

Conversion Of Biomass Waste Into Biobased Products And Their Contribution To Make Rural Areas Energy Self-Reliant

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ABSTRACT: *With the widespread use of biomass for energy purposes, present communication exploits this potential renewable source for the production of bio-based products including chemicals, polymers, materials, feed and bioenergy, pursuing a cascading approach (biorefinery). Both biochemical (chemicals, enzymes, and fermentative microorganisms) and thermo-chemical (heat and chemical) processes, are addressed. It is true that substantial breakthrough has been achieved but the fact remains that R&D efforts are still necessary to address both technological and non-technological barriers. Development and demonstration of qualified innovative processes, technologies and components for the generation of both electric and thermal power in small-sized plants and the production of second-generation biofuels and sustainable biobased products, are the main challenges that needs to be addressed. In the above context, ENEA, in cooperation with both national and international stakeholders, has a number of R&D activities and a strategic projects portfolio. The focal point of ENEA's activities as well as brief description of some prototype technologies, are described in the present communication.*

Keywords: *Biomass gasification, bioenergy, pre-treatment of biomass, biobased-products, innovative processes, thermochemical and biochemical conversion, lignocellulosic materials,*

1. INTRODUCTION

Clean energy production has become a vital scientific topic world-wide, requiring special attention, as huge carbon emissions due to global oil production has created threats of climate change. In this context, developing countries need more attention and bioenergy has come out as a significant component in many future energy scenarios. Many developing countries depend on biomass to fulfil their energy requirements. Biofuels seem to be a suitable

substitute for fossil fuels to avert an imminent energy crisis, along with reduction of carbon emissions to the atmosphere.

First generation biofuels are being exploited exhaustively since last three decades. The technology adopted for bioethanol production from sugar and starchy crops (sugar cane, sugar beet, maize, etc.) is matured enough to attain the liquid fuel competitive, in terms of price and performances, as compared to gasoline and diesel. However, it is proven to be grossly inadequate to fulfil the increasing global need. Additionally, their continued use has prompted towards global food for fuel crisis.

Hence, biofuel production which generally does not compete with food and agro-waste valorization from bio-based industries, has become a major challenge in countries building a sustainable bio based industry of tomorrow. Therefore, more priority should be given to make use of lignocellulosic biomass derived from woody forests and agricultural sectors.

The cellulosic ethanol production derives its raw materials from woodchips of slashes and tree tops, saw dusts and waste paper pulps which are commonly available forest biomass. The agriculture – based feedstocks like switch grass and miscanthus etc. contribute to cellulosic ethanol production.

The raw materials rich in lignocellulose require hydrolysis to form simple sugars before the distillation process. The hydrolysis can be done by acid or enzymatic treatments. These two approaches have been the subject of continuing research interest since 1970s, and huge investments have been made worldwide to gear up this route of bioethanol production. Use of lignocellulosic materials for power generation and bioethanol production has created huge interest worldwide. However, the argument lies against the second-generation fuels which is based on land availability and protection of global ecosystems.

The third-generation biofuel using algal biomass could be the panacea to increasing global requirements for fuels. Assessments by various scientific communities indicate that algae possess huge potential as a biomass resource for providing future green transport fuels and direct use in carbon sequestration in many parts of the world.

Biogas production from waste materials is one of the main research topics. Initiatives underway are aimed at the production and upgrade of biogas for electric power generation or for the grid. Innovative technologies are tested for the energetic valorisation of the digestate. R&TD on second generation biofuels is focused on both thermochemical and biochemical conversion processes of lignocellulosic materials [1-3]. More precisely, fermentation of carbohydrates into bioethanol, production of hydrogen through fermentation of humid biomass and biofuels from microalgae cultures are some of the main activities.

An important research infrastructure is available at ENEA Trisaia Research Centre for the biomass gasification to carbon monoxide and hydrogen, which represents a versatile platform for the production of energy and liquid biofuels, for instance, through the Fischer-Tropsch process.

Production of second-generation bioethanol to be used in the transport sector using a number of feedstocks, namely agroforestry biomass, poliannual and grass biomass crops, has been the focus in a number of R&D programmes. The process comprises the biomass pre-treatment, the enzymatic hydrolysis and fermentation, and finally the alcohol separation. Biomass pre-treatment is carried out with saturated steam at moderate temperatures (200 °C, approximately) enabling a deep biomass destructuration which facilitates the separation of its main components (cellulose, hemicellulose, lignin).

R&TD activities on microalgae and other photosynthetic micro-organisms for the production of energy and non-energy products through bench scale optimization and final testing of pilot plants. Also, the ENEA laboratories include a Genomics and Proteomics platform supporting the discovery of novel genes involved in the biological biomass degradation and in the biosynthesis of value added molecules.

Technologies And Processes For Biorefinery And Green Chemistry

A number of initiatives are underway in Europe to promote the development of a bio-based economy. Increasing the share of advanced biofuels in the transport sector and finding new bio-based products derived from renewable natural resources are only some of them.

As an example, a number of chemicals and advanced biofuels can be produced from sugars derived from lignocellulosic biomass using a biorefinery approach. Such approach consists in the maximum exploitation of the biomass barrel aimed at increasing the conversion efficiency. ENEA activities support the development of new integrated biorefinery models through the implementation of cutting-edge processes and technologies for the production and conversion of some platform molecules from the biomass conversion, namely sugars, lignin, and oils.

Already in the early 1990s, ENEA was pioneer in the evaluation of sustainable crops for industrial applications and test fields were planted with poliannual species at ENEA Trisaia Research Centre. The biomass productivities were monitored continuously over the years.

More recently, ENEA has strengthened some alliances with industrial stakeholders, including Biochemetex and Novamont, with significant investments in the construction of innovative biorefineries fed with poliannual crops. In particular, Giant Reed (*Arundo donax*) was selected as raw material for the BioChemtex Demo Plant in Crescentino (Vercelli, Italy) and tailor-made processes were developed under PRIT and BIOLYFE projects for the production of second-generation bioethanol. Common Cardoon (*Cynara cardunculus*) was selected by Novamont® as raw material for The Matrica Biorefinery in Porto Torres (Sardinia), and the development of a cardoon-based biorefinery was part of strategic projects in the Italian Cluster of the Green Chemistry (BIT3G, REBIOCHEM).

Amongst various biorefineries scheme, sugars platform involves the breakdown of raw materials into sugars, which can be fermented, dehydrated or hydrogenated to produce a spectrum of chemicals. As shown in Fig. 1, R&TD activities in cooperation with industries and research organizations are underway on the three main steps of the biomass conversion and include: i) biomass pre-treatment/fractionation to facilitate the enzymatic digestion; ii) hydrolysis at high solids content (the so-called high gravity hydrolysis); and iii) sugars upgrade and conversion to a number of biobased products, mainly through fermentation (e.g. bioethanol, microbial lipids, lactic acid).

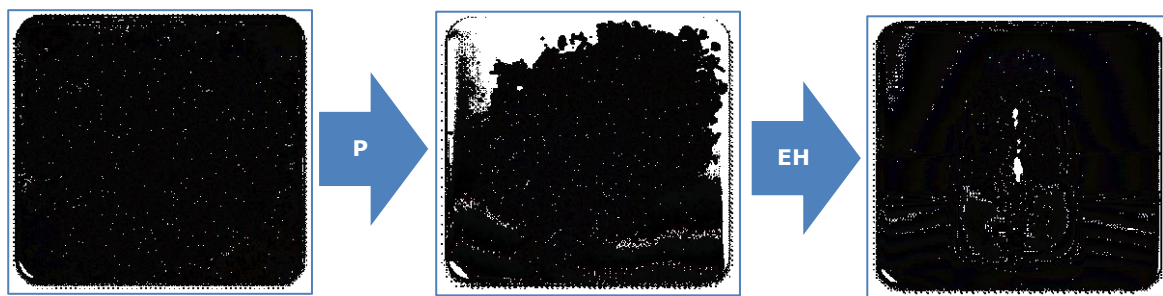


Fig. 1 Biomass-derived sugars through pre-treatment (P) and enzymatic hydrolysis (EH)

The cellulose and hemicellulose components are compactly packed by lignin layers and it hinders the enzymatic hydrolysis. The cellulose, hemicellulose, and lignin components have to be separated to use the forest waste, woody and herbaceous biomass for ethanol production. The lignin seal has to be broken to expose cellulose and hemicellulose for enzymatic action. Cellulose (primary sugar source in fibrous biomass) is surrounded by hemicellulose and lignin, hence pretreatment is required to liberate the cellulose from lignin sheath and render it accessible for a subsequent hydrolysis step. Mostly, the physical or chemical means of pretreatments are done for this purpose.

Physical treatment results in reduction of biomass physical size, whereas chemical pretreatment removes chemical barriers for the enzymes to access to the cellulose for microbial destruction.

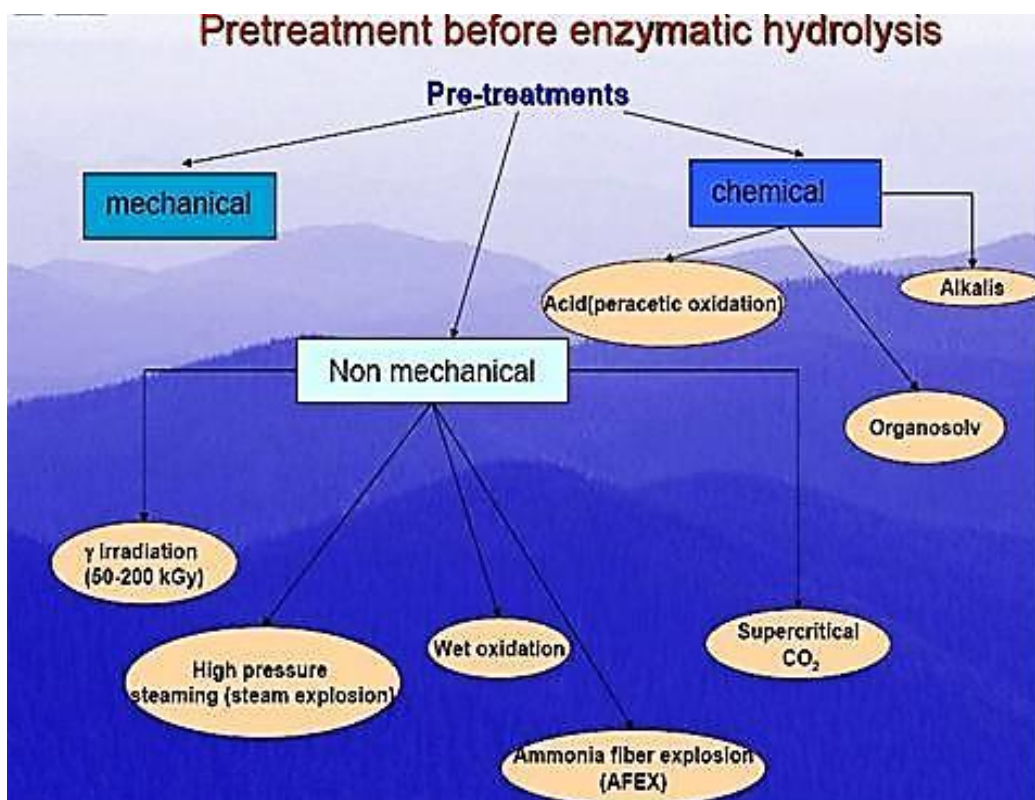


Fig. 2 Available pretreatment techniques [4]

The existing pretreatment techniques at present are acid hydrolysis, steam explosion, ammonia fiber expansion, Organosolv, Sulfite Pretreatment to Overcome Recalcitrance of

Lignocellulose (SPORL), alkaline wet oxidation method and ozone pretreatment method. For effective cellulose removal, an ideal pretreatment method should minimize the formation of degradation products, as their inhibitory action will affect subsequent hydrolysis and fermentation processes. In wet oxidation pretreatment technique, the substance is treated with water and air or oxygen at around 120°C temperature.

It was observed that significant amount of polysaccharides was lost due to degradation and byproduct formation (such as carboxylic acids), although the acidic wet oxidation (195°C, 15 min) method showed good fractionation of bagasse, and poor enzymatic convertibility of the pretreated feedstock was observed. The wet oxidation catalyzed transformation of hemicellulose (from solid phase to liquid phase) was found to give better results and there was not major hydrolysis of the solubilized hemicellulose compounds along with higher production of glucose by xylose steam explosion procedure.

Many pretreatment techniques are ineffective for high lignin containing feedstocks as of forest biomass. Two techniques such as Organosolv and SPORL can undergo more than 90% cellulose conversion for forest biomass, mainly of softwood species. SPORL is highly energy efficient (better sugar production per unit of energy consumption through pretreatment) and robust technique for forest biomass treatment with quite low yield of fermentation inhibitors. Organosolv pulping process is very effective in hardwoods processing and results in easy recovery of hydrophobic lignin product by dilution and precipitation.

It is highly necessary to use appropriate pretreatment method as various lignocellulosic compounds have different physicochemical properties. The hard woods and agriculture-based residues have primarily low lignin and high pentose content as compared to softwoods, and therefore high temperature treatment is ineffective for such biomass type, and there is more thermal degradation of pentose occurs.

The steam explosion (SE) method produces highly biodegradable substrate having less environmental effect and best suits for physical pre-treatment of straw as it causes partial hydrolysis of hemicellulose and enhances its enzymatic digestibility in the biomass residues. The SE method is a hydrothermal treatment technique for making easier and less impactful the separation between the different fractions of the common vegetal substrates (hemicelluloses, cellulose and lignin).

The technique is based on the inherent ability of the water vapour to enter and break the chemical bonding of polymeric, cellulose, hemicellulose and lignin components in the vegetal materials under high temperature and pressure. In this technique the materials are kept at temperature of 180°C -230°C for 1-10 minutes during which hemicelluloses are hydrolyzed and become soluble. Thereafter when the pressure is rapidly reconducted to the atmospheric level to get a decompress explosion that further scrapes the biomass.

The steam pretreatment process is influenced by many factors like temperature, residence time in the reactor, size of particle, moisture content and catalyst quantity. The final outcome is to avail the sugars (contained in the feed materials) to be metabolized easily by the microbes in subsequent bioconversion stage.

Pretreatment and fractionation through Steam Explosion (Fig. 3) can be considered as a flexible process scheme since it uses saturated steam to produce high degrees of biomass de-structuration.

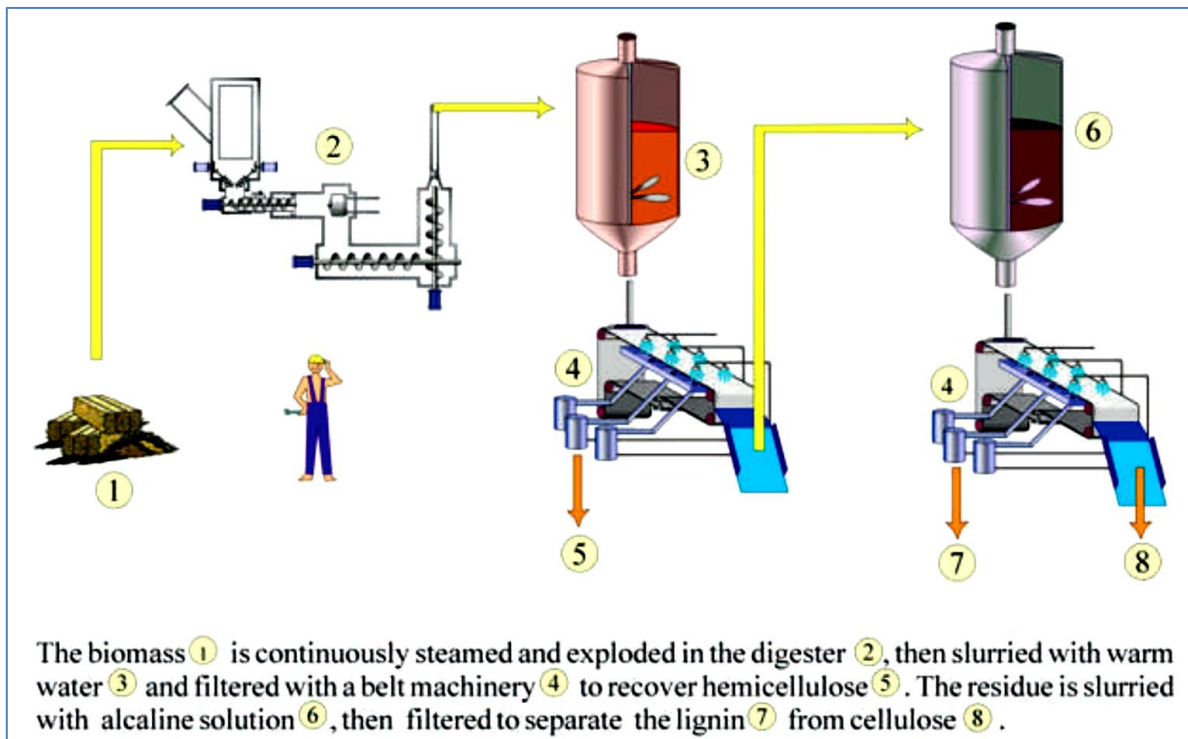


Fig. 3 ENEA Steam Explosion Continuous Plant

The use of small amounts of additives could catalyze the process at mild conditions. The type of additive could determine a different fractionation scheme. At the ENEA Trisaia Research Centre, the pilot station for biomass fractionation consists of three units of compatible size. The digester is able to process 300 kg/h biomass in the continuous mode. This technology is suitable to treat different biomass. The cellulose reach stream could reach purity of 80% and a lignin stream, containing less than 2% sugars, can be separated.

The reliability of a local biomass supply is a key element for biorefineries development. It is worth to note that a national GIS-based database and National Atlas of Biomass was created by ENEA enabling a detailed assessment of the distribution and type of biomass at province level (<http://www.atlantebiomasse.enea.it/>).

In addition, ENEA carries out analysis on the local biomass potential for instance in abandoned lands by applying an integrated evaluation of the agro-climatic vocation. The full development of biorefineries in the future will imply both technological and non-technological challenges. One main objective of the future research in the conversion of lignocellulosic materials will regard the exploitation of lignin, currently considered as a side stream and used for the production of heat and electricity to make biorefinery self-sufficient. The question is: how does the biorefinery energy balance look if part of the lignin is used to produce bioaromatics/ biochemicals?

THERMO-CHEMICAL PROCESSES FOR BIOMASS CONVERSION

Biomass can be suitable replacement to the conventionally produced fuels with sustainability, carbon-neutral and environment-friendly properties. Energy reserve per tonne of biomass is between about 1.5×10^3 and 3×10^3 kilowatt hours. Biomass can provide 1.4 times the approximate annual 150×10^3 terawatt-hours requirement for present world energy

consumption. The gasification technique has tremendous potential for conversion of biomass into both thermal and electric power generation.

Biomass gasification technique seems to be an efficient strategy to fulfil the future energy requirement along reduction of carbon emissions from fossil fuels.

Biomass is an important renewable energy resource including materials from plants, animals, leftover materials from agriculture and forestry processing sectors, woods from forests, and organic wastes from industry, human and animal origin. The energy that is present in biomass initially came from Sun. By the process of photosynthesis the CO₂ from the air is transformed to other carbon bearing molecules (sugars, starch, cellulose etc.) of plants. The chemical energy of plants, animals (animals consume plants or other animals), or their waste termed biomass energy or bioenergy. The projects related to biomass energy provide ample of opportunities in terms of business, healthy environment, and development in rural sector. The feedstock for biomass energy projects can be derived from widely available sources without affecting the food supply, forest trees and biodiversity of World.

AGRICULTURAL RESIDUES

Huge amount of crop residues are produced throughout the world but they were underutilized. The different types of residues include the agriculture based wastes such as straw, husk, leaves, peel, stubble, bagasse etc. The straw and husks produced as a byproduct of rice production can be converted into energy efficiently.

N be The cob produced during maize harvesting is left out in the field but it can be used as a biomass for energy production. Similarly, the fibrous bagasse produced in sugar cane harvesting can be a good source of energy. Significant quantities of biomass remain in the fields in the form of cob when maize is harvested which can be converted into energy. Besides, the shells and fibres produced from coconut harvesting can also be a good source of energy.

The existing practice is to do ploughing in the field and residues are mixed in the soil or burnt, left for decomposition, or may be grazed by cattle. The power and heat generation can be done by processing these residues into liquid fuels or through thermodynamic processing. The agriculture based residues are available season wise and possess differences as compared to solid fuels like wood, charcoal and char briquette etc. The major differences lies in their high content of volatile compounds and low density as well as less time needed for burning.

ANIMAL WASTE

Many animal wastes can also be converted to energy. The major component is manure of livestock animals and poultry birds which were applied in the field as a traditional practice. However, the controlled environmental conditions and anaerobic digestion process can enrich the manure and that can be applied later on. The anaerobic digestion can yield biogas from organic wastes which can be further utilized for internal combustion engines, for electricity generation or burnt for cooking, or water heating.

FORESTRY RESIDUES

The forest residues are generated from various sources like thinning of plantations, clearing of logged roads, natural process of attrition, and during stem wood extraction for pulp and

timber production. The harvesting procedures result in removal of 25 – 50 % of volume and thus residues will be available for biomass to be used for energy production. The harvesting can be in terms of young stand thinning, old stands cutting for timber and pulp which generates tops and branches to be used as biomass. Besides, the stands damaged due to insect attacks, diseases or due to fire, can also act as source of biomass. The forestry residues are generally having low density and fuel values making transportation cost higher and thus biomass reduction in the forest itself will be economical strategy.

WOOD WASTES

The wood wastes mainly come from saw mills, furniture production, building components, flooring, crafting industry etc. The wastes are mostly found in the processing industries like sawmills and plywood manufacturing companies. The amount of wood wastes varies as per the type of industry and the use of raw materials and finished products. The major wood wastes are from saw mills, plywood making, veneer, off cuts, trimmed parts and shaving products. Sawdust can arise from edging, cutting of logs, sizing and resizing etc. Generally, it is estimated that 1000 kg of wood in furniture industry will produce around 450 kg of waste (45 %). In a similar way, the wastes from sawmill industry will be around 520 kg out of 1000 kg wood (52 %).

INDUSTRIAL WASTES

The industrial waste coming from food industry has enormous potential to be used for bioenergy production. The wastes arising right from meat industry to confectionery can be collected and utilized as source of energy. The solid wastes such as fruit and vegetable peels and scraps, pulps and fibers coming from extracted sugars and starches, food materials not meeting the quality control parameters can be utilized instead of their disposal as landfill dumps.

The meat, poultry, fish, vegetable and fruit washing, fruit and vegetable blanching, cleaning and processing, wine industry produce huge liquid wastes which can be harnessed for energy production. These liquid wastes are rich in sugar, starch, and dissolved as well as solid organic components. There is tremendous potential for these wastes to undergo anaerobic digestion for biogas production, or fermentation for ethanol production and it will be a good model of waste – to – energy conversion.

Pollution is created by pulp and paper industry consuming enormous quantity of energy and water in various processes. Heterogeneous waste water is produced from these industries having materials from wood, chemicals, raw materials along with substances formed during processing. Black liquor can be judiciously utilized for production of biogas using anaerobic UASB technology.

Researches are going on to enhance the utilisation of biomass with a focus on the gasification technology (as shown in Fig. 1) and yielding gaseous energy with high value (suitable for direct application in CHP production) or gas synthesizing process for production of derived fuels (e.g. hydrogen, SNG, Fischer-Tropsch liquids, methanol, DME).

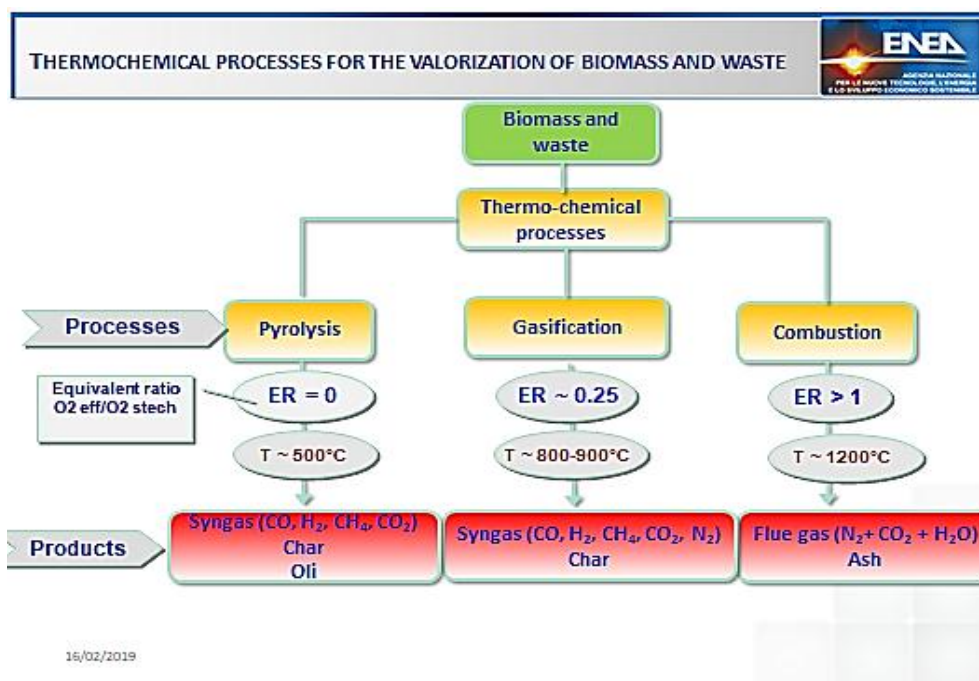
Conversion of biomass occurs at very high temperature and pressure in thermochemical process and there is flexibility in feedstock consumption as compared to biochemical biofuel

production. Gasification/pyrolysis is the initial step of thermochemical approach of biofuel generation. This technology is capital intensive but the final clean product is produced which has a direct use in engines.

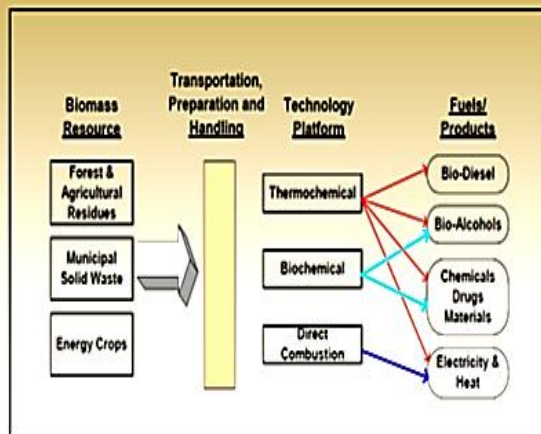
Anaerobic digestion of sewage can yield biogas as that of animal wastes. Ample amount of biogas can be generated by incineration and pyrolysis although less research has been conducted on its cost, turn down ratio, emissions, efficiencies etc. There is limited operational experience in this aspect which is evidenced from poor outcome of different prototypes.

The raw biogas is having several uses after transformation such as electricity production, steam or heat generation, or bio methane generation which can act as a substitute for natural gas in the internal combustion engines. Greenhouse gas emission can be cut down through the strategy of biomass to energy sustainable solution, adopting the use of secondary and tertiary biomass as a substitution for the use of fossil fuels. Agriculture and forest based industries in developing and emerging economies can produce a big amount of biomass residue and waste which could be used for energy production., but the biomass project is complex and its designing and development could be complex, which needs careful preparations and considerations.

The absence in many developing countries and emerging economies of high-quality project



Conversion approach



Biomass to electricity

Two main components:

1. An energy conversion system that converts biomass to useful steam, heat, or combustible gases
2. A prime mover (turbine, engine, etc.) that uses the steam, heat, or combustible gas to produce power

Note: Cogeneration or CHP is when you use the heat also

Biomass can be used directly through combustion for heat generation, or indirectly after conversion of various forms of biofuel.

COUNTER-CURRENT FIXED BED ("UP DRAFT") GASIFIER

The gasification agent such as steam, oxygen or air flows in a counter current configuration in a fixed bed of carbonaceous fuel like coal or biomass. Thermal efficiency is high as the temperatures in the gas exit are relatively low. However, this means that tar and methane production is significant at typical operation temperatures, so product gas must be extensively cleaned before use. The tar can be recycled to the reactor.

Biomass gasification (conversion of solid biomass fuel to gaseous form of combustible gas also known as producer gas) occurs sequentially through different thermochemical reactions. The steps include decomposition of a solid (say wood) by a reactive gas (say air) to give the product as a fuel. In this phenomena, biomass is undergoing four successive thermochemical processes like drying, pyrolysis, oxidation and reduction. The gas is a low-heating value fuel, with a calorific value between 1000- 1200 kcal/Nm³ (kCal per normal cubic meter). One Kg of biomass (air-dried) produces around 2.5-3.0 Nm³ of gas. Since the 1980's the research in biomass gasification has significantly increased in developing countries, as they aim to achieve energy security.

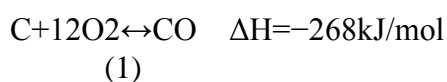
The gas mixture produced is called syngas (synthesis gas) or producer gas if it is generated without combustion in a controlled quantity of oxygen and/or steam. The power produced from gasification and combustion of the resultant gas is thought to be the source of renewable energy provided the gasified compounds were obtained from biomass.

The benefit of gasification is that the use of syngas i.e. synthesis gas H₂/CO is ideally more efficient as compared to direct combustion of the original fuel as it can be combusted at higher temperatures or even in fuel cells, so that the thermodynamic upper limit to the efficiency defined by Carnot's rule is higher or (in case of fuel cells) not applicable.

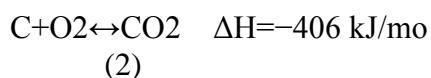
Chemistry of gasification

The reactions taking place in the gasifier can be summarized as indicated below:

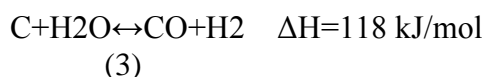
Partial oxidation:



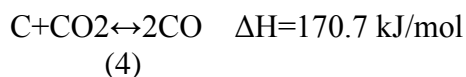
Complete oxidation:



Water gas phase reaction:

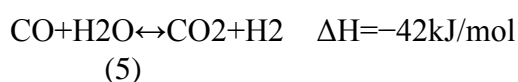


Boudouard reaction:

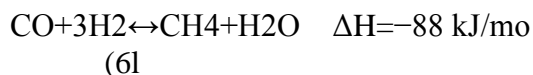


The heat needed for water gas phase and Boudouard reactions is provided by the complete and the partial oxidation reactions. The complete oxidation gives about 60% of the heat requirements during gasification. Along with the previous reactions which are common in combustion and gasification, hydrogen, steam, and carbon monoxide show further reactions as mentioned below:

Water gas shift reaction:

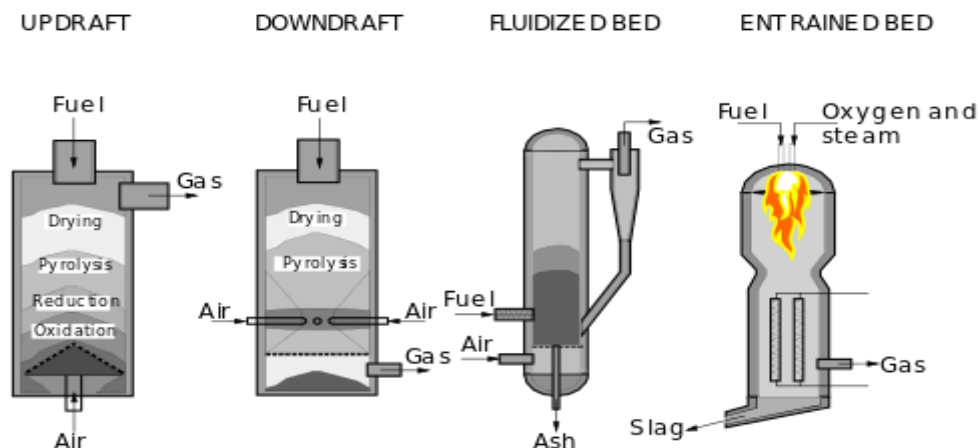


Methane formation:



The water gas shifts and methane production processes are in equilibrium and the regulating parameters are pressure, temperature and concentration of reaction species.

The different types of gasifiers that are existing and are in commercial use such as counter-current fixed bed, co-current fixed bed, fluidized bed, entrained flow, plasma, and free radical, is described below.



MAIN GASIFIER TYPES

COUNTER-CURRENT FIXED BED (UP DRAFT) GASIFIER

In this type of gasifier a fixed-bed of carbonaceous fuel such as coal or biomass, through which the gasification agent (eg. steam, oxygen and/or air) flows in counter-current configuration. The thermal efficiency is found to be high because the temperatures in the gas exit are comparatively low. This indicates that tar and CH₄ yield is significant at typical operation temperatures, hence product gas should be thoroughly cleaned before use. The tar can be recycled to the reactor.

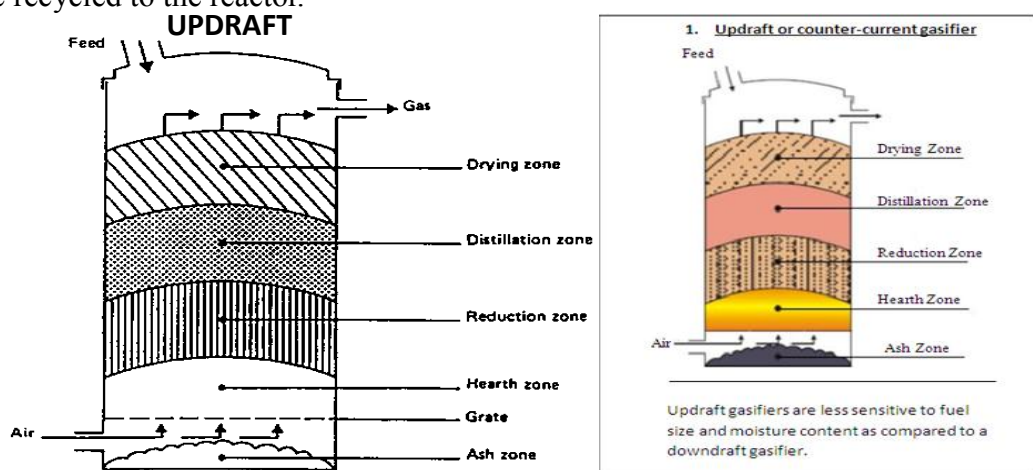


Figure . UP- DRAFT GASIFIER

Co-current fixed bed (down draft) gasifier

The problem of tar entrainment in gas stream has been solved by designing the co-current or down draft gasifiers, where the primary gasification air is introduced at or above the oxidation zone in the gasifier. The producer gas is removed at the bottom of the apparatus, hence the fuel and the gas move in the same direction. It is important that heat must be added to the upper region of the bed by combustion of small quantity of the fuel or giving from external heat source. The generated gas comes out of the gasifier at a very high temperature, and major part of this heat is transferred to the gasification agent added at the top of bed, resulting in an energy efficiency on level with the counter-current type. As all the tars should pass through the hot bed of char in this set up, level of tars is much lower than the counter-current type.

Functioning of downdraft gasifiers is better with internal-combustion engines. Air is drawn by the engine suction through the fuel bed, and towards the end gas is produced. The product gas is having Low tar level (0.015–3 g/nm³) which is another advantage for their use with internal-combustion engines. When we compare the ignition time, a downdraft gasifier needs shorter time (20–30 min.) to ignite and bring the plant up to the working temperature than the time required by an updraft gasifier.

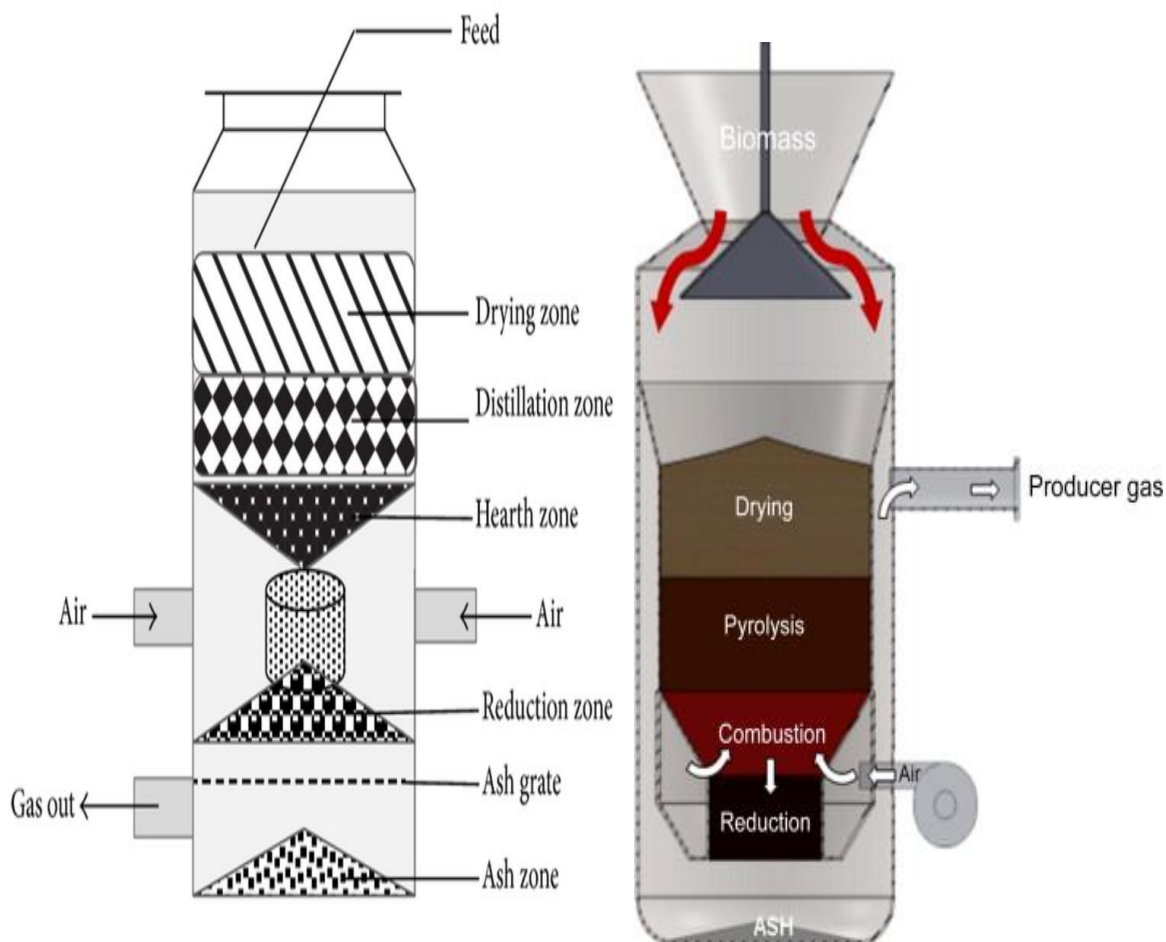


FIG. Fixed-bed downdraft gasifier or cocurrent gasifier

FLUIDIZED BED GASIFIER - In this case the fuel is fluidized in oxygen and steam/air. The fuel should be in highly active condition as temperatures are comparatively low in dry

ash gasifiers, and low grade coals are mostly suited for this purpose. The gasifiers causing agglomeration have little higher temperatures, and are suited for higher rank coals. The conversion efficiency can be rather low due to elutriation of carbonaceous material. The conversion can be enhanced by recycling or subsequent combustion of solids. The major benefits of fluidized bed gasifiers come from their feedstock flexibility culminating from easy temperature control, which can be adjusted below the melting or fusion point of the ash (such as rice husk), efficiently can deal with fluffy materials and fine-grained compounds (such as sawdust) without requirement of preprocessing. There can be problems with the feeding, bed instability and fly ash sintering in the gas channels with some of the biomass fuels.

Some of the other drawbacks of fluidized bed gasifier are high tar content of product gas (around 500 mg/m³ gas), incomplete burnout of carbon, and poor response to load changes.

As the control equipment needs to cater for the latter difficulty, very less fluidized bed gasifiers are not foreseen and the application range should be approximately set at above 500 kW of shaft power.

The fluidized bed gasifiers are best suited for fuels which form highly corrosive ash and damage the walls of slagging gasifiers. In general, biomass fuels possess higher levels of corrosive ash.

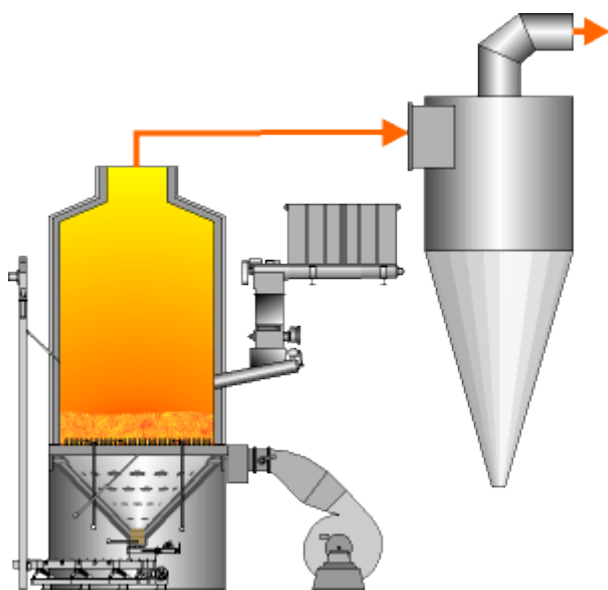


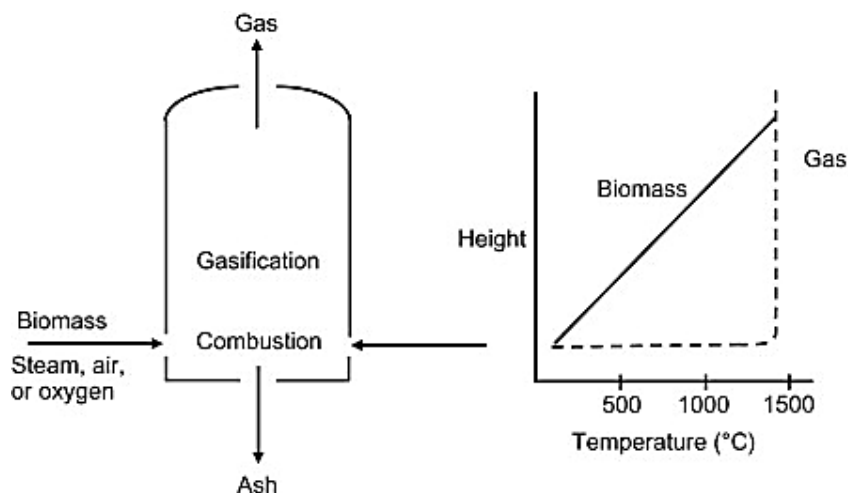
Fig. FLUIDIZED BED GASIFIER

BUBBLING FLUIDIZED BED GASIFIER. The positive aspects of bubbling fluidized-bed gasification are uniform syngas production; almost uniformity in the temperature distribution in all over part of the the reactor; ability to accept large range of fuel particle sizes; provision of high rate of heat transfer property between the inert materials, fuels and gases, high conversion rate with low amount of tar and unconverted carbon particles [13]. The drawbacks are the production of large bubble size which may cause gas bypass through the bed.

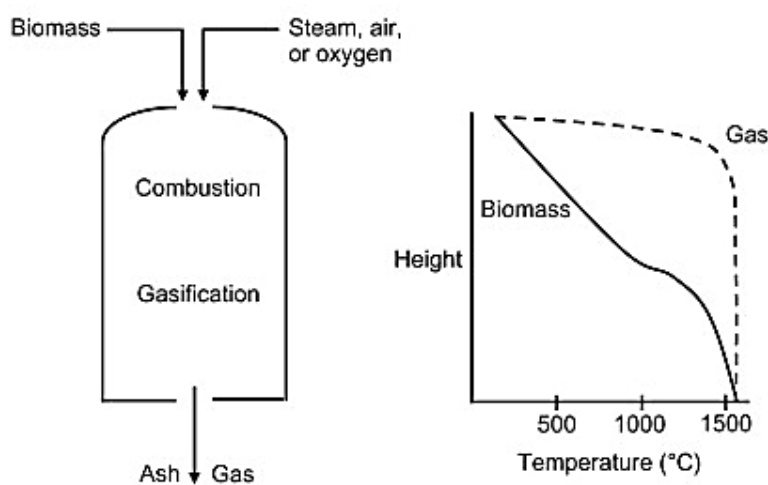
Major demerits of the fluidized bed gasifier lies in the high tar content of product gas (up to 500 mg/m³ gas),incomplete carbon burnout, and poor response to load changes.

ENTRAINED FLOW GASIFIER

In the concurrent flow, a dried pulverized solid, atomized liquid fuel, or the fuel slurry is gasified with the help of O₂ or less frequently air. The thermal efficiency is found to be lowered because the gas should be cooled before its cleaning with the presently available technology, although it is expected that higher temperatures and pressures will lead to high throughput achievement. The higher temperature means that tar and methane are absent in the generated gas; but the O₂ requirement is more as compared to the other gasifier types. All the existing entrained flow gasifiers remove most of the ash as the operating temperature is well above the ash fusion temperature.



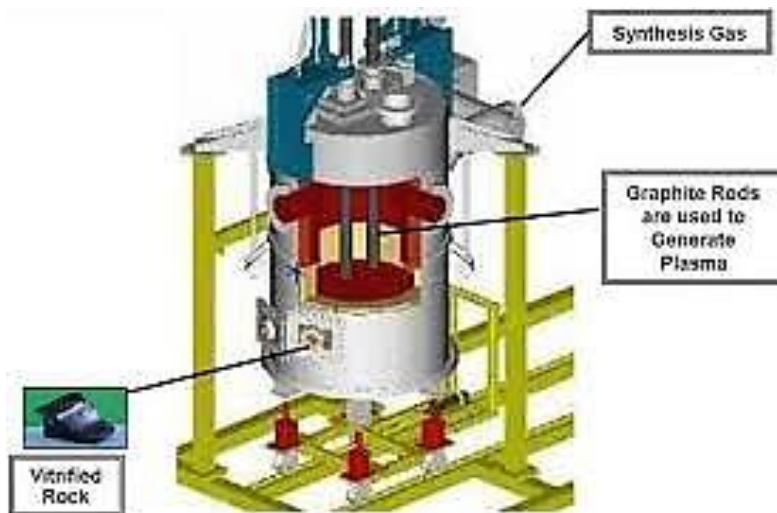
(a)



(b)

PLASMA GASIFIER

Plasma gasification, as shown in the figure below, is a method which transforms organic matter into synthetic gas, electricity, and slag by using the plasma. The hot gases coming out of the plasma torch or arc contact the solid wastes like municipal wastes, auto-shredder wastes, hospital wastes, hazardous waste materials and heat them to above 3,000 °F.

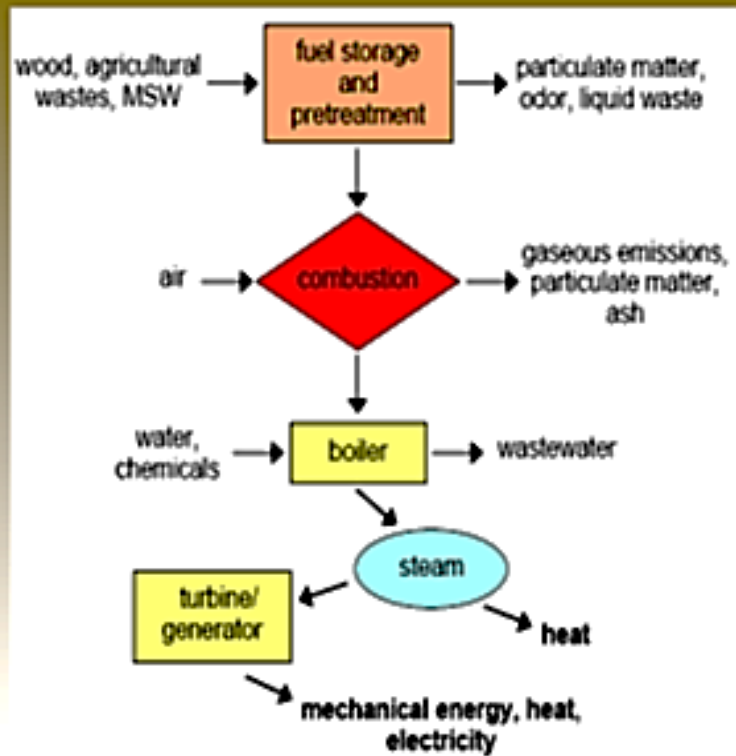


The very high heat generated supports the gasification reactions and the chemical bonds of the feedstock are broken down and finally converts them to a syngas. The syngas consists primarily of CO and H₂ — the fundamental structural units for chemicals, fertilizers, substitute natural gases, and liquid transport fuels. Besides, the syngas can be used in gas turbines or reciprocating engines to generate electricity, or combustion is done to yield steam for a steam turbine generator. Very high temperature is utilized for plasma gasification in an oxygen – deficient environment for absolute decomposition of waste materials into simple molecules, very similar to the process of pyrolysis. As the waste materials are converted to the basic elements, highly hazardous waste compounds become utilizable syngas. Glassy-like slag is produced after melting of the inorganic compounds and those are nonhazardous with solid hydrocarbons like coal, and oil sands, and oil shales.

Particularly because of the control equipment needed to cater for the latter difficulty, very small fluidized bed gasifiers are not foreseen and the application range must be tentatively set at above 500 kW (shaft power).

Typical industrial system

Direct combustion to produce steam to run turbine generators




UPDRAFT FIXED BED PLANT OF 150 KWTH




UPdraft fixed bed gasification plant based on 150 kWth reactor with steam/air gasifying agent, installed at ENEA Trisaia center, operates with feedstock of high biogenic fraction

and a generating producer gas of LHV 5-6 MJ/Nm³dry is implemented. The plant is equipped with a wet purification system operated with biodiesel.

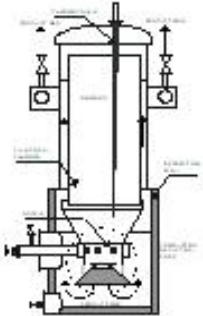
DOWNDRAFT FIXED BED PLANT OF 30-80 KWE

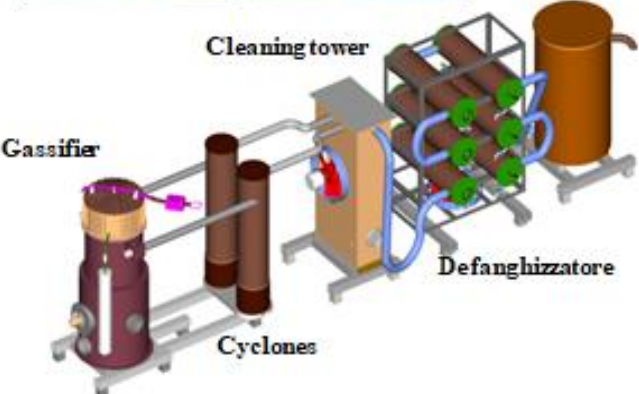





- ✓ Process study
- ✓ Development and optimization of plant components
- ✓ Sampling and analysis of gas, tar and emissions
- ✓ Performance analysis with enriched air
- ✓ Development of internal combustion engines

Bio-filter to expansion





Coupled with an endothermic engine
IVECO-AIFO



DAEWOO SOCOGES

ENEA ACTIVITIES ON BIOMASS/BIOFUELS (SUB MEGAWATT SCALE BIOMASS BASED POWER GENERATION FOR ENTREPRENEURS, NGOS, FINANCIAL INSTITUTIONS AND RELEVANT STAKEHOLDERS)

In Italy, efforts have been made with more focus for sharp enhancement of biomass use due to the tremendous potential for this type of energy source. Research and development activities on thermochemical conversion processes are based on gasification and pyrolysis and, thus, support the National and European industrial system to scout and focus on advanced new technologies.

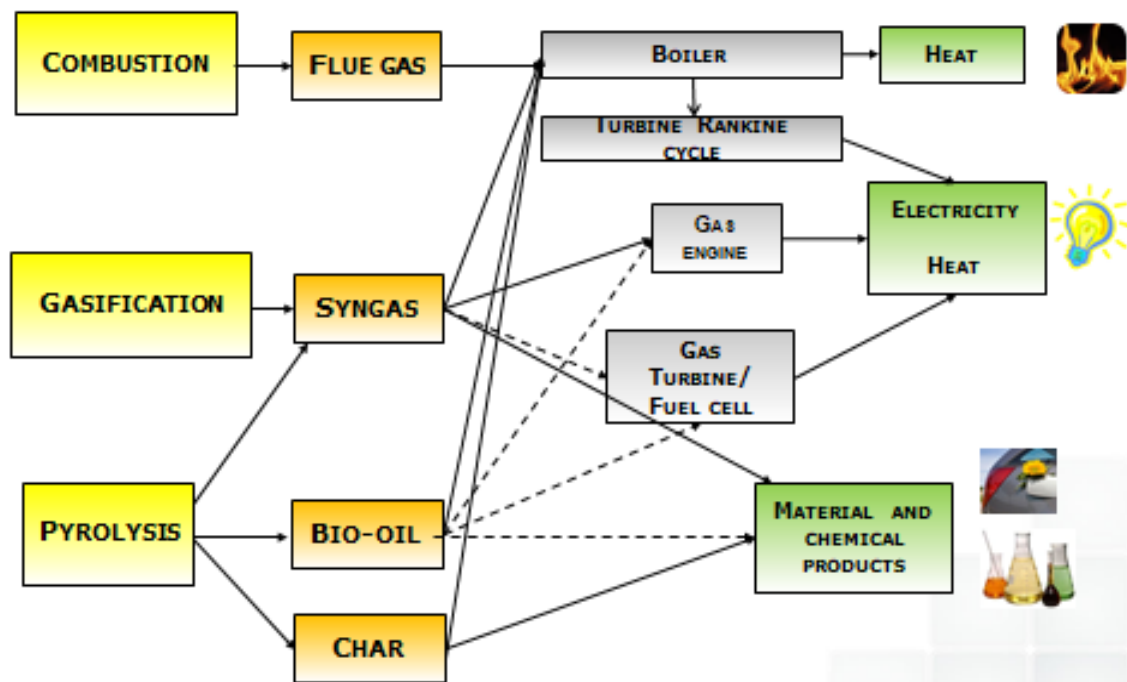
Various projects are accomplished and also going on in collaboration with national and international institutions in the process of thermochemical conversion of biomass through gasification.

Numbers of experimental plants with different technologies (fixed bed, BFB, FICFB gasifiers) and of different sizes (10kWth, 100kWth, 500kWth, 1MWth) are available at Trisaia.

Experimental investigations have been done to analyse the efficient field of application for fuel gas and power generation through different ways via internal combustion engine, gas turbines and high temperature fuel cell (MCFC).

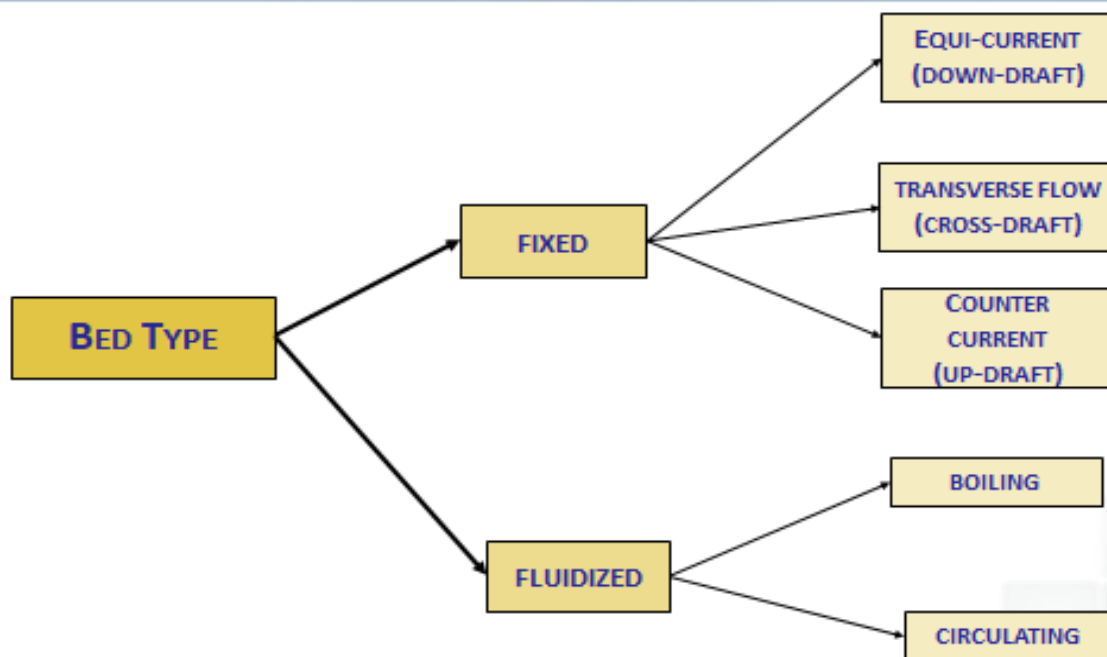
Research and development activities on thermochemical conversion processes are based on gasification and pyrolysis and, thus, support the National and European industrial system to scout and focus on advanced new technologies. The use of biomass gasification for syngas production to biofuels conversion has also been considered.

THERMOCHEMICAL PROCESSES FOR THE VALORIZATION OF BIOMASS AND WASTE




16/02/2019

CLASSIFICATION AND TYPES OF GASIFIERS FOR THE PRODUCTION OF ELECTRIC ENERGY 



16/02/2019

6

Thermochemical processes for the valorization of biomass and waste 

- ❖ **Air**, is the most simple technology but the gas produced has a low calorific value because it contains a large amount of nitrogen
- ❖ **Oxygen**, the absence of nitrogen allows to obtain a medium calorific value vector
- ❖ **Vapor**, it is cheaper. Oxygen and the gas obtained has higher hydrogen content but the process is endothermic.

| | Air | Oxygen/H ₂ O | Vapor |
|---------------------------|-----|-------------------------|-------|
| CO | 14 | 34 | 27 |
| CO ₂ | 15 | 27 | 20 |
| H ₂ | 10 | 32 | 38 |
| CH ₄ | 4 | 5 | 12 |
| N ₂ | 57 | 2 | 3 |
| PCI (MJ/Nm ³) | 4 | 9 | 11 |

- PCI natural gas about 35 MJ / Nm³
- A very diluted gas can not be transported over long distances
- A gas with PCI < 7 MJ / Nm³ can cause a significant drop in the performance of engines and boilers

7

ENEA has developed an industrial scale FICFB gasifier at Trisaia [13-14]. The design of the reactor and the use of steam as gasification agent gives this process a nearly nitrogen free

product gas with a high calorific value of around 12 MJ/Nm³ dry gas. By using a natural catalyst as bed material and gasification temperature above 800 °C, the tar content was

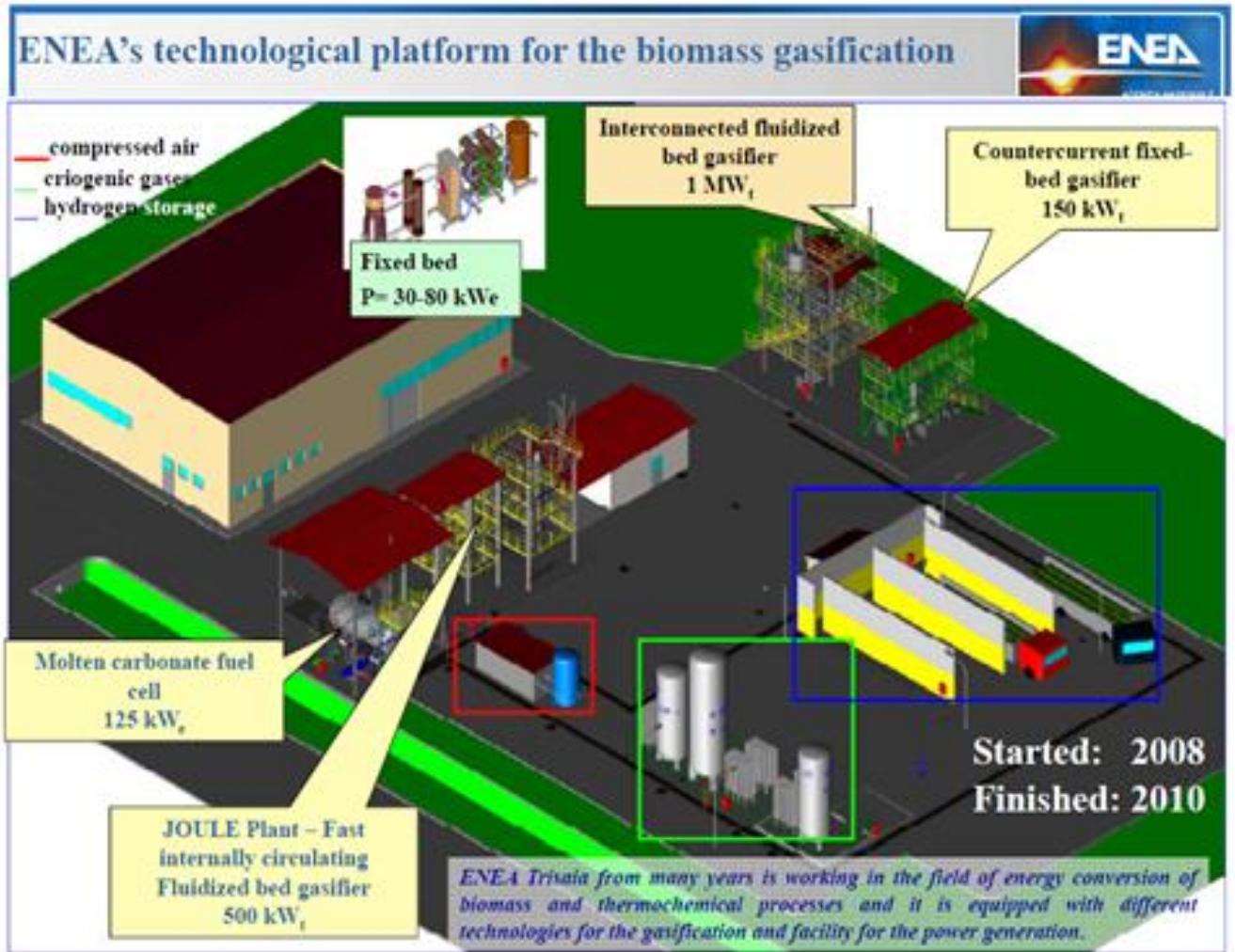


The 500 KW_e FICFB gasifier at Trisaia.

Fixed bed gasifier plants have been developed, most appropriate for their use, especially, in the developing countries as well as for their wide spread diffusion at the national level.

reduced below 5 g/Nm³.

Figure 4 Industrial scale FICFB gasifier designed, developed and experimented by ENEA

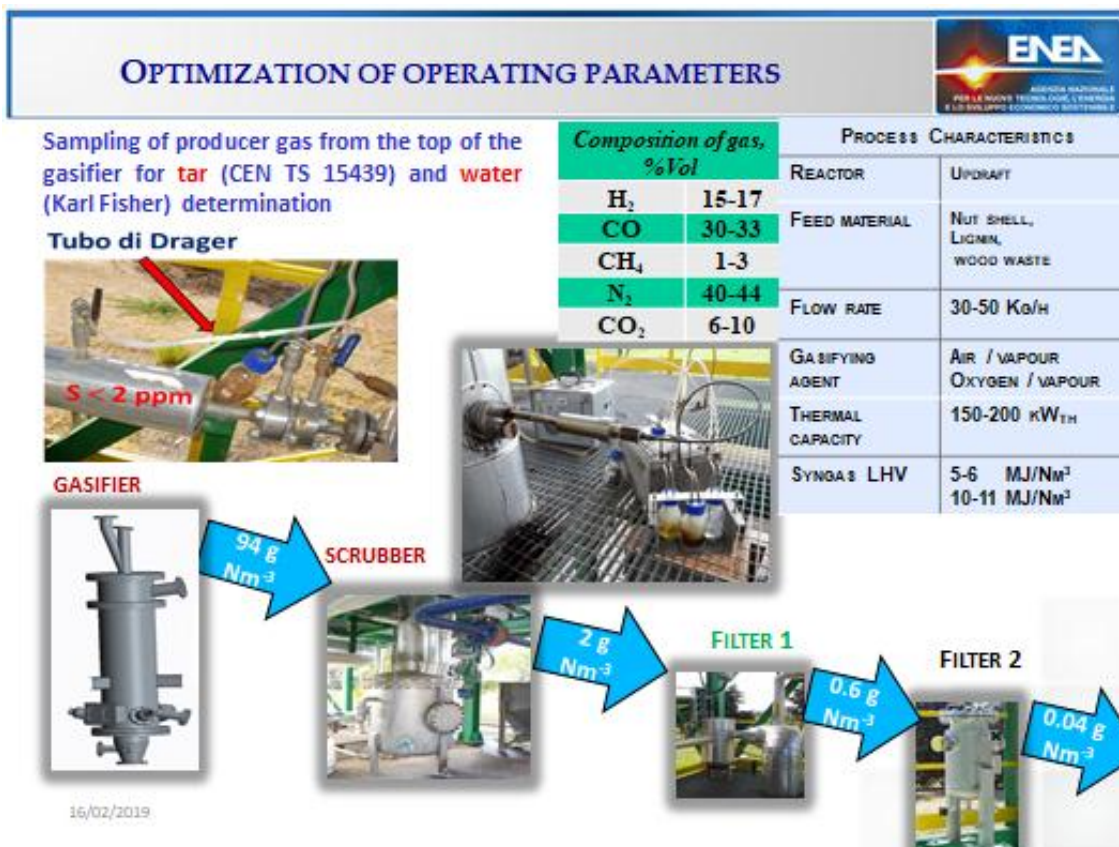


ENEA activities on Biomass/Biofuels



Pilot Plants for biomass gasification

| | <p>Fluidized bed –Internally Recirculating Enriched air/steam 1MWth Coupled with ICE for power generation</p> | <table border="1"> <thead> <tr> <th colspan="2">SYNGAS COMPOSITION</th> </tr> <tr> <th></th> <th>%Vol</th> </tr> </thead> <tbody> <tr> <td>H₂</td> <td>22</td> </tr> <tr> <td>CO</td> <td>37</td> </tr> <tr> <td>CH₄</td> <td>6.2</td> </tr> <tr> <td>H₂O</td> <td>6.8</td> </tr> <tr> <td>CO₂</td> <td>20.8</td> </tr> <tr> <td>N₂</td> <td>22</td> </tr> </tbody> </table> | SYNGAS COMPOSITION | | | %Vol | H ₂ | 22 | CO | 37 | CH ₄ | 6.2 | H ₂ O | 6.8 | CO ₂ | 20.8 | N ₂ | 22 | |
|--------------------|---|---|--------------------|--|--|------|----------------|------|----|------|-----------------|------|------------------|-----|-----------------|------|------------------|----|--|
| SYNGAS COMPOSITION | | | | | | | | | | | | | | | | | | | |
| | %Vol | | | | | | | | | | | | | | | | | | |
| H ₂ | 22 | | | | | | | | | | | | | | | | | | |
| CO | 37 | | | | | | | | | | | | | | | | | | |
| CH ₄ | 6.2 | | | | | | | | | | | | | | | | | | |
| H ₂ O | 6.8 | | | | | | | | | | | | | | | | | | |
| CO ₂ | 20.8 | | | | | | | | | | | | | | | | | | |
| N ₂ | 22 | | | | | | | | | | | | | | | | | | |
| | <p>Fluidized catalytic bed –Internally recirculating Air/steam 550kWth Coupled with ICE or FC for power generation, Fisher Tropsch</p> | <table border="1"> <thead> <tr> <th colspan="2">SYNGAS COMPOSITION</th> </tr> <tr> <th></th> <th>%Vol</th> </tr> </thead> <tbody> <tr> <td>H₂</td> <td>34.1</td> </tr> <tr> <td>CO</td> <td>25.1</td> </tr> <tr> <td>CH₄</td> <td>10.4</td> </tr> <tr> <td>N₂</td> <td>9.6</td> </tr> <tr> <td>CO₂</td> <td>20.8</td> </tr> </tbody> </table> | SYNGAS COMPOSITION | | | %Vol | H ₂ | 34.1 | CO | 25.1 | CH ₄ | 10.4 | N ₂ | 9.6 | CO ₂ | 20.8 | | | |
| SYNGAS COMPOSITION | | | | | | | | | | | | | | | | | | | |
| | %Vol | | | | | | | | | | | | | | | | | | |
| H ₂ | 34.1 | | | | | | | | | | | | | | | | | | |
| CO | 25.1 | | | | | | | | | | | | | | | | | | |
| CH ₄ | 10.4 | | | | | | | | | | | | | | | | | | |
| N ₂ | 9.6 | | | | | | | | | | | | | | | | | | |
| CO ₂ | 20.8 | | | | | | | | | | | | | | | | | | |
| | <p>UPDRAFT fixed bed Air/steam 200kWth Coupled with ICE for power generation, Fisher Tropsch</p> | <table border="1"> <thead> <tr> <th colspan="2">SYNGAS COMPOSITION</th> </tr> <tr> <th></th> <th>%Vol</th> </tr> </thead> <tbody> <tr> <td>H₂</td> <td>20</td> </tr> <tr> <td>CO</td> <td>21</td> </tr> <tr> <td>CH₄</td> <td>4</td> </tr> <tr> <td>N₂</td> <td>40</td> </tr> <tr> <td>CO₂</td> <td>6</td> </tr> <tr> <td>H₂O</td> <td>9</td> </tr> </tbody> </table> | SYNGAS COMPOSITION | | | %Vol | H ₂ | 20 | CO | 21 | CH ₄ | 4 | N ₂ | 40 | CO ₂ | 6 | H ₂ O | 9 | |
| SYNGAS COMPOSITION | | | | | | | | | | | | | | | | | | | |
| | %Vol | | | | | | | | | | | | | | | | | | |
| H ₂ | 20 | | | | | | | | | | | | | | | | | | |
| CO | 21 | | | | | | | | | | | | | | | | | | |
| CH ₄ | 4 | | | | | | | | | | | | | | | | | | |
| N ₂ | 40 | | | | | | | | | | | | | | | | | | |
| CO ₂ | 6 | | | | | | | | | | | | | | | | | | |
| H ₂ O | 9 | | | | | | | | | | | | | | | | | | |
| | <p>DOWNDRAFT fixed bed Air/steam 150-450kWth Coupled with ICE for power generation</p> | <table border="1"> <thead> <tr> <th colspan="2">SYNGAS COMPOSITION</th> </tr> <tr> <th></th> <th>%Vol</th> </tr> </thead> <tbody> <tr> <td>H₂</td> <td>15</td> </tr> <tr> <td>CO</td> <td>22</td> </tr> <tr> <td>CH₄</td> <td>3</td> </tr> <tr> <td>N₂</td> <td>40</td> </tr> <tr> <td>CO₂</td> <td>20</td> </tr> </tbody> </table> | SYNGAS COMPOSITION | | | %Vol | H ₂ | 15 | CO | 22 | CH ₄ | 3 | N ₂ | 40 | CO ₂ | 20 | | | |
| SYNGAS COMPOSITION | | | | | | | | | | | | | | | | | | | |
| | %Vol | | | | | | | | | | | | | | | | | | |
| H ₂ | 15 | | | | | | | | | | | | | | | | | | |
| CO | 22 | | | | | | | | | | | | | | | | | | |
| CH ₄ | 3 | | | | | | | | | | | | | | | | | | |
| N ₂ | 40 | | | | | | | | | | | | | | | | | | |
| CO ₂ | 20 | | | | | | | | | | | | | | | | | | |



The design of the reactor and the use of steam as gasification agent in ENEA's developed industrial scale FICFB gasifier at Trisaia [13-14], gives this process a nearly nitrogen free product gas with a high calorific value of around 12 MJ/Nm³ dry gas. By using a natural catalyst as bed material and gasification temperature above 800 °C, the tar content was reduced below 5 g/Nm³.

STEAM GASIFICATION PLANT



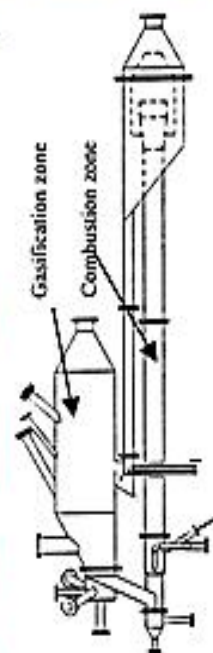
- Steam gasification, power 500 kWt.
- Gasifier boiling bed with internal circulation
- Gas produced "nitrogen free"
- Catalytic bed

Recirculated with the separation of the combustion zone from the gasification

Tar raw gas ~ 9 g/Nm³_{dry}

| Composition of gas, %Vol | |
|--------------------------------|---------|
| H ₂ | 34 - 32 |
| CO | 21 - 25 |
| CH ₄ | 9 - 10 |
| CO ₂ | 19 - 22 |
| C ₂ -C ₃ | 2-3 |
| N ₂ | 9 - 13 |

Yield raw gas 1-1.4 Nm³/kg_{dry}
 PCI raw gas 11-13 MJ/Nm³_{dry}



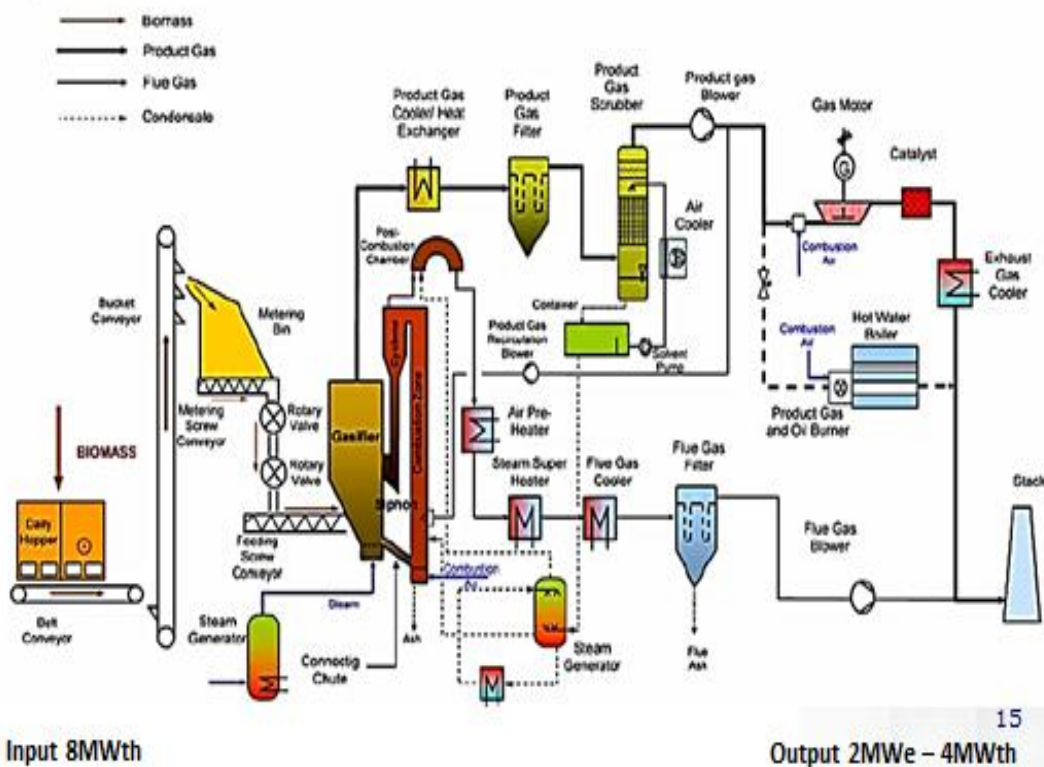
Industrial scale FICFB gasifier designed, developed and experimented by ENEA

DUAL FLUIDIZED BED GASIFIER GÜSSING-AUSTRIA



Biomass Gasification Power Plant

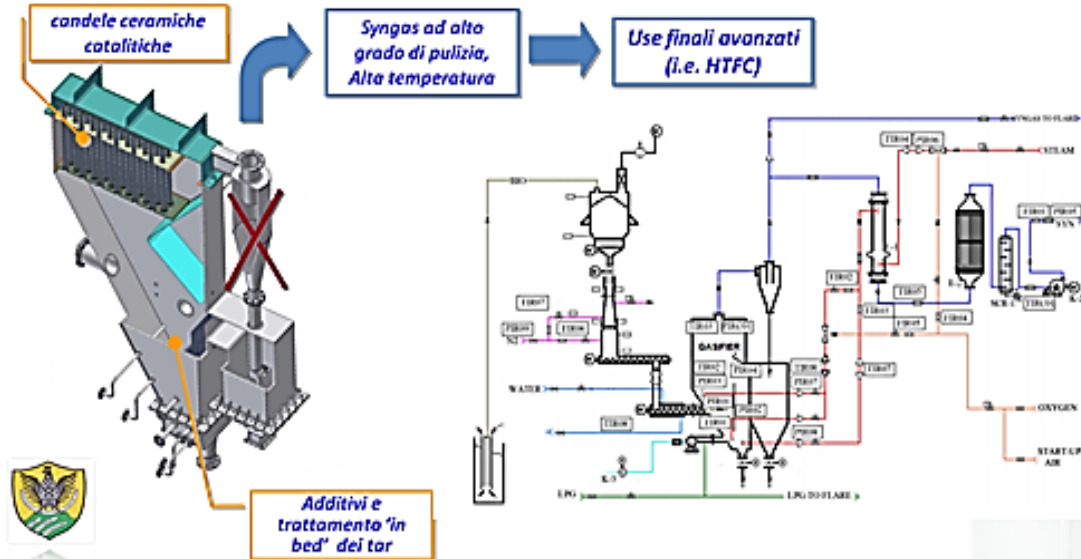
FLOW DIAGRAM



INTERNALLY CIRCULATING BUBBLING FLUIDIZED BED 1 MWth



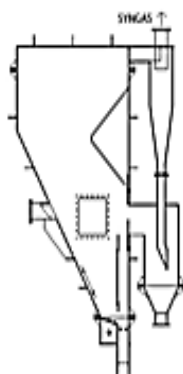
Integrated push of gas cleaning and conditioning directly in the gasification reactor. The reduction of costs for the purification is 20 -30% of the investment cost. compact and low thermal losses facility.



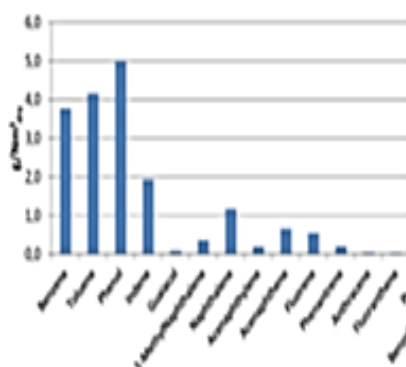
ENEA
16/02/2019

ICBFB gasifier with internal circulation
(1MWth ICBFB, Patented)

INTERNALLY CIRCULATING BUBBLING FLUIDIZED BED 1 MW_{th}



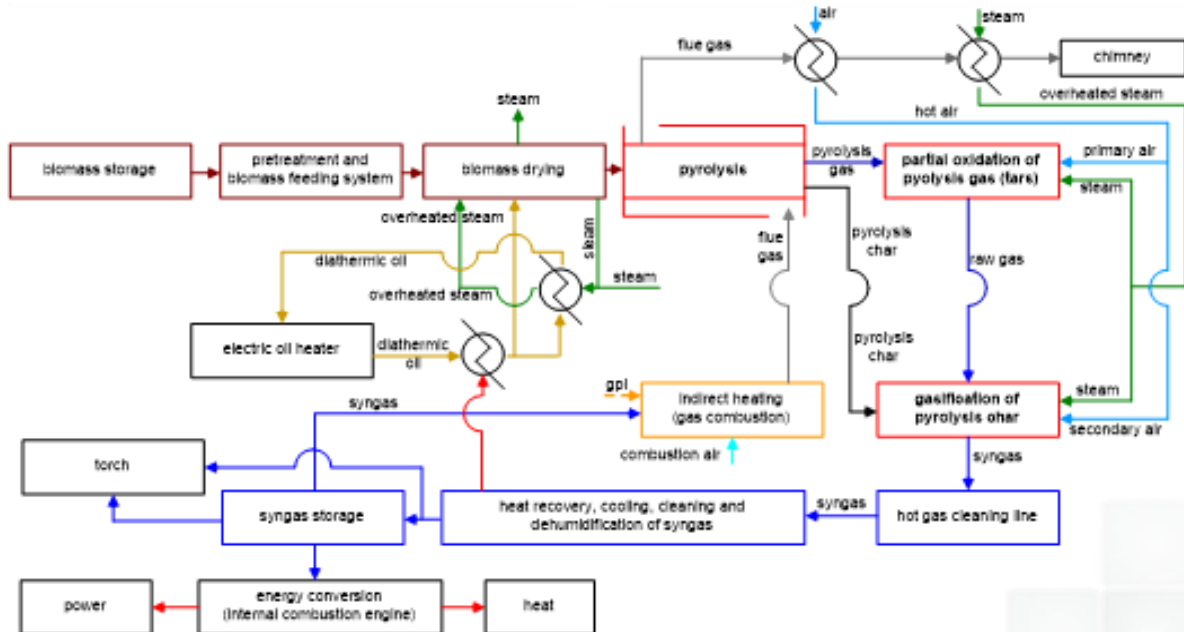
| Test | 35%-wt O ₂ | 50%-wt O ₂ | Steam/O ₂ |
|--|-----------------------|-----------------------|----------------------|
| Gas yield (Nm ³ /kg _{biomass, dry}) | 1.46 | 1.31 | 1.04 |
| Char residue (g/kg _{biomass, dry}) | n.a. | n.a. | 80-100 |
| Test duration (min) | 230 | 280 | 310 |
| Gas components | | (%v, Dry gas) | |
| CO | 18-23 | 20-25 | 28-32 |
| H ₂ | 7-9 | 11-13 | 30-33 |
| CH ₄ | 6-7 | 6-9 | 9-11 |
| CO ₂ | 17-24 | 19-25 | 22-27 |
| Light hydrocarbons | <1 | <1 | 1-2 |
| N ₂ | 41-45 | 30-37 | 2-5 ^a |
| O ₂ | <1 | <0,5 | <1 |
| H ₂ O (% v, wet gas) | na | na | 40-50 |
| LHV (MJ/Nm ³) | 5.9-6.7 | 6.3-8.4 | 10.9-11.7 |



| Contaminants | Steam/O ₂ |
|---|----------------------|
| Particles (g/Nm ³ _{dry}) | 6-10 |
| H ₂ S (ppm _v) | 40-50 |
| HCl (ppm _v) | 40-50 |
| NH ₃ (ppm _v) | 70-80 |
| Gravimetric tar (g/Nm ³ _{dry}) | 7-10 |
| Tot chromatographic tar (g/Nm ³ _{dry}) | 12-18 |

16/02/2019





- *Single specific units for pyrolysis, partial oxidation and gasification processes*
- *Separate routes for gaseous and solid products leaving pyrolysis unit*

Main technological innovations



Biomass drying by overheated steam and diathermic oil heat exchange



Indirect heated pyrolysis, with high level control of heat exchange, working temperatures and residence times

Partial oxidation of separated pyrolysis gases and vapors, for primary tars conversion and abatement (vortex partial combustion reactor)



Gasification of pyrolysis char in downdraft fixed bed reactor, with internal filtration of product gas on char and ash bed



Technical features

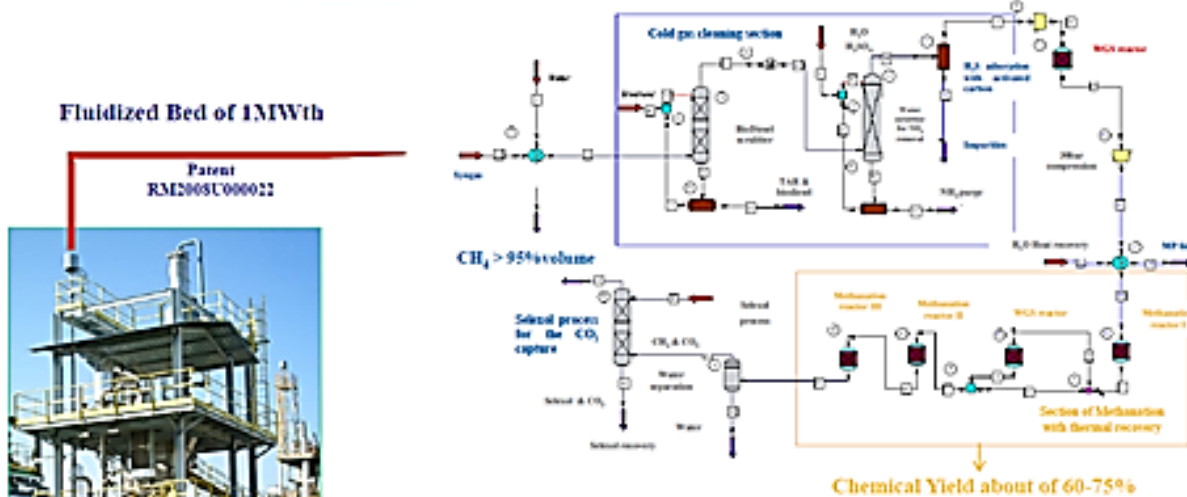
- Feeding fuel: lignocellulosic biomasses
- Biomass load: 150 kg/h
- Feeding biomass moisture content: up to 40 %
- Biomass moisture at pyrolysis inlet: ~ 10 %
- Syngas yields: ~ 300- 350 kg/h
- Syngas low heating value: ~ 6 – 7 MJ/Nm³
- Net power production: ~ 120 kWe
- Net thermal power availability: ~ 200 – 250 kWt



Goals and outcomes

- Utilization of a wide range of different biomass types for energy production
- High flexibility in biomass loads setting and modulation
- Lower equivalence ratio (less process air feeded) and higher syngas heating value
- Very low tars contents at gasification reactor outlet, thanks to selective partial oxidation of pyrolysis gaseous products, and syngas hot filtration on char bed

Current activity lines: Production of bio-SNG from syngas

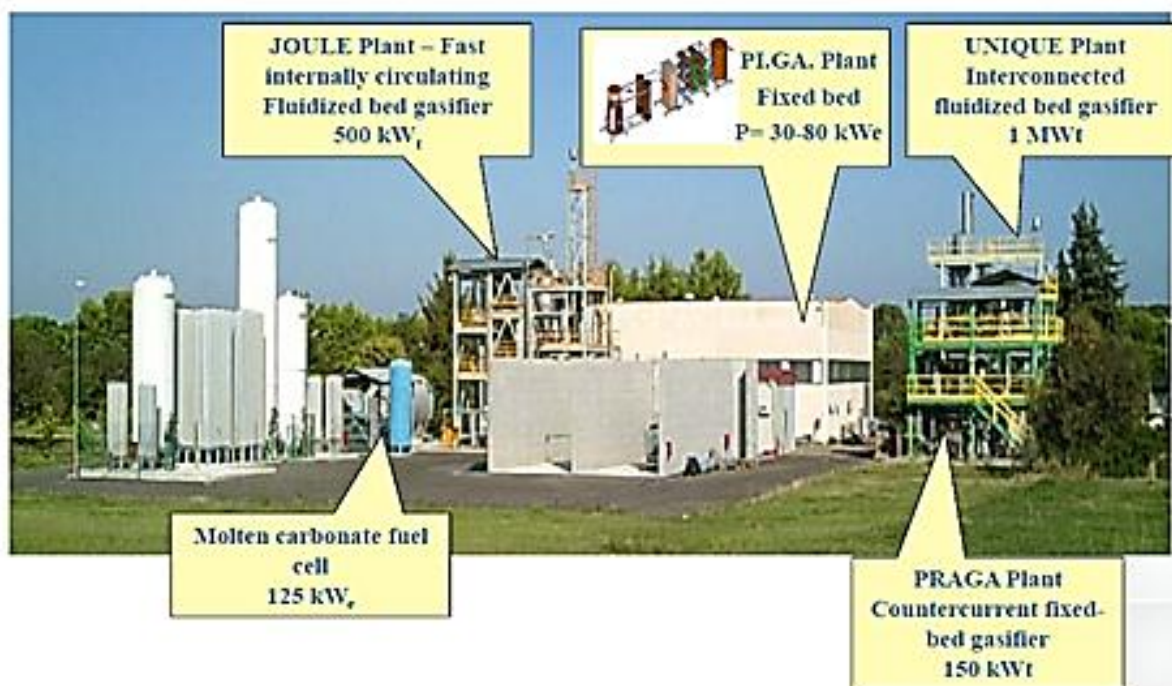


| SYNGAS COMPOSITION | |
|--------------------|------|
| Species | %Vol |
| H ₂ | 32 |
| CO | 17 |
| CH ₄ | 6.2 |
| N ₂ | 0.9 |
| CO ₂ | 20.9 |
| H ₂ O | 22 |

INTERMEDIA STAGES FOR PRODUCTION OF THE SYNTETIC NATURAL GAS

- Cold gas tars cleaning;
- Water scrubber for ammonia absorbing;
- Neutralization of acidic substances by use of low cost sorbents;
- CO-shift reactor for increase the H₂, CO ratio necessary for the methanation stages:
 $CO + 3H_2 = CH_4 + H_2O \quad \Delta H^{\circ}_{R_{298}} = -206.28 \text{ kJ/mol}$
- Compression stage for improve the thermodynamic conditions and for obtain a bio-SNG to high pressure suitable for the grid injection;
- Selexol process for CO₂ split-up from the syngas

Current state of the technological platform for the ENEA biomass gasification



Recently, an updraft fixed bed gasification plant based on 150 kW_{th} reactor with steam/air gasifying agent, operates with feedstock of high biogenic fraction and a generating producer gas of LHV 5-6 MJ/Nm³_{dry} is implemented. The plant is equipped with a wet purification system operated with biodiesel.

The produced gas was considered to generate a gaseous stream with a high H₂/CO ratio (> 2), to be used in the synthesis of biofuels (e.g. methanol), or to produce hydrogen of fuel cell grade. To this aim, after the biodiesel scrubbing, the gas stream is addressed to a section for gas upgrading and CO₂ removal.

As shown in Fig.5, a 500 kW_{th} staged pilot plant is based on a three stages gasification process carried out in different units.



Fig. 5 Three stages gasification pilot plant

The process starts with the pyrolysis of the supplied biomass. The pyrolysis gas is conveyed to a partial oxidation reactor where tars are mostly cracked and converted into lighter gases. Pyrolysis char is fed to an open core downdraft reactor, with air/steam primary and secondary lines. The char bed also acts as an active carbon filter for raw product gas. Overall, the ultimate results are a producer gas with a very low tar level content and the possibility of using a wide range of biomass feedstocks (including low value residues, e.g. AD sludge) as solid fuels.

Innovative thermal processes for treatment of residues and wastes were developed in order to recover carbon fibres and energy from end-of-life composites, produce activated carbon and energy from scrap tires and waste biomass, produce high added value technical ceramics and energy from scrap tires and waste glass, convert chemical energy of non-recyclable waste (refuse derived fuel, automotive shredder residues, manure, sewage sludge, waste plastics) in more flexible energetic vectors such as char, bio-oil, and syngas. Preliminary tests conducted on bench scale continuous rotary kiln with mass rate of about 1 kg/h provided useful information for the scale-up of pyrolysis/gasification process of tires, sewage sludge, ASR, and digestate.

A pilot scale rotary kiln system to process automotive shredder residues and waste biomass at a maximum mass rate of 10 kg/h and equipped with a gravity settler to collect char, has been built. The raw gas is purified by the gas treatment system composed of an spray tower, panel filter and a scrubber working with alkaline solution.

Also, a rotary kiln plant, with treatment capacity of 30 kg/h, was built up with an industrial partner SICAV Srl . It is a 4 meters long rotating drum reactor with internal diameter of 0.4 m. The main purpose of this plant was to develop and optimize a thermochemical process to convert waste/biomass to solid products with high added value “Activated carbon” and synthesis gas.

A “batch” fixed bed pyrolysis plant with reactor capacity of 5 m³ has also been realized to recover carbon fibres from scraps and composite waste materials (Fig. 6). The ENEA-

patented process allows the recovery of the carbon fibres that still retain 90% of the mechanical properties of virgin fibres. Moreover, the recovery cost is about 20% lower than the commercial cost.

REVIEW OF COMMERCIAL' GASIFICATION PLANTS

An extensive review of gasifier manufacturers in Europe, USA and Canada, identified 50 manufacturers offering 'commercial' gasification plants from which:

- 75% of the designs were downdraft type,
- 20% of the designs were fluidized bed systems,
- 2.5% of the designs were updraft type, and
- 2.5% were of various other designs.

However, scanty informations were available related to the cost, efficiency level, emissions level, turn down ratio and actual operating hours experience which is limited and less confidence is there on the technology, due to poor outcome of the prototypes.

Atmospheric Circulating Fluidized Bed Gasifiers (ACFBG) have proven to be very efficient with variety of feedstocks and scaling up is easy relatively from few MWth up to 100 MWth. Moreover, for capacities more than 100 MWth, confidence prevails that the industry could provide reliable operating gasifiers.

Many industrial companies such as TPS, FOSTER WHEELER, BATTELLE, LURGI and AUSTRIAN ENERGY are adopting this system for wide and large scale application.

The ACFBG have high market attractiveness and are technically well proven of their efficiency. Atmospheric Downdraft Gasifiers (ADG) are suitable for small scale utilizations (<1.5 MWth), both in developed as well as developing economies. Although so much advancements are there, the issue of efficient tar removal is there which needs to be addressed and automation is needed more specifically in small scale operations. In addition, recent progress on catalytic conversion of tar gives better option and that is why ADG can be considered as having average technical strength.

There is higher amount of tar in fuel gas and there is issue of gas cleaning, so Atmospheric Updraft Gasifier (AUG) has obviously no market attractiveness with respect of power applications. Atmospheric Bubbling Fluidized Bed Gasifiers (ABFBG) have shown confidence due to feedstock variety at pilot as well as small and medium scale application up to about 25 MWth. ABFBG are more beneficial for small and medium range capacities. The companies which are promoting ABFBG are CARBONA and DINAMEC.

The gasifiers like Atmospheric Cyclonic Gasifiers (ACG) are still not proven of their efficiency but have simple technology for biomass feedstock use. Finally, Atmospheric Entrained Bed Gasifiers (AEBG) are still at the very early stage of development.

The Fast Internally Circulating Fluidized Bed Gasifier (FICFB) is reliable for large scale utilization and for small scale applications downdraft gasifiers are most widely used.

Presently 87 gasification facilities are in the active condition. Out of them 54 are found in Task 33 member countries whereas remaining 33 are found in other countries.

(Austria 9, NZ 1, Denmark 7, Norway 0, Italy 0, Sweden 4, Finland 4, Switzerland 4, Germany 7, Turkey 2, Japan 2, Netherlands 6 and USA 8).

Co-firing (4 gasification facilities); CHP (37 gasification facilities), Synthesis (34 gasification facilities); Other innovative (12 gasification facilities)

It is imported to emphasize that most of the total 87 gasification facilities are in operational condition (59%), along with it 14% are under construction, 3% are in commissioning and 16% are planned. Only 8% of all the gasification facilities are on hold condition. Almost half of all the gasification facilities are commercial in nature (47 %), some are pilot plants (27%), and some are demo plants (26%).

Basing on the successful operations of the Güssing plant, the FICFB gasifier has been commercialized in 6 plants in Europe in different stages such as planning, construction and operation.

The Pressurized fluidized bed systems either circulating (PCFBG) or bubbling (PBFBG) are complex in nature due to their installation related issues along with the additional costs relating to construction of all the pressurized vessels. At present due to the problems such as scaling, removal of tar, and price no company is developing pressurized systems for downdraft, updraft, cyclonic or entrained bed gasifiers for biomass feedstocks, and it is not expected to develop in near future due to the above mentioned issues. Bubbling fluidized bed gasifiers is expected to be competitive for medium scale applications. The large-scale fluidized bed systems have been successful due to success in co-firing projects whereas moving bed gasifiers are still struggling to achieve this fit.

Various gasification techniques and gas cleaning or conditioning processes are under investigation to exploit the use of low-value feedstocks like forest biomass residues, agroindustrial wastes, and residues from wood industries.

Recently, gasifiers are manufactured with a dedication to produce syngas (for internal combustion engines), synthetic biofuels (such as sun diesel, methanol) and hydrogen. The steps followed in this method are use of heat and chemicals for breaking down biomass into syngas (CO and H₂) and reassembling these into product like ethanol.

This methodology has significance as around one-third of cellulose biomass and lignin-rich parts are not easily convertible by biochemical process. The forest residues and mill products are having higher content of lignins, hence not appropriate for biochemical process of conversion, rather thermo chemical method is suited for them. In the integrated biorefinery system lignin containing residues derived from biochemical method can be utilized for thermo chemical conversion.

The syngas produced from biomass carries contaminants like tar and sulphur which hinder the conversion of syngas into products. These contaminants should be excluded by tar – reforming catalysts which have shown to be higher level of tar conversion where 97 % of tar can be converted to syngas. This approach along with cleaning the syngas, reduces the cost of ethanol production.

The primary constituents of syngas are CO, H₂ and less amount of CH₄. Liquid fuel is produced whenever the catalyst (CH₄ is inert) is used and these gases are passed over the catalyst. The CO and H₂ react when passed over a catalyst (the CH₄ is inert) to produce liquid

fuel. The type of catalyst decides the type of biofuel produced. Recent research findings have shown that partial deactivation of tar - reforming catalyst by sulphur poisoning can improve its efficiency for further use. Microorganisms can play crucial role and undergo fermentation of the gas and thus pure ethanol or pure butanol can be produced from syngas [12].

The second approach for conversion of syngas to liquid fuel is the combined thermo/biochemical approach to produce pure alcohol. This methodology is less developed as compared to the catalytic process discussed above. This approach if made feasible in a commercial way, then lignin-rich feedstock alongwith hemicellulosic and cellulosic components can be used for fuel generation, unlike the case for purely biochemical "cellulosic ethanol" discussed earlier. With this option, specially-designed micro-organisms ferment the syngas to ethanol or butanol.

Presently, many instrument parts are available to produce thermo-chemical biofuel through catalytic synthesis process. Still, the areas which need to be improvised are biomass feeding to large scale pressurized gasifiers and raw gas cleaning up generated by the gasifier. When there is biomass of low bulk density then it is challenging to feed into a pressurized gasifier with efficiency and cost effective manner.

Progress in the area of syngas clean-up is needed with more focus on removal of tar as tolerance to contaminants is low particularly for the downstream fuel synthesis processes. From 1970s focus is more on tar removal because they are problematic contaminants and although the removal processes (converting to light permanent gas) are known, still the methods are not efficient and cost effective. More researches, developmental works and demonstration efforts are being pursued for syngas fermentation.

The reaction rates are enhanced because fermentation vessel functions at slightly above ambient temperature (37 °C) but at moderate pressure (40psi). As ethanol is toxic to the culture its concentration is maintained below 3% v/v in the reactor. The organism consumes CO, CO₂, and H₂ to produce ethanol and acetic acid. The acetic acid production is minimized by the recycle of distillation bottoms containing some acid back to the fermenter. The major benefit in this technique is the utilization of bark along with softwood, sawdust and shavings. No coproducts will be there except the excess energy produced by the system. This energy would be in the form of methane and could be used in a variety of applications including a gas turbine cogeneration system.

Dimethyl ether (DME) which is a colourless gas at normal temperature and pressure is also an efficient diesel engine fuel due to its high cetane number and there is no soot production during combustion period. Nevertheless, adequate purification of the product gas is achieved and involvement of a high temperature ceramic filter in the cleaning section performs the function. Involvement of specific catalysts can result in increase of H₂ content more than 50% and quality could also be enhanced.

The ENEA has been successful in developing industrial scale FICFB gasifier (Fig. 4) at Trisaia [13-14], through its intensive research work on thermochemical conversion of waste biomass for both thermal and electric power. The design of the reactor and the use of steam as gasification agent gives this process a nearly A nitrogen-free product gas with a very high calorific value of approximately 12 MJ/Nm³ dry gas is given by the reactor designed along with use of steam gasification agent. By using a natural catalyst as bed material and gasification temperature above 800 °C, the tar content was reduced below 5 g/Nm³.

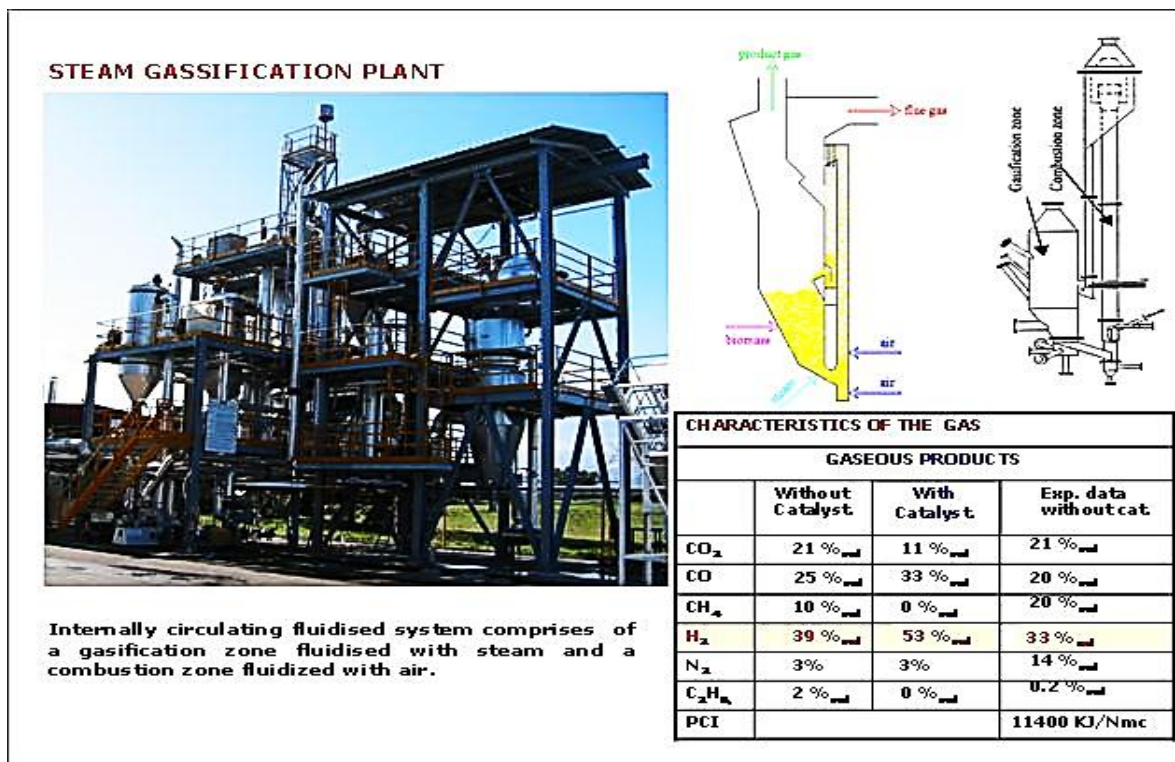


Fig. 4 Industrial scale FICFB gasifier designed, developed and experimented by ENEA

Research and development activities on thermochemical conversion processes are based on gasification and pyrolysis and, thus, support the National and European industrial system to scout and focus on advanced new technologies.

In relation to the exploitation of biomass, activities are mainly focused on the development of gasification processes for the production of gaseous energy carriers of higher value, available for direct application in CHP production or, after proper cleaning and conditioning, as a gas of synthesis to produce derived fuels (e.g. hydrogen, SNG, Fischer-Tropsch liquids, methanol, DME). From the produced gas, chemicals can also be synthesized.

R&D activities are mainly focused on the development of small to medium size technologies for power production using low value feedstocks. Five pilot-scale gasification plants, based on different reactor design (fixed bed, fluidized bed and staged gasifiers), effective gas cleaning and conditioning unit and size ranging from 120 kW_{th} to 1000 kW_{th}, are available at the ENEA Trisaia Research Centre.

Recently, an updraft fixed bed gasification plant based on 150 kW_{th} reactor with steam/air gasifying agent, operates with feedstock of high biogenic fraction and a generating producer gas of LHV 5-6 MJ/Nm³_{dry} is implemented. The plant is equipped with a wet purification system operated with biodiesel.

The produced gas was considered to generate a gaseous stream with a high H₂/CO ratio (> 2), to be used in the synthesis of biofuels (e.g. methanol), or to produce hydrogen of fuel cell grade. To this aim, after the biodiesel scrubbing, the gas stream is addressed to a section for gas upgrading and CO₂ removal.

As shown in Fig.5, a 500 kW_{th} staged pilot plant is based on a three stages gasification process carried out in different units.



Fig. 5 Three stages gasification pilot plant

The process starts with the pyrolysis of the supplied biomass. The pyrolysis gas is conveyed to a partial oxidation reactor where tars are mostly cracked and converted into lighter gases. Pyrolysis char is fed to an open core downdraft reactor, with air/steam primary and secondary lines. The char bed also acts as an active carbon filter for raw product gas. Overall, the ultimate results are a producer gas with a very low tar level content and the possibility of using a wide range of biomass feedstocks (including low value residues, e.g. AD sludge) as solid fuels.

Innovative thermal processes for treatment of residues and wastes were developed in order to recover carbon fibres and energy from end-of-life composites, produce activated carbon and energy from scrap tires and waste biomass, produce high added value technical ceramics and energy from scrap tires and waste glass, convert chemical energy of non-recyclable waste (refuse derived fuel, automotive shredder residues, manure, sewage sludge, waste plastics) in more flexible energetic vectors such as char, bio-oil, and syngas. Preliminary tests conducted on bench scale continuous rotary kiln with mass rate of about 1 kg/h provided useful information for the scale-up of pyrolysis/gasification process of tires, sewage sludge, ASR, and digestate.

A pilot scale rotary kiln system to process automotive shredder residues and waste biomass at a maximum mass rate of 10 kg/h and equipped with a gravity settler to collect char, has been built. The raw gas is purified by the gas treatment system composed of an spray tower, panel filter and a scrubber working with alkaline solution.

Also, a rotary kiln plant, with treatment capacity of 30 kg/h, was built up with an industrial partner SICAV Srl . It is a 4 meters long rotating drum reactor with internal diameter of 0.4 m. The main purpose of this plant was to develop and optimize a thermochemical process to convert waste/biomass to solid products with high added value “Activated carbon” and synthesis gas.

A “batch” fixed bed pyrolysis plant with reactor capacity of 5 m³ has also been realized to recover carbon fibres from scraps and composite waste materials (Fig. 6). The ENEA-patented process allows the recovery of the carbon fibres that still retain 90% of the mechanical properties of virgin fibres. Moreover, the recovery cost is about 20% lower than the commercial cost.

The patented process was validated in the continuous rotary kiln (Fig.6). Moreover it was sold to a SME that is building up an industrial plant for the recovery of carbon fibres by ENEA patent.



Fig. 6 Pyrolysis fixed bed plant

A fluidized bed gasifier was built to treat refuse derived fuel with a mass rate of 10 kg/h. It has a raw gas cleaning section and catalytic modules of steam reforming and water gas shift for hydrogen enrichment. A technological integrated platform was realized to dispose waste tires, to produce high added value material, such as nanometric silicon carbide, to recovery power.

BIOMASS AND BIOTECHNOLOGY FOR ENERGY

Development of efficient biomass conversion processes and innovative technologies for the conversion of different biomass (including no-food crops and microalgae) into biofuels and chemicals by means of biological processes are the main goals of R&D activities on Biomass and Biotechnology for Energy. Activities are mainly focused on the selection and use of microbial pools for the production of second-generation biofuels, applying the biorefinery concept and microbial ecology approach for sustainable energy production.

Research activities are mainly focused on the enhancement of biogas production from lignocellulosic wastes by a biological co-treatment and its scale-up, development of two-stage anaerobic digestion processes for hydrogen and methane production from organic wastes, ethanol and hydrogen production from raw glycerol arising from biodiesel industry

by anaerobic fermentation with mixed bacteria cultures and experimental cultivation of microalgae to produce biofuels and/or high-value products for chemicals. Such goals are pursued through selection of functional consortia by means of bio-augmentation, acclimatization and enrichment and the statistical optimization, in order to increase their productivity and stability for a further scale-up and industrial exploitation.

Lignocellulosic substrates represent the main potential energetic stock among organic wastes. When lignocellulosic wastes are used as sole substrate, the hydrolysis step represents the bottleneck of the whole process; if they are used in co-digestion with other substrates, they become the limiting factor of the process efficiency. Recently, biological treatments of lignocellulosic wastes are gaining more attention thanks to the low energy requests, mild operational conditions, and low production of toxic and unwanted by-products.

An innovative approach (based on the development of microbial processes for hydrolysis of lignocellulosic materials by Anaerobic Ruminant Fungi - ARF) through Anaerobic Digestion (AD) of lignocellulosic biomass was tested at ENEA in two different series of experiments, where the second experiment was a scale-up (10x) of the best results obtained in the first one. A mathematical model to predict methane production was calibrated on the first experiment while data from the scale-up experiment were used to validate it.

The bio-augmentation approach is innovative because the breakdown of lignocellulosic biomass promoted by ARF is not performed upstream, as imposed by typical pre-treatments, but it is totally integrated and concurrent within the AD process. The obtained results enlighten interesting perspectives for the application of bio-augmentation in the AD process, providing a co-treatment of lignocellulosic wastes. Moreover, the microbial bio-augmentation leads to even better results in a greater process scale. This aspect is under investigation with increasing process scale.

Several research activities have been and are presently carried out on the development of advanced anaerobic digestion processes, aimed at increasing energy production from organic wastes (manure, crude glycerol, cheese whey) through a two-stage fermenter, made of two separate reactors, the first producing hydrogen and the second one methane. Anaerobic digestion of ricotta cheese whey (RCW) has been extensively studied at ENEA.

The results of these research show that the two-phase reactor configuration improves the energy efficiency of the process in terms of total energy production and methane quality. The two-stage process has been patented (ENEA-CRA Patent number PCT/IB2014/059942), leading to the construction of a pilot plant with a size of a first stage reactor of 0.3 m³ volume and a second stage reactor of 3 m³ at the Monterotondo (Roma) Research Centre of CREA (Fig. 7), and some full-scale plants are currently in advanced stages of construction.

Furthermore, ENEA has developed a technology making use of raw glycerol - by-product of the industrial biodiesel production - by way of innovative anaerobic fermentation processes to obtain bioethanol, hydrogen or synthesis intermediates (lactic and succinic acid, 1-3 propanediol) for chemical industry. Enrichment of activated sewage sludge allowed to select a suitable microbial culture able to grow on crude glycerol as the only carbon source, using this simple medium without any extra-nutrient supplements.



Fig. 7 Two-stage anaerobic digestion pilot plant at CREA Research Centre [15]

The process developed at ENEA laboratories has been patented (Patent No. RM2011A000480). It is to be noted that in the framework of European R/S project “GRAIL”, trials on both lab-scale fermenters and pilot plant are in progress. Next step of the research will involve the development of a continuous process, both at lab as well as pilot plant scale.

Preliminary tests for the scale-up of the process have been carried out on a pilot bioreactor of 50 L at the ENEA Trisaia Research Centre (Fig. 8) and appears to be quite promising for beginning the continuous fermentation. Cultivation of microalgae to produce biofuels, food products with high nutritional power and/or high-value products for chemical industry are in progress at the ENEA Casaccia Research Centre.

The main target of these research is the realization of innovative, simplified and low-cost systems for microalgal cultures, both at laboratory scale (PET used bottles), as well as outdoors .

A brief of activities, already completed or in progress, is given below:

- Bioenergy: use of liquid digestate as fertilizer for microalgae crops to be used for biogas production;
- Green chemistry: *Botryococcus braunii* and *Dunaliella salina* production experiments for enhancing their content in oleic acid and dienes;
- Production of nutraceuticals: production of *Arthrospira platensis* (spirulina) to be used as a food supplement or as a source of natural dyes (phycocyanin) for food, cosmetics and chemical analysis;
- Restoration of cultural heritage: screening and evaluation of micro- and macro-algae for the production of polysaccharides extracts to be applied on paper works (manuscripts, books, drawings) deteriorated or at risk of deterioration.



Fig. 8 Pilot fermenter (50 L) at ENEA Trisaia Research Centre [16]

PREFERRED TECHNOLOGY ROUTE

At present there is no clear distinction in terms of technical and commercial advantages among the 2 pathways. In both the techniques persistent development and assessment is going on and yet many technical and environmental issues to be overcome.

In both the cases of biochemical pathways many things have to be performed such as feedstock characteristics; making cost-effective and perfecting pretreatment; improving the enzyme efficiency and reducing their cost of generation; and enriching overall process of integration. The major advantage of biochemical process is the less cost involvement and cheaper biofuels could be produced as compared to that of thermo-chemical route.

In general, it is found that there are less technical barriers to the thermo-chemical route as much of the technology has already been proven and established. The major hurdle seems to be the availability of large quantity of feedstock with a genuine price. However, efficient and cost-effective gasification of biomass, yet to be achieved.

One of the important differences among the biochemical and thermochemical pathways is that the lignin component is the residue for enzymatic hydrolysis method and so it can be utilized for heat and power production. Through the BTL process this is converted into syngas along with the cellulose and hemicellulose biomass components.

Both the pathways have the potential to convert biomass to energy carrier such as biofuels resulting in overall biomass to biofuel conversion efficiency of approximately 35%. The overall efficiency of the process can be enhanced when additional heat, power and coproduct generation are involved in the total system.

Another important difference is that biochemical routes generate ethanol while thermochemical routes can produce a range of longer chain hydrocarbons from the synthesis gas. These include biofuels better suited for aviation and marine purposes.

Still, there is no added advantage is found among the two pathways in terms of commercial or technical point of view and in due course of time it can be predicted which one is superior over the other.

Advancement in engineering processes and bio-organisms is the need at present for 2nd generation biochemical ethanol production and low cost generation of lignocellulose based feedstocks like switchgrass, will aid to commercial ethanol production with costs being competitive with ethanol from corn.

In the long-run, both low feedstock costs and large production scales are projected to be needed to reach costs below corn-ethanol costs. Due to the existence of natural climatic condition many developing countries have advantages and higher probability for sustainable low cost biomass production.

As equipments required for biofuel production are available commercially due to their utilization in fossil fuel conversion, the second generation thermochemical systems with further development and demonstration efforts, could be in form of commercial production within a few years. Large scale biomass FTL production facility could be developed with the existing technologies. The thermochemical biofuel production process could be integrated with the facility which is generating biomass by products ready to use for energy as in the pulp and paper industry which can be competitive at much lower oil prices and at smaller scale application.

The thermochemically produced biofuels can be competitive with the oil prices in countries where biomass generation cost is lower and construction and labor costs are also lower.

Various studies have been done for production of biofuels such as bioethanol and biodiesel using different types of biomass, but the approach needs to be improvised further for cost-effective production [17-21]. The process of production, transformation and efficient use of biomethanol has been comprehensively analysed by Barisano et al. (2020) with significant findings [22]. In a similar way critical analysis has been done on bio-oil production process parameters through biomass pyrolysis [23]. Bio-oil that is derived from biomass has been comprehensively reviewed by Sharma et al. with future projections of the potential of renewable energy [24]. Strategies and management of solid wastes in cities like Indore and Srinagar has been discussed thoroughly and directions for optimum management of biomass has been highlighted [25, 26]. Various biomass like lignocellulosic biomass, coconut husks, organic wastes, dairy industry wastes, distillery waste water have been treated for production of useful products with success [27-31].

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