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## TRANSPORT FUEL BY BIOMASS GASIFICATION

*The present work focuses on the importance and the feasibility to produce transport fuel on large-scale by biomass gasification. Biofuels will help to reduce greenhouse gas, increase the security of energy supplies and enhance the no-food use of abandoned lands. However, there are political, economical, social and technological problems that must be solved before the commercialization of such processes.*

**T**he high dependence of most modern transport, agricultural and industrial systems on the relative low cost and high availability of oil caused its production decline and severe increases in prices in the last years. It is now evident that this critical commodity heads into decline due to natural depletion. Even if a debate [1] rages over the precise date of the world peak oil (the point in time when the maximum rate of global petroleum extraction is reached) it is undoubted that the Age of Oil that started in the mid 19<sup>th</sup> Century, will finish soon and the Humanity shall face the greatest challenge it has never faced: the adaptation to the loss of fossil fuels.

There are no reliable renewable alternatives to oil, carbon and natural gas, at the moment [2]. Hydro, geothermal, solar, wind, tides and biomass have to be used all together to cover not even a 13% of world energy demand (Fig. 1). Before World War II, hydropower covered almost a 65% of the Italian energy demand [3]. Every water jump,

from the Alps to the Apennines, is used to produce electricity. Due to the increased energy demand, hydropower covers now only a 15%. Even if improvements such as the micro-hydroelectric for small waterfalls and the revamping of the old plants are going to be applied, this value is intended to further decrease in the future. Despite of the first geothermal plant all over the world was built in Italy (Larderello, 1913), this energy has been the fortune of Iceland and not of Italy, due to the fact that there

aren't so many sources in Italy and most of them are concentrated in Tuscany only. Nevertheless, Italians extract from Mother Earth about 5 TWh per year [4].

Nowadays solar is the most appreciated and studied between all weather-dependent renewable sources (wind, tides...). Sometimes it happens to learn from mass media that if a grand part of the Sahara Desert (the reported surface always changes) is covered with photovoltaic panels it will be possible to withdraw all energy that Humanity needs. Sure, until the first sand storm

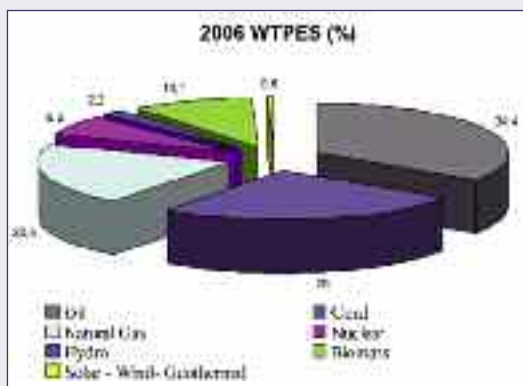


Fig. 1 - 2006 World Total Primary Energy Supply

occurs, that will bury those expensive panels meters below the ground! Despite of the high cost of investments and the poor efficiency (about 10-15% and this value usually decreases with aging), solar energy has a lot of potential and on improving the technology, it will cover more and more of the world energy demand.

Therefore, at the moment biomass is the most promising renewable energy source, already furnishing almost a 10% of the World Total Primary Energy Supply.

There are several ways to produce fuel and power from biomass [5, 6]. Diesel blends can be obtained from vegetable oils (soybean, rapeseed) by trans-esterification of the long chain fatty acids with methanol or higher alcohols and basic catalysts. However, a considerable amount (about a 10 wt.%) of glycerol is obtained, thus starting the so called "Glycerol Challenge", a way to use this by-product instead of disposing it.

Bioethanol can be currently produced by fermentation of vegetable starch (sugar cane, corn and sugar beet) and Brazil is the largest producer all over the world. Bioethanol has been recently charged with being the principal cause of increased cereals price. Even if everyone could agree or disagree with this accusation, it is undoubted that starchy crops have a EROEI (*Energy Return On Energy Invested*) not exceeding 1.3, a very low value compared to other fuels [7, 8]. However, a new technology capable to produce ethanol from cellulose (2<sup>nd</sup> generation bioethanol) is under development. The use of cellulosic crops such as switchgrass is estimated to increase the EROI up to 6 [9].

The biogas, having a methane content of 50-75 vol.%, can be produced by digestion of urban waste and animal manure. It has been evaluated that a pig of 100 kg can produce up to 20 Nm<sup>3</sup> of methane per year. Organic matter is collected into digesters connected to a net of pipes that usually feed a power station, since the conversion in transport fuels is not convenient.

On the other hand, lignocellulosic biomass (wood and dedicated energy crops) and residues (bark, husks, straw, paper mill wastes) can be converted by thermal processes (pyrolysis, gasification) to liquid fuels such as Fischer-Tropsch (FT) diesel blends or dimethyl ether (a clean-burning alternative to diesel). The productivity in terms of yield and process time is very high, since thermal conversion takes place in very

short reaction times (typically seconds or minutes).

Pressurized oxygen circulating fluidized bed (CFB) gasification is the best large-scale technology for the clean, sustainable use of biomass for fuel generation [10, 11]. The biomass generated gas mainly contains CH<sub>4</sub>, light hydrocarbons, CO, CO<sub>2</sub>, H<sub>2</sub> and it needs to be upgraded before its conversion to liquid fuel. The process has to overcome a number of technical and non-technical barriers before industry will implement its commercialization [12].

The present work is an attempt to highlight the political, economical, social and technical (PEST) obstacles to the commercialization of the production of liquid fuels from biomass (BTL) and focusing on technical problems that must be solved.

## Political concerns

Since the energy providers have considerable investments in fossil fuels, there is a concern about that those companies, always seeking to protect their interests, do not really support renewable energy. It is not completely true, since most major energy suppliers have their own programs on renewable energy. However, industry will only invest in projects that have an acceptable return at an acceptable risk, regardless of the environmental benefits. Technology improvements can do much to minimize the risk, but it couldn't be enough to promote biofuels. However, governments have the tools to render more attractive the investments by means of fiscal incentives on biofuels or additional taxation on fossil fuels.

Due to the growing interest in reducing the CO<sub>2</sub> emissions (e.g. the Kyoto Protocol) civilized Countries are trying to support renewable fuels more and more, like the European Union that obliged its members to cover at least the 12% of own total energy demand from renewable within 2010.

However, there is a nonsense concerning the production of biofuels, since most Countries buy the feedstock outside Europe, in a simpler way than growing own crops but consuming more energy in transportation than that produced by the conversion of the biomass.

## Economical concerns

First of all, it is consolidated that economies of scale are a vital feature of the development of power plants, in which the larger a process can be built, the cheaper it becomes.

Unfortunately, biomass has a low energy density, can be obtained only on a seasonal base and has to be harvested and collected over large areas.

For example, on fulfilling the electricity demand of a small town district (about 1,000 family flats without any hospital or industry), a 10 MW<sub>el</sub> power station operating at a modest efficiency of 35% will require about 40,000 t per year of wood on a dry basis which will require about 4,000 ha of land [13]. This places a practical upper limit on the benefits of scale.

However, there are still some tips that can help to achieve scale economy: i) the development of sustainable forestry can ensure a large enough supply of clean wood, as it has been long demonstrated in Northern Europe;



Geothermal power plant of Larderello (1950)

# CRITICAL REVIEWS

ii) BTL plants should feature the technical possibility to operate with different feedstock (wood, charcoal, herbaceous crops, industrial and domestic organic wastes...), otherwise they have to be built in proximity of the places where biomass is concentrated (standing forests, saw and paper mills...) in order to maintain a constant supply all over the year;

iii) dedicated energy crops (switchgrass, miscanthus, eucalyptus and poplar) have rapid growth, low mineral content and high biomass yield. In this way, the ratio of power produced per surface of land can even double.

Second, biofuels have to still compete with fossil fuels. With the updated price of oil at 65 \$ per barrel (but peaks over passed 150 \$), biofuels are more expensive than fossil fuels. However, taking in account that the price of fossil fuels is intended to increase more and more, due to the depletion of the natural deposits, biofuels will become proportionally more and more economical attractive.

Finally, huge investments are involved in the whole raw of production of fuels from biomass gasification (plant, pipes, employers, feedstock...). On the other side, this conversion can be routed via a conventional petrochemical refinery, since a refinery is usually well equipped to handle variable feedstock. The advantage is that all necessary infrastructures for the separation, purification and distribution of biofuels are already in place, bringing down the investment cost [14].

## Social concerns

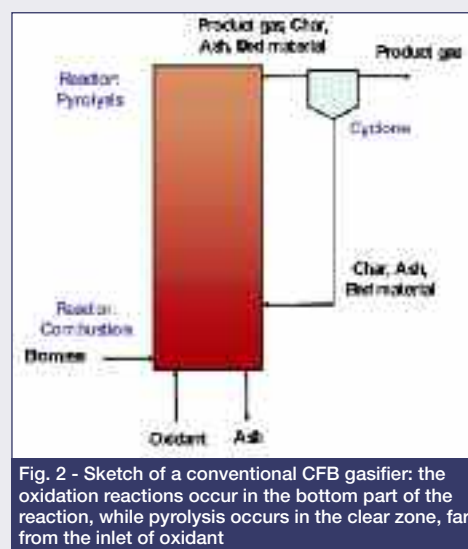
The most important social concern is the potential conflict between the use of land and water resources for energy and fuel or for food production. Surely crops require lands and water to grow, but abandoned lands and plants that require a low water feed can be used instead. In this way biofuels may create a lot of job opportunities, helping to revitalize rural communities. Finally, we cannot forget that the price of the food is always chained to the price of the energy used to grow, collect and transport it.

Then, NIMBY (Not In My BackYard)! The perception of the population about this new technology is very important. There is a widespread approval of renewable energy and biofuels, as long as the plant has to be built in proximity! Therefore, a careful attention has to be placed on selling the idea to the citizen.

Last but not least, a widespread and uncontrolled use of natural forests can cause deforestation, with serious ecological and social ramifications. Therefore careful strategies that balance deforestation and reforestation have to been adopted, like in Northern Europe where a considerable amount of forestland is used for energy purposes without any complaint.

## The technical feasibility of gasification and gas cleaning

Gasification is the conversion by partial oxidation at elevated temperature of a carbonaceous feedstock into a gaseous energy carrier consisting of permanent, non-condensable gases. Ideally, the process produces only a non-condensable gas and an ash residue. However, since gasification



from the injection of the oxidant, cracks them into methane, hydrogen and carbon. Fluidized beds provide many features not available in the fixed-bed types, including high rates of heat and mass transfer and good mixing of the solid phase, which means that reaction rates are high and the temperature is more or less constant in the bed. The most common design between fluidized bed reactors is the circulating type, due to its highest carbon conversion obtained by means of the recycle system and to the confidence in scaling up such a reactor in applications that generate over 150 MW<sub>th</sub> for operations at atmospheric or elevated pressures, using air or oxygen as gasifying agent (Fig. 2). In these gasifiers a bed material is used to maintain fluidization and to provide a large heat transfer area. Sand, magnesite (MgO) or magnesium carbonates (MgCO<sub>3</sub>) are usually chosen as bed material. The latter are basic and do not react with alkali from the biomass, have high strength so that they will not be worn down and are cheap (even if more expensive than sand). Loss of fluidization due to bed sintering is one of the commonly encountered problems (Fig. 3). The main parameters of a gasifying process are [16]:

- i) temperature: gasification is generally carried out at 750-900 °C, but higher temperatures allow a higher conversion of tars into gaseous compounds, however increasing the overall cost of the process;
- ii) pressure: all the gasifier types can be operated at either atmospheric or elevated pressure. With increasing pressure, the gasifier and other process equipments can be made smaller in size. However, less energy is consumed by gas compression in atmospheric gasification;
- iii) gasifying media: air or oxygen. The pres-



ence of nitrogen decreases the heating value of the produced gas and increases the size of downstream equipments. If the produced gas is intended for fuel production, oxygen should be used. Steam should be added to dilute the oxygen when maintaining enough gas flow is necessary but avoiding combustion of the biomass. Obviously, operating in an oxygen/steam flow is more expensive than operating in air.

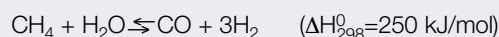
Depending on the biomass feedstock and gasifier operative conditions, there are several contaminants present in the product gas (tars, ash,  $\text{NH}_3$ ,  $\text{H}_2\text{S}$ ,  $\text{HCl}$ ,  $\text{HCN}$ ...). Tar formation is one of the major problems to deal with during biomass gasification [17]. Tars may be defined as organic molecules with a weight greater than that of benzene and the most common are refractory polyaromatic compounds with 4 and 5 rings. Upon condensation, these contaminants block downstream pipelines and foul catalytic bed and reactor. Ash is made of inorganic components derived from the biomass feedstock ( $\text{SiO}_2$ ,  $\text{MgO}$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{K}_2\text{O}$ ,  $\text{Na}_2\text{O}$ ,  $\text{P}_2\text{O}_5$ ...). A part of ash melts into the gasifier and it can be easily removed from the bottom. However, the part which leaves with the product gas (fly ash) contains the most of alkali metals, responsible of hot corrosion above 600 °C. Nitrogen-, sulphur-, and chlorine compounds are also of concern because they are precursor of  $\text{NO}_x$  and  $\text{SO}_2$  and also because they can poison the catalysts placed in the downstream equipments. Therefore, all these contaminants have to be removed from the flue gas. Removal technologies can broadly be divided into two approaches: cleaning after the gasifier (secondary methods) and treatments inside the gasifier (primary methods). Although secondary methods are proven to be effective, treatments inside the gasifier are gaining much attention as the gasifier is optimized to produce a gas with a low tar concentration. There is a potential of using some active bed additives such as dolomite or olivine inside the gasifier [18-21]. Ni-based catalysts are reported to be very effective not only for tar reduction, but also for reforming methane [22-24]. Since the cracking of tars inside the gasifier can significantly improve the heating value of the produced gas, the catalytic cracking is a preferred way to removal methods. However, in the gasifier environment, the lifetime of Ni catalysts is very short, due to the high amount of sulphur compounds and other contaminants.

The gas clean up methods can be classified into two distinct routes: 'wet' low temperature cleaning and 'dry' high temperature cleaning. Conventional 'wet' low-temperature cleaning is the preferred technology in the short term. This technology has the highest removal efficiency and it is well established, but requires additional wastewater and solid treatments. Firstly, a gas filter collects particulate matter. Bags work at low temperature, while candles at higher temperatures. Ceramic candles are commonly used for atmospheric gasification, while metal candles are suitable for pressurized systems. In new configurations, a Ni based catalyst is loaded on the filter to additional crack tars. Then a scrubber operating with a  $\text{NaOH}$  solution removes the acid contaminants and another scrubber with a  $\text{H}_2\text{SO}_4$  solution removes the basic ones. Finally, a  $\text{ZnO}$  guard bed is a very efficiency sulphur trap at low temperature, even for few ppm of  $\text{H}_2\text{S}$ . However the bed has to be constantly replaced and the produced  $\text{ZnS}$  has to be discharged and treated.

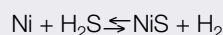
Hot gas cleaning [25] consists of several filters and separation units in which the high temperature of the product gas can be maintained, achieving efficiency benefits and lower operational costs. Hot gas cleaning is specifically advantageous when preceding gas upgrading stages, because these process steps have high inlet temperatures. However, after atmospheric gasification it does not improve efficiency, because the subsequent essential compression requires syngas cooling anyway. Hot gas cleaning is not a commercial process yet, since it is still in the experimental phase. The Växjö Värnamo Biomass Gasification Centre (VBGC) in Sweden is a unique plant and an important site for the research on this field [26]. At the moment, the Värnamo plant is the heart of the CHRISGAS European project [27], which aims to convert the biomass generated gas to an enriched hydrogen stream, thus having a high added value. The know-how resulting from the project is aiming to be representative of a variety of European conditions and will support a large-scale implementation.

### The technical feasibility of the gas upgrading and the gas to liquid conversion

The exit gas from the gasifier needs to be improved to synthesis gas in order to produce fuels. Nowadays, the consolidated technology for syngas generation is the steam reforming of natural gas (SR), in which methane and steam are catalytically and endothermically converted to hydrogen and carbon monoxide [28]:



A different approach is autothermal reforming (ATR, [29]). The process is "autothermal" in that the endothermic reforming reactions proceed with the assistance of the internal combustion (or oxidation) of a portion of the feed hydrocarbons, in contrast to the external combustion of fuel characteristic of conventional tubular reforming. Plants based on oxygen-blown autothermal reforming at low steam to carbon (S/C) ratios are the preferred option for large-scale applications [30]. The commercial plants commonly use supported nickel catalysts [31, 32]. The catalyst contains 15-25 wt.% nickel oxide on a mineral carrier ( $\alpha\text{-Al}_2\text{O}_3$ , aluminosilicates, magnesia and  $\text{MgAl}$  spinel). Before start up, nickel oxide must be reduced to metallic nickel with hydrogen but also with the feedgas itself at high temperature (above 600 °C, depending of the reducing stream). Required properties of the carriers are relatively high specific surface area, low pressure drop and high mechanical resistance at temperatures up to 1,000 °C. The main poison for Ni based catalysts is sulphur and concentrations as low as 50 ppm can completely deactivate the catalysts [33]. During biomass thermal conversion and SR/ATR, all S compounds are converted to  $\text{H}_2\text{S}$  that chemisorbs on metal sites forming  $\text{NiS}$ , in according to the equilibrium:



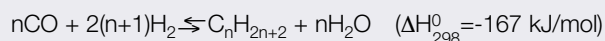
The low melting point and high surface mobility of  $\text{NiS}$  also accelerate



the sintering process of Ni crystallites. Since the formation of NiS is an exothermic process, activity loss can be partially recovered by raising the reaction temperature, however accelerating the thermal degradation of the catalyst and increasing the carbon formation by cracking reactions. In the specific case of biomass gasification, a number of alkaline salts and heavy metals and metal oxides particles may act as additional poisons by enhancing the sintering of the Ni crystallites or being adsorbed on the Ni sites [34, 35]. While acid supports such as alumina react with alkali to form crystalline phases, basic supports (like MgO) do not react directly with them, however alkali cause coverage of the surface and plugging of the pores. Another cause of activity loss is the carbon deposition that can be avoided if a high S/C ratio is employed [36, 37]. The presence of tars in the reforming reactor enhances coking and it is the main cause of carbon formation in BTL processes. Therefore, an optimal hot gas cleaning stage and the development of more tolerant catalysts are key points for the feasibility of the gas upgrading step.

Many researchers have been studying alternative active phases to Ni based reforming catalyst in the last years [38-40]. These studies claim that Pt and Rh based catalysts were the most active in model reforming, but their performances have to be still confirmed by processing a real biomass generated gas.

The reformed gas can be directly converted to liquid fuel by the FT process [41]:



The FT synthesis produces hydrocarbons of different length from syn-gas. The relation between the hydrocarbon yield and the chain growth probability is described by the Anderson-Schulz-Flory distribution [42].

There are two main kinds of FT reactors: fixed bed reactor and slurry [43]. The latter is preferred in large-scale applications [44].

A variety of catalysts can be used for the FT process, but the most common contain cobalt, iron and nickel. Cobalt seems to be the most active catalyst, although iron also promotes the water gas shift reaction. Nickel is seldom used, since it tends to favor methanation. In addition to the active metal, the catalysts typically contain a number of promoters, including potassium and copper, as well as high surface area binders/supports such as silica, alumina or zeolites. Like in the reforming, the FT catalysts are sensitive to the presence of sulphur containing compounds among other poisons. The sensitivity of the catalyst to sulphur is higher for cobalt and nickel based catalysts than for their iron counterpart. Therefore iron catalysts are preferred for lower quality feed-stock such as biomass. Moreover, the lower cost of iron makes sacrificial catalyst at the front of a reactor bed economical.

Generally, the FT process is operated in the temperature range of 150-300 °C and at 20-40 atm of pressure. Higher temperatures lead to faster reactions and higher conversion rates, but also tend to favor methanation. Increasing the pressure leads to higher conversion rates and also favors formation of long-chained alkanes both of which are desirable. Even higher pressures would be favorable, the benefits do not justify the

additional costs of high-pressure equipment.

The optimal H<sub>2</sub>:CO ratio is around 2. However, iron based catalysts, on promoting the water gas shift reaction, can tolerate significantly lower ratios. This can be important for the direct conversion of a not upgraded biomass generated gas, which tend to have relatively low H<sub>2</sub>:CO ratios (<1).

The large hydrocarbons can be then hydrocracked to form diesel of excellent quality. The overall carbon efficiency of the hydrocracking step is close to 100%.

The FT fuels are totally free of sulphur, nitrogen, nickel, vanadium, asphaltenes and aromatics, which all are typically found in mineral oil products. Cetane number (CN) is essentially a measure of the delay before ignition. The higher is the CN the shorter is the delay, achieving better motor performances. Thus having a high CN, FT diesel is commonly added to poor quality fractions, such as hydrotreated light cycle oils [45], in order to meet the properties required by the international laws.

## Conclusions

This work presented a critical review on the importance and the feasibility of BTL via gasification, reforming and FT synthesis. Since biomass is a renewable and CO<sub>2</sub> neutral source, the ability to produce biomass-derived vehicle fuel on a large-scale will help to reduce greenhouse gas and pollution, increase the security of energy supplies and enhance the no-food use of abandoned lands. However, the BTL route has to overcome a number of barriers before its commercialization.

There are still a lot of technological improvements that must be made (set up of an efficient hot gas clean up, development of catalysts for reforming insensitive to the contaminants generated during gasification), improvements that require the rebuild of the existing plants and therefore involving huge investments. On the other side, this conversion can be routed in a petrochemical refinery, bringing down the investment cost.

Besides the technical and the economical barriers, BTL has also to face political and social concerns. First, there is the conflict between the use of land and water resources for energy and fuel or for food production. Second, there is a widespread approval of renewable energy and biofuels, as long as the plant has to be built in proximity!

Therefore, a careful attention has to be placed on selling the idea to



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the citizen.

Finally, since all energy companies protect their interests, they will support renewable energy and biofuels but maintaining fossil fuels always on a competitive edge. Nevertheless, the European policy is still providing incentives to green fuel producers, the economics of processing bio-

mass are improving, the concerns about greenhouse gas emission are growing and the Humanity is feeling the impellent necessity to get free from the slavery of fossil fuels.

Therefore, BTL on a large-scale will become more and more relevant in the next years.

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## RIASSUNTO

### L'importanza e la fattibilità di produrre combustibili per gassificazione di biomasse

La produzione su larga scala di combustibili da gassificazione di biomasse permetterà non solo di ridurre i gas serra ma anche di affrancarci dalla trappola energetica rappresentata dai combustibili fossili. Tuttavia, ci sono ancora molte barriere da superare per la commercializzazione di questo processo. Miglioramenti tecnologici prevedono un sistema di purificazione del gas ad alta temperatura e lo sviluppo di catalizzatori più tolleranti verso i contaminanti prodotti dalla gassificazione delle biomasse. Altre barriere (politiche, economiche e sociali) potranno essere abbattute con strategie mirate dei governi atte ad incentivare la produzione di biocombustibili.