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Fuels from Biomass

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ABSTRACT

Against the climate change due to greenhouse gas emissions, one of the several solutions is the use of biofuels. Biofuels are biomethane, biodiesel, bioethanol, GTL, DME, biobutanol, biohydrogen and BTL. Biomethane is produced by anaerobic fermentation of organic wastes. Bioethanol is produced from fermentation of sugar crops but also from lignocellulosic wastes. Biobutanol is produced by fermentation of food crops or from lignocellulosic wastes. GTL and DME and biohydrogen are produced essentially by gasification of biomass. However, agricultural and forest waste and energy crops that make up marginal land should be used as biomass.

1. INTRODUCTION

It is now clear to everyone that the last decades have been the hottest ones since 1850, when global thermometric measurements began; particularly we have passed the hottest sixty years of the last 1400 years. Since 1950, changes have been observed in extreme meteorological and climatic events, the number of cold days and nights is decreased and the number of hot days and hot nights is increased; there are more lands emerged with an increase in the number of events of intense precipitation compared to a decrease in their number in Europe and North America and the frequency or intensity of intense (or extreme) rainfall is increased. The ice caps in Greenland and Antarctica have lost mass over the last thirty years, particularly the ice cap in Greenland is decreased faster in recent years: the average rate of decline has increased over the past decade. The rate of rising global average marine level has accelerated over the past two centuries.

It is "extremely likely" that more than half of the observed increase in surface temperature from 1951 to 2018 was caused by the anthropogenic effect on the climate (greenhouse gas emissions, aerosols and land use changes). There will be an increase from 2 to 4 °C in global temperatures at the end of the century and an increase from 50 to 80 cm in sea level at the end of the century. The ice will continue to melt and in particularly the annual extension of the arctic ice will be subject to decrease during the century. In conclusion, according to the IPCC, the United Nations Organization, founded in 1988, the emissions of greenhouse gases by human activities are the cause of the warming of the oceans, the melting of the ice, the reduction of the snow cover, the raising of the average global marine level and global warming is occurring.

In the year 2017 the UN IPCC conference was held in Marrakesh to find a solution that prevents the planet from warming up more than 2 °C, a limit indicated as crucial by climate experts and which should prompt us to intervene immediately to avoid disastrous climate changes, but in reality no new decision for immediate intervention has been taken. At this point, the only alternative is to demonstrate in fact that there are technologies of energy saving in the production of electricity, in the treatment of wastes, in construction, transport and in the industrial production sectors, such as to lead to positive effects in the economy and considerable savings on fossil fuels [1-2]. Faced with the presence of an economic crisis, many governments do not feel to let the world of production accept new limits imposed on greenhouse gas emissions, despite being aware of the seriousness of the climate problem, for fear that this will bring new costs and reduce competitiveness. In view of these disappointing results, a different approach is needed, which achieves better results, through energy efficiency, technological innovation, the use of renewable sources and, finally, the change in lifestyles. Such a "Copernican revolution" could make environmental respect so economically advantageous that it can be embraced voluntarily rather than imposed by regulation. Pope Benedict XVI had appealed to the participants in the 2011 United Nations Conference on Climate changes, which clearly underlined that there is no good future for humanity on earth if we do not educate everyone to a more responsible lifestyle towards creation. There is no future if we do not change the "lifestyles" and this is the first strategy that calls us into question as citizens of the world. The second strategy, which has to do with innovation, calls us into questions as technicians. The savings and the increase in energy efficiency and the lower waste of raw materials in the chemical sector in recent years have been one of the engines. It is also time to make a gradual transition from the chemical processing of fossil substrates to biomass-based chemistry. Despite the lack of proposals for immediate restrictions on greenhouse gas emissions, the future of the planet may not be so dramatic if research activities in Europe and around the world succeed in developing new technologies and processes capable of reducing greenhouse gas emissions, even at a lower cost than fossil technologies currently in use, using biomass as fuels. Today, chemistry has the great task of indicating new raw materials starting from biomass and new ways of their transformation, so efficient and profitable to impose itself by necessity to the old fossil model, even with the help of biogenetics.

2. FROM BONFIRE TO BIOREFINERIES

Biomass, of which lignocellulosic substances are the most significant fraction, have returned to the spotlight since 2006, following the energy crisis and the increase in pollution of large cities. Everyone is now aware of the urgent need to diversify energy sources, especially in Europe. The use of biomass for energy, one of the available options, has nothing new, dates back to the prehistory of man [3-4], but the simple combustion is no longer viable, because it is not very efficient from an energy point of view and is also highly polluting. There are two strategies that can be pursued to use lignocellulosic substances: transformations in the fuel supply chain and in the thermal supply chains. We talk about the supply chain because the goal is not to produce only energy, but also fuels, valuable chemicals and materials. Chemistry, as it has been in the past with coal and oil, is still a by-product or a co-product of energy. This is why the supply chains are also called biorefineries. An example of a fuel chain is that of ethanol consisting of the chemical and enzymatic hydrolysis of hemicellulose and cellulose to sugars and their subsequent fermentation to ethanol. In the thermal supply chains one example is the gasification of the whole biomass to synthesis gas or pyrolysis to obtain in this case liquid fractions (the bio-oil) similar to those obtained from crude oil. The advantages of using biomass are many and consist in being neutral compared to the emission of CO_2, in being able to contribute to achieve the goal set by the European Community for the percentage of renewable energy to be used in the coming years, in order to increase the agricultural income and avoid the deterioration of mountain areas and abandoned areas, and, finally, the possibility of obtaining less polluting fuels and more biodegradable chemicals. There are also the negative aspects, such as the loss of biodiversity, if territories that are currently uncultivated are cultivated, the increase in land use and water consumption, with the consequent greater polluting load, the problem of hunger in the world, that the most fortunate countries cannot forget, and the current cost of biomass and transformation processes. Precisely for this reason, when we talk about biomass we must immediately think of the use of wastes from agro-forestry, from the food industry, from the processing of paper and wood and from the organic component of urban and industrial wastes. Then, one can think of the partial exploitation of crops already used for human and animal feed (biodiesel from oils and ethanol from sugary substances). Finally, in a longer time, we can think of the use of new crops dedicated to industrial uses, obtained by selection or genetic modification. Of these energetic crops are known lignocellulosic raw materials as the miscanthus and the switch oil or fats as the jatropha and the algae and terpenes. In particular are interesting microalgaes that can produce energy as simple fuels or by transformation to biogas or oils. In comparison with terrestrial biomass, microalgae can make an order of magnitude more energy per territory. The interest of chemistry is twofold, both because research efforts are still needed in transforming unreactive substances into fuels, using simpler low-cost processes, and because it is necessary to transform into value products the new raw materials for chemistry that will be made available by the various supply chains or by-products and co-products of fuel production. So from firewood in a bonfire or from burning in a boiler, we have now moved on to a chain of molecules from a biorefinery that can be oxidized in a turbine or motor or transformed into valuable chemical products.

3. ENERGY FROM BIOMASS

The use of renewable resources and the use of alternative technologies for the production of energy, such as solar photovoltaics, hydrogen, wind and the use of biomass is now widely accepted throughout the world as the main solution to tackle climate changes, even if there are still many people who consider that environmental policies are a brake on economic development and they believe that companies are penalized in their economic budgets by the impact of environmental legislation [5-7].

Many industries have introduced since many years in their development strategies the will to be consistent with sustainable development and they believe that green image increases the consideration of the general public, making it easier to attract investments. Some analysts believe that the image of a company is determined more by intangible parameters, such as that of an ethical or sustainable production, rather than the value of the production and of the plants.

The environment can open up new market opportunities for energy and chemistry behind a radical change in technology. When we talk about eco-economics, we are talking about new production technologies with low environmental impact, water, air and soil purification technologies, recycling and wastes treatment, thermal insulation materials and the use as raw materials biomass. Although, we cannot say that the era of fossil fuels has ended, we must note that we are in a period of transition and therefore the next few years will be characterized by the presence of hybrid technologies, where in addition to fossil raw materials biomass will be used. The future challenge is motivated by the observation that compared to 130 billion tons of fossil raw material reserves, there are 150 billion tons of biomass produced per year: with an annual consumption of 7 billion tons of fossil raw materials and as many of the renewable raw materials used, the latter, for human, animal and industrial uses.

Biomass should be understood as waste from wood processing industries, forestry, agricultural and food industries, or urban waste, sewage sludge or dedicated land or aquatic crops. In order to be sustainable, biofuels must be less expensive than those obtained from oil, lead to a strong reduction of toxic emissions, do not create social problems (no competition with food and be animal and to create a profit for agriculture.

4. BIOFUELS AGAINST CLIMATE CHANGES

When we speak about biofuels, in Europe, biodiesel and ETBE are essentially used, the latter being used as an additive for gasolines, while in the world they also mean bioethanol, biobutanol and fuels obtained from synthesis gas or hydrogen produced from biomass and green fuels obtained for thermal transformations of biomass [8-11]. The addition of 5 % ETBE to gasoline will lead to the production of bioethanol obtained from species with a high content of carbohydrates (sugar and starch) and at longer times from lignocellulosic biomass or dedicated crops, such as sugar sorghum and Jerusalem artichoke. Biodiesel can be mixed with fossil fuels or used pure with minor engine modifications and does not require, as for all other alternative fuels, construction of special infrastructures for their development. Biofuels undoubtedly lead to a reduction of CO_2 and SOx production and are renewable feedstocks, but do not lead to complete elimination of particulate matter and NOx. The biofuels that have currently being studied and mostly already produced in the world are the following: biomethane, bioethanol, FAME (biodiesel), HVO (biodiesel and biocherosene), GTL (bioalkanes), DME (alternative to biodiesel), biobutanol (alternative to gasoline and diesel), biohydrogen, and BTL (gasoline, diesel and kerosene.

4.1 Biomethane

Biomethane is obtained by purification of biogas that is generated by anaerobic digestion of organic wastes or landfills and in Italy [12-13]. Enea has worked on the various technologies for the purification of biogas to obtain biomethane. The biomass used for the production of biomethane are the following: wastes from livestock farms, dedicated energy crops (ideal crops in marginal lands), food wastes, urban organic wastes, sewage sludges, wastes from agricultural activities and slaughter wastes. Anaerobic digestion is carried out in suitable digesters in the absence of oxygen, using a first group of bacteria to start the degradation of organic matter to intermediate compounds, such as hydrogen, acetic acid and carbon dioxide, and a second group of bacteria, formed by metanigenic microorganisms, which transform these intermediates into methane. The biomass is demolished in variable percentages between 40 and 60 % at temperatures ranging from 10-25 °C to 55 °C. Biogas has a mean methane content of 63 % and CO_2 of 36 % and impurities of NH_3 and H_2S are present. Liquid and solid wastes are introduced into the digesters: for example the biogas cogeneration plant of the Bruni (Sutri-Viterbo) is fed by bovine sludge (16,200 t / year), bovine manure (3,600 t / year) products of dedicated cultivation, such as maize (1,500 t / year), vegetable wastes and vegetation waters (1,000 t / year), agro-industrial residues (700 t / year). Fertilizers are obtained as a by-product of anaerobic digestion. The landfill must have an impermeable bottom and cover (usually polyethylene), percolate collection pipes and chimneys to collect biogas emissions. In the landfills the first phase of transformation is "aerobic" and then anaerobic. Biogas is used directly for the production of electricity by combustion in engines of generators or cogenerators or for direct combustion in the boiler for heating. In Italy, biogas is produced in 1,264 anaerobic digestion plants and in about 100 landfills. From biogas, after removal of the CO_2 and purification in order to eliminate the other impurities present, it is possible biomethane that can be introduced into the gas distribution network to be used as fuel for domestic purposes, for the production of electricity in gas turbine plants or for biofuels for automotive. The potential of methane production in Italy from anaerobic digestion of biomass from wastes and zootechnical dejections could reach a value of 8 billion Nm^3 / year in 2030 (including the addition of 400,000 hectares of dedicated crops): this quantity is equivalent to current national production of natural gas or that of the Rovigo regasification plant that has a value of 8 billion Nm^3 / year (including the addition of 400,000 hectares of dedicated crops).

4.2 Bioethanol

Ethanol is also used as ETBE, synthesized from isobutene and ethyl alcohol, as an anti-knock additive for gasoline added up to a concentration of 15 %, as an alternative to MTBE (methyltertiary butylether), which has been eliminated because it is toxic to the environment [14-15]. The use of bioethanol reduces CO_2, SOx, NOx and aromatics emissions. Current world production comes from sugar cane (Brazil), corn (USA) and beetroot (Europe). Other possible raw materials under study are energy crops such as miscanthus, sugary sorghum, cassava and panic, but the ideal choice for the future is the use of lignocellulosic wastes with Proesa technology developed by Beta Renewable Mossi & Ghisolfi Group companies. Proesa technology is based on the use of raw materials from lignocellulosic wastes or energy crops. The first plant, with a capacity of 40 kt / a, was built in 2013 in Crescentino (VA), using as raw material reeds (Arundo Donax) and wheat straw grown in the area. A second plant has been built in Brazil in 2014 using bagasse, waste from sugar production. Beta Renewable is the company that owns the Proesa technology and is a joint venture between Chemtex (Mossi & Ghisolfi company) and the Danish company Novozymes. Proesa technology transforms lignocellulosic substances into high temperature C5-C6 sugars, with steam to separate cellulose and hemicellulose from lignin, with a second step with a reaction of hydrolysis of C5-C6 sugars with enzymes and subsequent fermentation in the presence of yeasts is formed ethanol, which, finally, is separated from the lignin which is used produce energy in situ. Proesa technology makes it possible to use other non-edible biomasses such as miscanthus, switch grass and sorghum with CO_2 emissions savings of up to 85 %.

4.3 Biodiesel

There are two types of biofuels FAME and HVO that can use in diesel engines (6-11). FAME (Fatty Acid Methyl Ester) is the methyl ester of natural oils and fats and can be mixed with fossil fuel diesel for 7 % [16-20]. Animal fats are used in Japan, Australia and Canada, fryer oils in Germany, Austria and China, fish oils in Norway and Canada and algae in New Zealand which grow in basins fed by water treatment plants. As a by-product of transesterification, glycerol is obtained which must be used to give added value to the process. Germany, France and Italy are the biggest producers in Europe and in Italy the majority of the raw material comes from abroad for transesterification with basic, homogeneous or heterogeneous catalysis with methanol of oils from agricultural crops or animal fats. The oils used are different depending on the region: palm, jatropha and coconut in Asia, rapeseed in Europe, soy in North America and South America and palm and jatropha in Africa.

HVO (Hydrogenated Vegetable Oil) is obtained with the technology "Ecofining by hydrogenation of natural oils and fats and can be mixed with fossil fuels up to 30 %". This biodiesel called "green diesel" produced by the "Ecofining" process is obtained by hydrogenating of esters with C16-C18 carbon atoms and formation of alkanes with coproduction of propane. Eni in Marghera in 2013 has created a biorefinery that can use vegetable oils and animal fats, the first case in the world to reconvert a conventional refinery into a biorefinery using the "Ecofining" technology, patented and developed by Eni together with the American company UOP. The biorefinery started with a first phase of conversion of existing plants and then have been built new ones. The production of HVO in Marghera, where the main product is "green diesel", that cover 50 % of the EU's biodiesel needs, with an initial production of 300 million t. / y and then 500 million t/a. The raw material, palm oil, is arriving by boat in Marghera from Malaysia and Indonesia, while later non-food grade oils will also be used, such as waste oils from food industries, animal oils and fats, spent oils, oil from energy crops, such as Jatropha and algae. The plant consists of a hydrodeoxygenation and a hydroisomerization reactor and / or a hydrocracking reactor. The Isomerization serves to increase the cold properties of diesel, and produces iso-alkanes and gasoline as by-products in quantities up to 10 %; the hydrocracking is used to produce jet fuel. In Marghera, the hydrogenation reactor and the isomerization reactor have been obtained by modifying slightly existing plants in the refinery, in particular hydrodesulphurization reactors of petroleum fractions, while an upstream oil pretreatment plant has been realized to eliminate impurities containing Na, Ca and P. Propane obtained as a co-product can be used to produce the hydrogen necessary for reforming reaction. The advantages of this process compared to the production of traditional biodiesel, FAME, obtained by transesterification are numerous. First of all it is possible to use oils that contain fatty acids and to use different types of oils, even of low quality, that is to say low price, in fact the quality of the diesel obtained is not affected by the variability of the type of oil in charge. In addition, it is possible to place the production inside an oil refinery using the existing structures (tanks and handling), so there is no problem of integration. Finally, with the Ecofining process, a diesel with a higher calorific value is obtained, with excellent stability, low solvent power and low water solubility, modulating cold properties and high cetane number (> 80). HVO is a mixture of alkanes hydrocarbons, does not contain sulfur and aromatics and the cold properties can be optimized by playing on the severity of the hydroisomerization. The HVO diesel has a cetane number of 70-90 % against 50-65 % of FAME and 50% of the fossil diesel; its cloud point is from -5 to -20 °C against the -5 / -15 °C of FAME and the -5 °C of diesel from fossil fuels. As a consequence HVO burns more easily than that obtained from crude oil and can be used at lower temperatures, therefore in colder locations. The cetane index is similar to that of the diesel obtained from Fischer-Tropsch processes via the production of synthesis gas from coal or methane or biomass (GTL fuels). The use of HVO leads to a reduction in emissions of NOx and particulate matter. It is worth mentioning that the Finnish Neste Oil has already built two plants of 170,000 t / y, the first in 2007 in Porvoo in Finland, one in Rotterdam of 800,000 t / y and one in Singapore of 800,000 t / y with the NExBTL technology, similar at that point set by Eni and UOP. In this way, new plants have been built, placed inside a refinery, but with separate units, to use the control laboratories and the energy production plants. The production of biomass diesel is important for Europe, where it will arrive in 2020 to produce 25 million liters. In Asia and South America it will reach 13 million, 5 million liters in North America. Biofuels will be a sustainable alternative provided they are not in competition with the food sector. In Marghera it will be necessary to evaluate new raw materials alternative to palm oil. The oils obtained from algae and those obtained from lignocellulosic residues transformed first into C5-C6 sugars and then to lipids in the presence of yeasts before being inserted into biorefinery reactors are being studied. A second biorefinery will be made in Gela. The problem is what biomass should be used in the future as raw materials by eliminating palm oil from Malaysia. If currently the raw materials used are first generation biomass, there is agricultural products for human and animal food, other types of biomass are being studied, the so-called second and third generation ones. Second-generation biomasses are agricultural or forestry waste or derived from energy crops (not usable for food) based on lignocellulosic substances. These fermentation biomass can produce sugars that, in the presence of oleaginous yeasts, produce lipids similar to vegetable oils, which can then be converted into green diesel by the Ecofining process. A pilot plant for this production was made at the Donegani Institute in Novara. It is also possible to use organic waste, transforming it by liquefaction into a bio-oil which is then hydrogenated to green diesel. A pilot plant was also set up at the Donegani Institute. The third generation biomass is the one that grows in marginal land, there is not usable for agricultural crops or in the sea (algae) and a pilot plant for the transformation of algae to greediesel has been realized in Gela. The plant in Marghera os started with palm oil from abroad, but over the years will change the raw material. The use of biomass for the production of energy and fuels can enter competition instead human and animal food if produced in large quantities, but not, if we are talking about additives, components of formulations or small percentages such as those set by the European Commission for 2020, 10 % of total fuels, quantities that will be met very well from the Marghera biorefinery and from the planned one of Gela. In Marghera, it was proposed to build the first plant in Italy to produce energy from algae, although so far it has not yet been realized. The bioelectric power plant foresees the presence of two structures: one dedicated to the "cultivation" of algae and another suitable for converting biomass into energy; plants for growing algae should be located in Marghera. The microalgae can also be used for the phytoremediation of wastewater, feeding on substances present in the purification water and also with carbon dioxide present in large quantities in the area, thanks to the presence of the coal power plant.

4.4 GTL and DME

The GTL (Gas To Liquid) consists of C13-C18 alkanes obtained by Fischer-Tropsch reactions between CO and H_2 (synthesis gas) produced by biomass gasification [21-24]. The GTL can be obtained from the gasification of lignocellulosic biomass and the obtained alkanes can be isomerized and hydrocracked to obtain a diesel fuel. The Jet fuel is based on kerosene, which consists of C12-C15 alkanes that can be obtained with the GTL process (and also with the Ecofining process), achieving a final cracking of the obtained diesel.

The DME (dimethyl ether) is obtained as the GTL from the synthesis gas obtained from biomass through the synthesis of methanol and its dimerization and can be a substitute for diesel and is already used in China and Japan (14.15).

4.5 Biobutanol

Biobutanol means 1- butanol, 2- butanol and isobutanol and the advantages of the availability of biobutanol at low prices and in large quantities from biomass are many and are the following: the possibility of using it as an alternative to ethanol up to 100 % in gasoline and in diesel and jet fuel as an additive up to 20 % without engine modification and with the same fossil fuel infrastructure; the possibility of obtaining starting from butanol alkanes for chemical synthesis usable as conventional gasoline, diesel and jet fuel; the possibility of using it for the production of hydrogen in situ in fuel cell engines; the possibility of producing solvents and intermediates for use in different sectors of the chemical industry. Butanol can be prepared from all current and future raw materials: crude-oil, natural gas, coal but also biomass and is therefore an emblematic example of what the future of the chemical industry may be [25-34]. There are purely chemical processes starting from fossil fuels and lignocellulosic wastes, there are biotechnological processes starting from sugars, starchy or cellulose substrates and mixed biochemical processes always starting from biomass. We need to wait for the realization of the first biomass demonstration plants to find out what the winning technology will be. The synthesis of biobutanol from biomass can take place with the following technologies: the anaerobic fermentation of substrates based om sugars available as such or derived from starch or cellulose to 1-butanol or isobutanol and to a lesser extent the fermentation to synthesis gas and its transformation to butanol; the mixed bio and chemical synthesis through the production by fermentation of intermediates such as ethanol, 1,3-butanediol, butyraldeyde or butyric acid and their chemical transformation following one of the three biobutanols; chemical synthesis through the gasification of biomass (possibly via a prior pyrolysis) and the subsequent transformation of the obtained synthesis gas or to a mixture of alcohols from which 1- butanol and isobutanol are possible to be obtained; or production of methanol from synthesis gas and subsequently transformation to propylene and then its oxosynthesis are separated and final hydrogenation to 1-butanol and isobutanol. Biobutanol is an ideal substitute for gasoline, ethanol and diesel. When compared to gasoline, biobutanol has the advantage that its combustion in the engine produces lower amounts of CO, NOx, SOx and hydrocarbons emissions and that being more biodegradable any leakage into the environment causes less damage. It should also be remembered that the use of biobutanol in comparison to petroleum gasoline reduces CO_2 emissions as an alternative fuel to petrol or as an additive. Butanol can also be used to produce biodiesel, not by esterifying fatty acids with methanol, but with butanol, and this fuel is called but obiodiesel (a completely green diesel). Biobutanol has also been successfully tested in mixture with diesel up to 20 % (better if together with its dehydration product the dibutyl ether) without modification of the engine, improving different properties of the diesel, as the lubricating power the oxidative properties, the behavior to cold and its environmental impact following the reduction of toxic emissions. Biobutanol can be alternative to bioethanol and the advantages compared to this biofuel, already on the market for years, are the following: a greater calorific value (higher specific energy and energy density), only slightly lower than gasoline, and this allows to use it in smaller quantities or better to make more kilometers with a liter; a lower tendency to disperse in the presence of water and a lower corrosive power that make it possible to use the same transport and gasoline distribution structures and in particular to mix it with petrol already in refineries, while ethanol must be only before of its use; Biobutanol does not causes harmful swelling of tires and plastics in the fuel system and in the engine and can be used up to 100 % without making changes to the engine and with the same performance; a lower vapor pressure compared to ethanol and petrol which makes it easy to mix and makes it safer (less flammable). Finally, biobutanol can be synthesized with the same bioethanol equipment with only slight changes in the fermentation stage and the separation and purification system and also with the same raw materials. In 2005 a car (a buik of 92) without any modification traveled in the USA 15,000 km with 100 % butanol, however, the current interest is to use it in mixture with 16 % petrol against 10 % of ethanol, compositions that correspond to the same oxygen content. Some recent industrial biobutanol realizations are reported below.

Syntec biofuel Inc (www.syntecbiofuel.com) a Canadian company has studied the gasification of municipal waste and agriculture in CO and H_2 and their transformation to a mixture of alcohols and has for now achieved a yield of 400 liters of alcohols (ethanol, methanol, n-butanol and n-propanol) for tonne of biomass working with a laboratory fluidized bed reactor 0.5 to 2Kg / ha 815 °C and 10 Atm. In January 2010 signed an agreement for the development of the process with the. Energy & Environmental Research Center (EERC) and the University of North Dakota (UND).

Range Fuel (www.rangefuels.com) American company will inaugurate in a few months a commercial plant of 400 million liters of alcohol (essentially ethanol and methanol) to be used as fuels, with a gasification plant of lignocellulosic residues with synthesis gas that will be subsequently transformed into alcohols with a catalytic process. With this plant the company in the future could also produce a mixture of alcohols including butanol, Butamax Advanced biofuels (www.butamax.com) a company created by BP and Dupont together with British Sugar will build in Saltend (Hull - UK), it seems in 2011, a pilot plant of 20,000 liters a year of 1-butanol and 2 –b utanol and then in 2012-2013 a retrofitting of an existing ethanol plant of 420 million liters per year starting from sugar beet and starch and with the aim of creating in 2022 the construction of different plants with a total production of 120 billion liters a year of biobutanol. It seems that the microorganism used is the Clostridium Beijerinckii 600,000 t / y in 2010. Currently 70 % of the oil is imported, in the future the national production should cover 80 %. The most suitable crops for our country to produce biodiesel are sunflower, rapeseed and soybean.

4.6 Biohydrogen

Hydrogen from biomass can be obtained by synthesis gas produced by gasification or pyrolysis. Gasification is a combustion carried out between 700-900 °C, in lack of oxygen (1/3 of that required for complete combustion to CO_2 and H_2O is used) [35-37]. The gas obtained in processes contains CO (15-30 %), H_2 (10-20 %), CH_4 (2-4 %), CO_2 (5-15 %), H_2O (6-8 %), N_2 (45-60 %) and small amounts of light and particulate hydrocarbons.

The pyrolysis is the high temperature treatment (400-550 °C) in the absence of oxygen to produce three fractions: a gaseous fraction (15 %) that is generally used to supply heat to the reaction itself, which is endothermic, a liquid fraction (50-60 %), which can be used to produce biofuel, consisting of heavy and oxygenated hydrocarbons and a solid fraction (20-30 %) consisting of products similar to bituminous or anthracitic coal. The economy of gasification depends on many factors, such as the size of the plant, the cost of biomass and above all of its transport, the price of hydrogen from fossil fuels and the incentives for the use of renewable raw materials. Given the importance of transport costs, which become penalizing for distances already greater than 60 km from the plant, the most advantageous solution seems a two-stage process: small pyrolysis plants near the production of biomass to obtain a liquid, more easily transportable , which will be sent to a large centralized gasification Starting from the gas obtained in the gasification, hydrogen is obtained, through a first reforming reaction which transforms the fractions of hydrocarbons still present to synthesis gas, and a subsequent reaction to convert all the CO with water to CO_2 and hydrogen. The current problems in the industrial realization of these processes are due to the presence, in the gas obtained from gasification, of enormous quantities of impurities (P, Na, K, S and particulate) which quickly deactivate the downstream catalysts (which have been developed for the gases derived from relatively cleaner fossil fuels) and it is therefore necessary to insert purification plants.

4.7 BTL

BTL (biomass to liquids) is obtained by hydro-liquefaction of biomass at 250-400 °C, 50 -250 Atm, the presence of a catalyst and water as solvent. The presence of hydrogen allows to obtain alkanes and to a lesser extent aromatics. The advantages of this technology with respect to gasification are that it is not necessary to dry the biomass. The obtained hydrocarbons must be subjected to cracking and isomerization processes to obtain diesel or jet fuel [38-39].

5. CONCLUSIONS

Some numbers cannot be forgotten when we treat biofuels and we want to reflect on their prospects for a future development. There are currently around a billion people suffering from hunger in the world, of which over 150 million are children, of whom 3 million underweight are dying every year. It is expected that three billion people will be at risk of hunger over the next 30-40 years and that in the next decade the water resource will decrease by 30-35 % and to feed the world it is necessary to double the production of cereals and rice by 2050. There will be more than 30 million hectares, once used for food crops, converted for the production of fuels and which, in the next 8-10 years, can double. The European Commission estimates that the target of 10 % of biofuels in 2020 leads to an additional demand of 30 million tons of raw materials. There is a fear that by decreasing the area destined for the cultivation of cereals, prices could explode again and this would lead to increases the basic necessities, starting with bread, then moving on to milk and meat. Faced with these numbers there are those who say that it is immoral to allocate the territory to the production of biofuels. To respond to these fears we must remember that the problems of food shortages are mainly in Africa and are due to natural disasters, wars and lack of water. In Africa, 80 % of the population lives in the countryside and agriculture could be the backbone of the economy, as it was in Ghana and Malawi, to accumulate new resources.

Currently biofuels are obtained from the residues of agro-industrial activities, from biomass of forests especially in many less developed economies, and from dedicated crops, such as those for the production of ethanol and biodiesel. To solve the problems of hunger in the world, specifically referring to biofuels, we need to encourage those of second generation, there is those obtained from the transformation of agro-industrial wastes, especially lignocellulosic ones and multiannual crops and to increase, however, the production of renewable energy from biomass in a balanced way. Furthermore, a world bank of agricultural products needs to be created in order to avoid and discourage financial speculation, creating global agricultural reserves, leading to a rapid increase in agricultural production in developing countries, granting them access to an adequate amount of water and food. and to give more support to science, research, technology, education, dissemination and innovation. The advantages of devoting a part of the agricultural resources to energy production are many, such as environmental, the possibility of diversifying the energy sources to increase the security of their availability, to decrease the energy dependence on imports from the few producers of crude oil and offer agriculture a new source of income, trying to allocate the production of biofuels in abandoned or under-productive land. It should not be forgotten that the production of biofuels is now an important source of income in several countries such as Brazil, Argentina, Malaysia and the United States.

However, it is necessary to rationalize the use of forests, limiting their killing, with a targeted exploitation and to favor the sustainable use of biofuels produced from biomass deriving from different agro-industrial and human wastes. Hunger and malnutrition, food emergencies are being fought with an increase in investments to increase productivity in developing countries, strengthening rural development and trying to solve the many difficulties of agriculture, eliminating state subsidies to biofuels and trying to consume less meat [36-37].

REFERENCES

[1] Cuhum HL, Overend RP. (2001). Biomass and renewable fuels. Fuel Processing Technology 71(1-3): 187-195. https://doi.org/10.1016/S0378-3820(01)00146-1

[2] Catalán-Martínez D, Domine ME, Serra JE. (2018). Liquid fuels from biomass: An energy self-sustained process integrating H_2 recovery and liquid refining. Fuel 212: 353-363. https://doi.org/10.1016/j.fuel.2017.10.014

[3] Bioenergy (Biofuels and biomass). https://www.eesi.org/topics/bioenergy-biofuels-biomass/description

[4] European Commission (2015). Workshop “Integrated biorefineries and innovations in the optimal use of biomass” https://ec.europa.eu/research/bioeconomy/pdf/workshop

_on_optimal_use_of_biomass_integrated_biorefineries_10Dec2015.pdf
[5] Qureshi N, Hodge DB, Vertes AA. (2014). Integrated biochemical processes for liquid biofuels. Elsevier.
[6] McKendry P. (2002). Energy production from biomass (part 1): Overview of biomass. Bioresource Technology 83(1): 37-46. https://doi.org/10.1016/S0960-8524(01)00118-3
[7] What is biomass? RE Energy Holding. https://www.reenergyholdings.com/renewable-energy/what-is-biomass
[8] Trifirò F. (2016). Carburanti alternativi per contrastare i cambiamenti climatici e l'inquinamento delle città. La Chimica e l'Industria News Letters 3(1).
[9] Anniversary - Climate Action is More Urgent than Ever. https://unfccc.int/
[10] COP21 Decision. https://unfccc.int/process-and-meetings/conferences/past-conferences/paris-climate-change-conference-november-2015/cop-21/cop-21-decisions
[11] European Commission (2013). EU launches clean fuel strategy. europa.eu/rapid/press-release_IP-13-40_en.htm
[12] Biomasse utilizzabili per la produzione di biogas (2009). http://www.nextville.it/Biogas/559/Da_quali_biomasse
[13] La tecnologia del biogas made in Germany. http://www.envitec-biogas.it/
[14] Proesa Technology. https://www.bio.org/sites/default/files/files/beta%20renewables%20proesa%20technology%20june%22013_bio_michele_rubino.pdf
[15] Cobror R. (2012). La produzione industriale di bioetanolo. Un passo deciso verso la Bioeconomia. La Chimica e l'Industria 3: 80-82.
[16] Rozzi R, Trifirò F. (2007). Chimica nella vita quotidiana: l'olio diesel il top dei prodotti chimici. La Chimica el' Industria 89(7): 162-168.
[17] Un nuovo piano di sviluppo per Gela. https://www.eni.com/it_IT/media/dossier/nuovo-piano-sviluppo-gela.page
[18] When did second generation green diesel demo plant project start? https://www.eni.com/en_IT/results.page?question=when+di+second+generation+green+diesel+demo+plant+project+start
[19] Bioraffinerie Eni (2016). https://www.eni.com/it_IT/innovazione/piattaforme-tecnologiche/bio-refinery.page
[20] Perego C, Ricci M. (2012). Diesel from Biomass. Catal. Sci. Technol. 2: 1776-1786.
[21] Trifirò F. (2012). Polo verde a Marghera: Forse parte una nuova chimica. La Chimica e l'Industria 94(9): 86-87.
[22] Natural gas and its advantages http://www.shell.com/energy-and-innovation/natural-gas/gas-to-liquids.html
[23] Bond JQ, Upadhye AA, Olcay H, Tompsett GA, Jae J, Xing R, Alonso DM, Wang D, Zhang TY, Kumar R, Foster A, Sen SM, Maravelias CT, Malina R, Barrett SRH, Lobo R, Wyman CE, Dumesic JA, Huber GW. (2014). Production of renewable jet fuel range alkanes and commodity chemicals from integrated catalytic processing of biomass. Energy Environ. Sci. 7(4): 1500-1524. https://doi.org/10.1039/c3ee43846e
[24] Basile F, Albertazzi S, Barbera D, Benito P, Einvall J, Brandin J, Fornasari G, Trifirò F, Vaccaria A. (2011). Steam reforming of hot gas from gasified wood and herbaceous biomass. Biomass and Bioenergy 35(1): 116-122. https://doi.org/10.1016/j.biombioe.2011.06.047
[25] Albertazzi S, Basile F, Trifirò F. (2006). Gas di sintesi da pirolosi e gassificazione di biomassa lignocellulosica. La Chimica e l'Industria 88(2): 64, 69.
[26] Leadbeater NL, Barnard TM, Stencel LM. (2008). Batch and continuous-flow preparation of biodiesel derived from butanol and facilitated by microwave heat. Energy & Fuels 22(3): 2005-2008. https://doi.org/10.1021/ef700748t
[27] McLaren JS. (2008). The economic realities, sustainable opportunities, and technical promises of biofuels. Journal of Agrobiotechnology Management & Economy 11(1): 8-20.
[28] Napoli F, Olivieri G, Russo ME, Marzocchella A. (2009). Production of biobutanol by clostridium acetobutylicum. Combustion Colloquia IV(2): 1-6.
[29] Festel GW. (2008). Biofuels economic aspects. Chemical Engineering & Technology 31(5): 715-720. https://doi.org/10.1002/ceat.200700335
[30] Qureshi N, Li XL, Hughes S, Saha BC, Cotta MA. (2006). Butanol production from corn fiber xylan using Cl0ostridium acetobutlycum. Biotechnol Prog. 22: 673-680.
[31] Ezeji TC, Qureshi N, Blaschek HP. (2007). Bioproduction of butanol from biomass: From genes to bioreactors. Current Opinion in Biotechnology 18(3): 220-227. https://doi.org/10.1016/j.copbio.2007.04.002
[32] Durre P. (2007). Biobutanol: An attractive biofuel. Biotechnology Journal 2(12): 1525-1534. https://doi.org/10.1002/biot.200700168
[33] Atsumi S, Higashide W, Liao JC. (2009). Direct photosynthetic recycling of carbon dioxide to isobutyraldehyde. Nat Biotechnology 27(12): 1177-1180. https://doi.org/10.1038/nbt.1586
[34] Olson ES, Sharma RK, Aulich TR. (2004). The higher-alcohols biorefinery: improvement of the catalyst for ethanol conversion. Applied Biochemistry Biotechnology 113-116: 913-932. https://doi.org/10.1385/ABAB:115:1-3:0913
[35] Wright MM, Brown RC, Boateng AA. (2008). Distributed processing of biomass to bio-oil for subsequent production of Fischer-Tropsch liquids. Biofpr 2(3): 229-238. https://doi.org/10.1002/bbb.73
[36] Chandrasekhar K, Lee YJ, Lee DW. (2015). Biohydrogen production: strategies to improve process efficiency through microbial route. Int. J. Mol. Sci. 16(4): 8266-8293. https://doi.org/10.3390/ijms16048266
[37] Pandey A, Chang JS, Larroche C. (2913). Bihydrogen. (book) Elsevier.
[38] Stocker M. (2008). Biofuels and biomass-to-liquid fuels in the biorefinery: Catalytic conversion of lignocellulosic biomass using porous materials. Angewandte Chemie (International ed. in English) 47(48): 9200-9211. https://doi.org/10.1002/anie.200801476
[39] Zhang SP, Yan YJ, Li TC, Ren ZW. (2005). Upgrading of liquid fuel from the pyrolysis of biomass. Bioresource Technology 96(5): 545-550.

https://doi.org/10.1016/j.biortech.2004.06.015