired. It is as well supposed to reduce the heating value, but the analysis shows, that this is no significant effect in the evaluated samples.

Though fully upgraded pyrolysis oil with the new technique were not produced, the improvement of the oil characteristics cannot be overseen: An essential rise in the energy input leads to a clearly visible increase in pH value, water content and H/C value of the BCO. From the results of single compounds analysis (GC-MS) it is assumed that the most significant effect is the destruction of acetic acid by the electrical discharge.

Work Package 4: Derivation of scale-up guidelines for the CFB pyrolyzer

- There is a multitude of parameters and combinations thereof, which give lots of possibilities to influence the circulation rates of bed material (as the most important measured parameter) in an appropriate way.
- The nature of scale-up efforts is not to achieve fundamental and total knowledge of a process, not even only of the fluid mechanics, but to predict more general tendencies and dependencies which help to minimise the possibility of expensive errors in reaching commercial operation.
- Specific circulation rates far above the minimum requested unnecessarily increase the ratio of the specific circulation rate of bed material to the specific feed rate. Too high values of this ratio usually leads to a reduction of the liquids yield of the products. Too long gas residence times in the riser will cause the problem of secondary cracking of the product vapors and again lead to a reduction of the liquids yield of the product.
- In CFB-reactors usually the particle size distribution should not be too narrow, with it being desirable to have at least a tenfold variation between the sizes of the 5% and 95% cumulative particle sizes.
- Experiments to study the fluid mechanic behaviour have been carried out at three different cold flow models corresponding to CFB flash pyrolyzers with 10, 135 and 1000 kg/h

biomass feed rate. As there is good agreement between the 10 kg/h pyrolyzer test rig and the cold flow model it may be concluded that appropriate scaled and designed cold flow models are well suited for the derivation of the above stated fluid mechanic scale-up criteria for the new CFB flash pyrolysis reactor design.

- For further evaluation of the scaling criteria and validation of cold flow model results any additional data is useful. For this purpose exploitation and operation of a CFB pyrolyzer pilot plant with approximately 100 kg/h biomass flow rate would be desirable. Furthermore the 10 kg/h cold flow model may be used for further parametric studies to support improving the CFB flash pyrolysis test rig.

Work Package 5: Pyrolysis liquids incorporation to niche markets

- Even though, most of the standard methods for the analysis of petroleum products can be used for BCO, it is crucial to modify existing standard methods or to develop new analytical methods.
- Fuel (BCO) quality is the critical issue for its incorporation to the energy and chemicals market. The main properties of interest are viscosity, contaminant levels of char and ash, and stability.

Work Package 6: Safety and environmental analysis including technoeconomic analysis

The following conclusions can be derived from the economic analysis for the candidate biomass feedstocks:

- financial support on agriculture is necessary in order to obtain competitive unit cost for the delivered feedstock,
- Arundo Donax plantations and pine residues exhibit the lowest cost per ton of delivered feed,
- cumulative losses during harvesting and storage have to be reduced in order to obtain higher feed yields per hectare of cultivated area.

The following conclusions can be drawn from the integrated technoeconomic analysis of the plant:

- The cost analysis of the upstream process predicted costs (per dry ton of biomass) ranging from 29 up to 85 ECU depending on the type of biomass, the size of the plant considered and the technological scenario used. When literature data are used for the yields upstream process costs decrease considerably ranging from 18 up to 55 ECU.
- The cost of converting biomass to Bio-Oil and/or heat (without taking into consideration the cost of biomass) ranges from 26 to 30 ECU's per GJ of delivered energy for a plant with processing capacity of 1 ton/h using pine as feed. The overall cost (adding feedstock costs) ranges from 45 to 56 ECU and per GJ of delivered energy using pine as feed. Economies of scale will reduce these costs to 30 and 40 ECU respectively for a plant processing capacity of 15 tons/h. Heavy oil with a sulphur content of 3.5% costs range from 2 up to 4 ECU (1990) per GJ of delivered energy¹.
- Considering a more efficient scheme for the size reduction process and a specific energy consumption of the upgrading reactor equal to 2 kWh per kg of Bio-Crude Oil (BCO) the

¹ European Commission (1997) "1997-Annual Energy Review", Directorate General for Energy DGXVII, September 1997, Special Issue.

overall cost ranges from 20 up to 28 ECU per GJ of delivered energy when Arundo Donax is used as feedstock.

- From the analysis of the pyrolysis process optimal temperatures in the riser section for particle sizes from 1.0 mm up to 1.5 mm range from 490 up to 525 °C. Optimal gas residence times range between 0.7 up 0.75 sec. For particle sizes from 1.5 mm up to 2.0 mm optimal temperatures in the riser section range from 475 up to 550 °C. For both cases riser temperatures in the zone of 500 °C are expected to maximize the liquid yield.

The following conclusions can be drawn from the results of the probabilistic analysis of the integrated process and the estimates of the gaseous emissions of pollutants, particulate emissions and solid waste:

- Preliminary analysis of the complex, introduced changes on the conceptual design (a tank for buffer storage of the Bio-Crude Oil (BCO)) to increase considerably the reliability and availability of the plant. From the analysis the critical components of the system, are identified. Sensitivities of the plant's availability and Mean Time Between Failures (MTBF) with respect to these components, are calculated. The effects on the overall cost, plant operation time and liquid yield of introducing redundancies with regard some critical components were thoroughly investigated and the outcome of the analysis were presented.
- From the results obtained plant operation estimates for a plant with processing capacity of 1 ton/h are expected equal to 8050 h per year. For a 5 tons/hour plant the estimated operation time is equal to 7700 h per year whereas for a 15 tons/hour plant this time is expected equal to 7300 h per year.
- Estimates for the gaseous emissions and the amount of generated solid waste of a plant with processing capacity of 1 ton/h of moisture ash free biomass are calculated. Sulfur dioxide emissions are extrapolated from the content of the considered biomass feedstock. Generated solid waste considers both the wasted material during size reduction and the solid waste generated from the pyrolytic process. In addition, estimates of gas emissions and fertilizer requirements (where applicable) for the upstream processes are calculated.
- For bigger plants a small reduction of the plant operation time is expected due to increased maintenance workload. Sulfur dioxide emissions vary from 1.5 tons/y to 17.5 tons/y. NO_x emissions for pyrolytic conversion vary from 0.3 to 1.7 tons/year for a plant processing capacity of 1 ton/h. These variations are the result of the sulfur and N content of the considered biomass feedstocks. For the upstream processes NO_x emissions are expected to vary from 27 to 82 tons per year for plant processing capacity of 1 ton/hour while HC emissions vary from 4 to 13 tons per year for the same plant. Fertilizer estimates for N vary from 348 up 435 tons per year when eucalyptus is considered whereas for miscanthus the annual fertilizer requirement, for 1 ton/h plant processing capacity, is estimated equal to 54 tons. For K₂O fertilizer requirement vary from 174 to 261 tons for eucalyptus whereas for Miscanthus this value is equal to 134 tons.

4 Exploitation plans and anticipated benefits

The exploitation plans of the project results are the following:

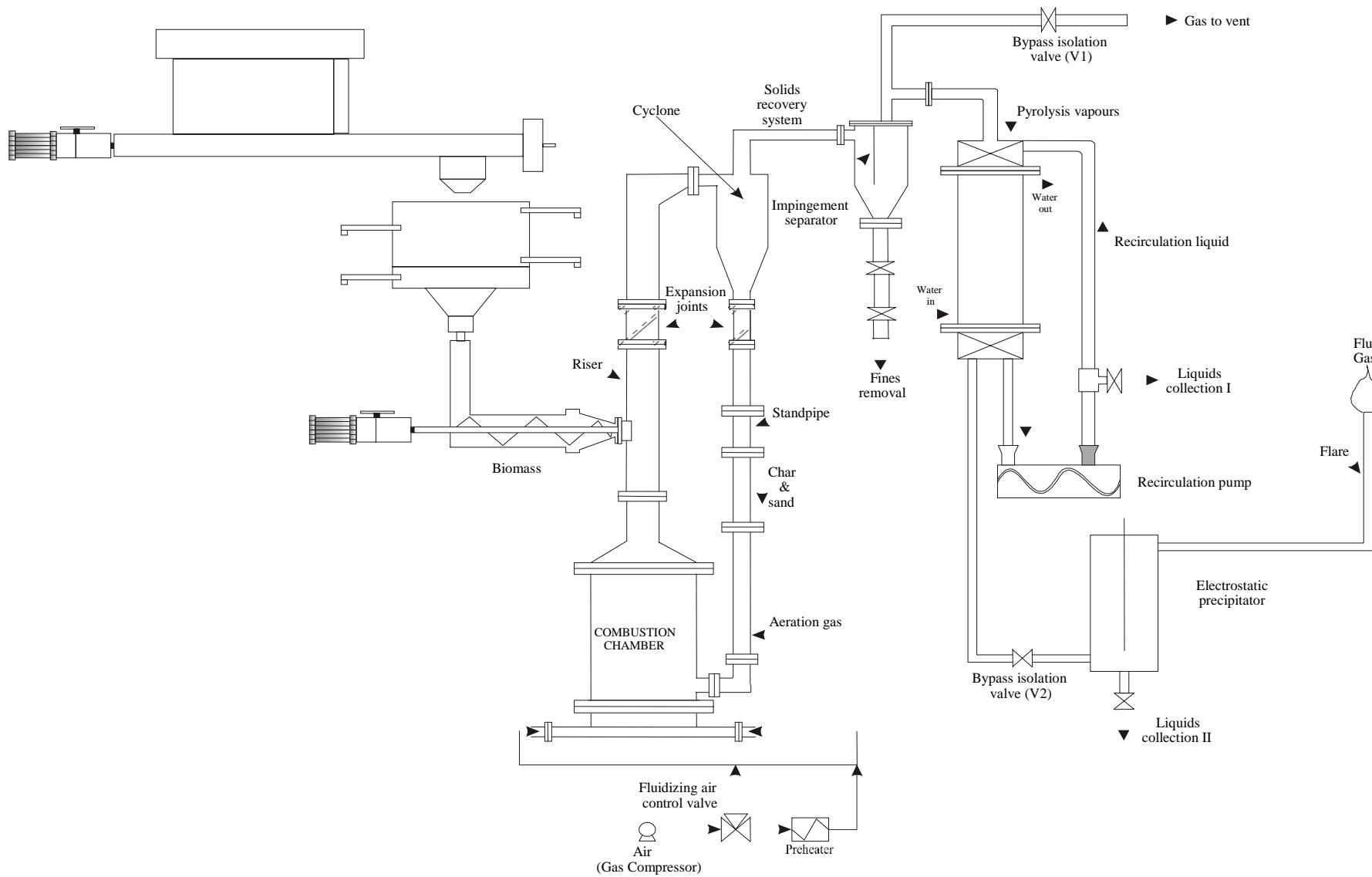
- The improved BSU flash pyrolyzer located in Athens will be utilized in another research project funded by the European Commission (JOR3-CT98-0310) for the production of pyrolysis liquids.
- The methodology and equipment developed by UnS/IPE have the potential to be used for the on-line upgrading of the pyrolysis products in other pyrolyzers.
- The cold flow models developed by TUV have great potential (because of their immediate availability and low costs) for further fluid mechanic investigations necessary during development of the design as well as during the increase of the size of pyrolyzers.
- The integrated safety, environmental, and technoeconomic analysis performed in the course of this project, may serve as a good guideline for future large scale pyrolysis plants.
- No industrial exploitation plans for the project exist.

The scientific benefits of the project include:

- an innovative approach to unresolved issues concerning flash pyrolysis such as hot gas filtration and direct vapour quenching
- assessment of different feedstocks behaviour, as far as conversion to produce pyrolysis liquids is concerned
- a major breakthrough in pyrolysis liquids upgrading technology
- derivation of concrete scale-up rules to minimize risks associated to changing fluid dynamics in larger systems.

The technical benefits of the project include:

- the development of an integrated scheme for biomass conversion, including feedstock handling (feedstock logistics), primary conversion (flash pyrolysis) and secondary treatment (pyrolysis vapour upgrading)
- the technoeconomic assessment of the integrated biomass conversion concept
- the exploitation of low-value resources (forestal and agricultural residues) by converting them to an easily handled, higher energy density product
- the exploration of the array of possibilities for further utilisation of pyrolysis products in niche markets, such as their incorporation in refinery infrastructure.



Process Flowsheet of the Bench Scale Flash Pyrolysis Unit