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Analysis of the alternative routes in the catalytic transformation of lignocellulosic materials☆

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ABSTRACT

The large interest on a bio-based economy has stimulated a fast growing R&D on the 2nd generation processes for converting lignocellulosic biomass, but it is still often difficult to have a comprehensive picture of the different possibilities and routes, and especially of the critical factors for selecting one route over the competing ones. This perspective review analyses these aspects, with focus on the identification of the critical elements for the evaluation of the different routes, providing at the same time an update on the main trends and tendencies in R&D in this field. The focus is on the catalytic transformation of lignocellulosic materials. After a short introduction, two main aspects are discussed: (i) the socio-political context and the eco-impact of biofuels, and (ii) how to utilize the biomass in a sustainable perspective. The final part of the review uses the concepts developed in the first part to discuss a new vision for converting lignocellulosic raw materials in an integrated chemo-catalytic biorefinery. Aspects highlighted regards in particular the problem of depolimerization/hydrolysis of cellulose and the different possibilities to convert the products formed (sugars and furfurals) to biofuels and chemicals.

1. Introduction

There are many reasons pushing forward the need to accelerate the transition to a low carbon footprint society based on the use of renewable energies [1]: (i) the decrease of the reserves of fossil fuels, (ii) their impact on the environment in terms of greenhouse gas emissions and (iii) the geopolitical issues related to the marked fluctuation of the oil prices and to the localization of fossil fuel resources in certain areas. Most of the current renewable energy options (wind, solar, tides, hydro, geo, etc.) are suited to produce electrical energy. However, the density (by volume and by weight) of energy storage in batteries is about two orders of magnitude lower than that of the fuels used currently in vehicles (gasoline or diesel). Notwithstanding the intense research on nanostructured batteries [2,3], it is unlikely that this gap could be filled. It is thus expected that hybrid cars will dominate the market in the next 20 years, while electric cars will be mainly used in niche applications. The International Energy Agency – IEA – estimated that in 2030 they will cover about 1% of the sector [4]. This means that liquid fuels will continue to be the dominating energy vector for vehicles in the short-medium term scenario.

The transport sector accounts for about one third of the world energy consumption, which is actually about 500 EJ (around 12.000 MToe) [4]. While the energy consumption of the other sectors (residential, industrial, etc.) is expected to decrease or stabilize due to the introduction of new energy-saving technologies, the benefits due to the introduction of more energy-efficient devices in the transport sector is expected to not compensate the faster expansion in the number of circulating cars, particularly in emerging countries (Asia and Latino-America). In vehicles, only about one fifth of the energy is used for the motion, while the remaining is waste energy. It is thus in theory possible a large improvement of energy-efficiency in cars, but from the practical point of view, either due to the need to develop further the materials (for example, to produce electrical energy from low temperature streams by thermoelectric effect) or to the low cost-effectiveness of the new technologies (fuel cells), the improvement of the energy-efficiency of the cars will be limited. Therefore, the reduction of the carbon footprint of transport for the next two decades will depend mainly on the introduction of fuels deriving from renewable resources such as biomass. This is the reason for the political push in introducing biofuels, and the still growing excitement on the development of biofuels. On the other hand, there are increasing estimations that the cost of biofuels in the next two decades will be still higher with respect to the cost of fossil fuels. Therefore, biofuel market will heavily depend also in the future on economic subsidies. This fact has a number of consequences also in terms of R&D on biofuels, because poses a number of constrains which should be considered

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in evaluating the different possible options and routes in biomass transformation.

There are many other relevant aspects to assess the different production technology options: technical, economic and environmental aspects, e.g. the three components of sustainability. Many reviews and books on biofuels have discussed the technical aspects and in minor amount also the economic and environmental aspects of the production of biofuels and the role of catalysis in these processes [5–20]. However, it is still often difficult to have a comprehensive picture of the different possibilities and routes, and especially of the critical factors for selecting one route over the competing ones. In addition, there is a fast changing R&D panorama in this area, and often the aspects valid for one country cannot be directly translated to other countries.

There is thus still the need of an analysis of the field, with focus on the identification of the critical elements for the analysis of the different routes, and an update on the main trends and tendencies in R&D. This perspective review has thus the aim to introduce the general aspects related to the sustainability of the biofuel production, in the attempt to provide the critical elements necessary for the evaluation of the different (2nd generation) possible routes and options in transforming biomass. The focus will be on the catalytic transformation of lignocellulosic materials.

2. The socio-political context and the eco-impact of biofuels

With an estimated cost of the oil barrel stabilized around 100 US$ for the next decade [4], the cost for producing fuels from biomass will probably remain more expensive than that from oil (at equivalent energy content), apart in very peculiar situations. Even an increase in the oil cost will probably not change significantly this situation, due to the training effect of oil cost on those of biomass production, transport and transformation. It is difficult to make precise forecasts in the energy sector, due to the extremely complex situation and the often confuse indications on the real costs. However, it is highly probably that the market for biofuels will considerably depend on the continuation of economic subsidies (in one form or another) to this sector. The International Energy Agency [4] indicates that in 2030 the biofuels will cover only about 14% of the energy mix for transport (in developed countries such as Europe) with respect to the actual value of about 6%. Therefore, the rate of growing of the biofuel market will be limited by the presence of economic subsidies.

The costs of producing biofuels depend significantly on the feedstock, process and location. Location determines access to particular feedstocks and energy supplies. Their prices depend largely from the market developments at the global scale. For established processes (1st generation) the processes currently used for producing ethanol and biodiesel do not vary so greatly, because the fixed costs of the latter are lower, but higher the raw material cost. Therefore, the plant scale has a significant impact. For 2nd generation plants, there are large uncertain in the cost estimation. Moreover, rapid developments in the design of plants in order to make the use of energy more efficient, or to improve the profitability of by-products, may have a large effect on the economics of new plants. Location, in terms of labour cost, access to biomass, transport costs, etc. has also a large influence. It is thus possible only to make roughly indicative estimations of the relative costs of biofuel production, and of the expected changes in the costs.

Steenblik [21] of the Global Subsidies Initiative (GSI) reported a detailed study, supported by OECD and the International Transport Forum, on the economics of biofuels and of current policy measures to support their production and consumption. Based on the data from IEA they reported a comparison of the current and projected future ethanol and biodiesel production costs, compared with pre-tax gasoline and diesel prices. Their results are in essence in agreement with the estimation of the German Biomass Research Centre (DBFZ) [18] regarding the economic assessment of the biofuel production cost. Fig. 1 summarizes some of the relevant elements of this analysis by comparing the actual and future (year 2030) estimated cost of production of selected biofuels (at fuel equivalent conditions) with respect to the average pre-tax prices for fuels from fossil resources.

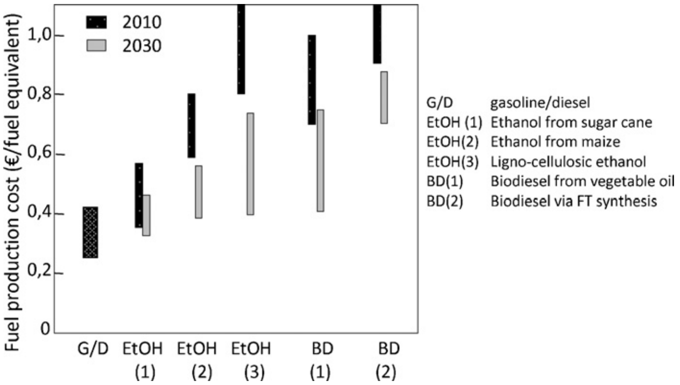

Fig. 1. Current and projected future ethanol (EtOH) and biodiesel (BD) production costs from selected routes, compared with pre-tax prices for fuels from fossil resources.

Even considering the large uncertain in some estimations, and the large dependence from country to country, it may be concluded that on the average for the next two decade the products costs for biofuels will be higher than the expected (pre-tax) prices for fossil fuels. Therefore, only with subsidies the biofuel market could expand.

It should be remarked that the structure of the public subsidies to the biofuels is quite complex, and often not very transparent [21]. Fig. 2 summarizes the general structure of subsidies provided at different points in the supply chain for biofuels, from production of feedstock to final consumers. Different countries have different policies for these different subsidies, which in addition do not influence the biofuel sector only. Therefore, it is very difficult to separate the different aspects in the cost structure for biofuels. On the other hand, Fig. 2 clearly evidences the concepts that (i) the structure of subsidies goes much beyond the simple subsidies to the biofuel cost (tax exemption), which is often only considered, and (ii) the biofuel chain is highly interconnected with many other social aspects.

There are many motivations, which justify these subsidies, even it was remarked that current biofuel support policies in OECD (Organisation for Economic Co-operation and Development) countries are not technological neutral [21]:

- biofuels reduce the carbon footprint of mobility which requires liquid fuels which can be integrated into the actual infrastructure (distribution, compatibility with actual fuels and engines, etc.); the alternative is to produce fuels from natural gas or coal (GTL and CTL processes), but which are also more expensive than fuels from oil (Fig. 1),
- the possible use of biomass wastes, with the double benefit of reducing their environmental impact and the efficient valorization of unused resources,
- the benefits for local agriculture and land preservation, with the creation of energy districts where biomass is used more efficiently through integration between the production of food, energy and raw materials for chemical industry,
- significant opportunity for creating and maintaining employment,

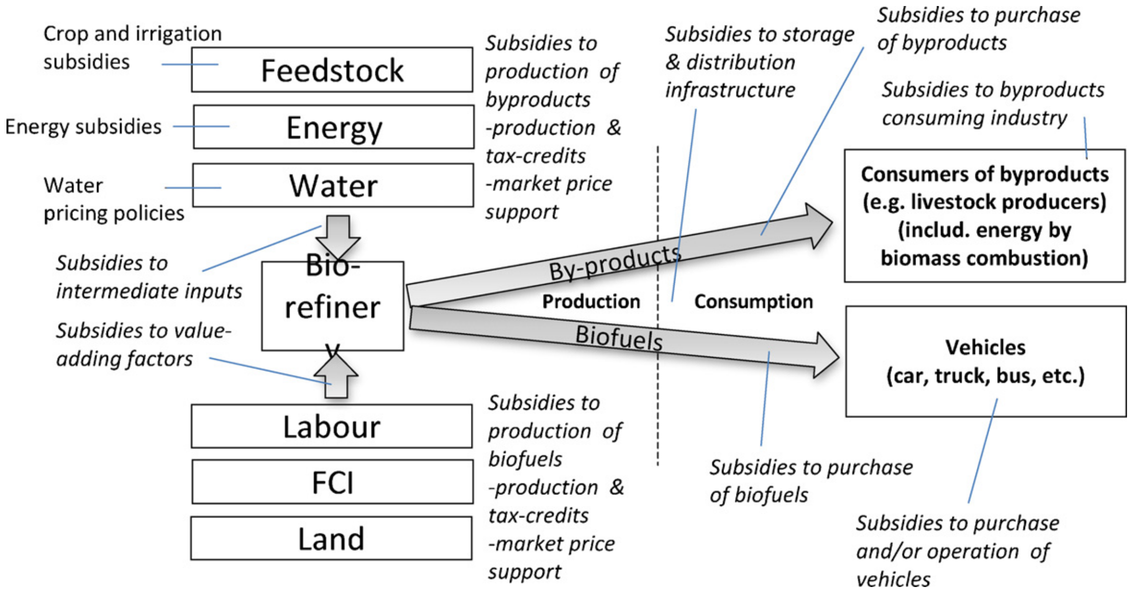

Fig. 2. Subsidies provided at different points in the biofuel supply chain.

Adapted from Ref. [21].

- reduced dependence on fossil fuels and thus a positive impact on energy economy and geopolitical strategies.

There are thus significant social motivations to push the production and use of biofuels. There are also some additional aspects, which were often not considered. The introduction of biofuels had a significant impact on the energy market particularly that related to fossil fuels, which was dominated from relatively few energy companies. One of the reasons of this monopoly-like character was the need of very large investments for oil extraction and refining. First generation biofuels (ethanol from sugar cane or corn, biodiesel from vegetable oils) do not require very large investments for the production plant (fixed capital investment – FCI), particularly in the case of biodiesel. This has created the opportunity for a large number of new investors to enter the market, favoring a fast spreading of the technology. However, the raw materials for this first generation biofuels are in direct competition to their use as food or other valuable productions. Many interesting and higher value oleochemical products could be produced from vegetable oils, for example [5].

The second generation of biofuels is instead in principle not in competition with food, and in addition is characterized from a much larger use of the biomass. Vegetable oils (palm oil, for example) constitute about 5% of the biomass, and it is thus necessary to make a progressive full use of the biomass. There are many possible routes for this second-generation biofuels (see later). Some are already close to commercialization (although often there are still many techno-economic aspects to solve), while other are at an earlier stage of development. Between the aspects often not fully taken into consideration, the FCI is an important one. The biofuels are significantly subsidized by public to be economically competitive, as discussed before. Therefore, the interest of society over that of the companies is an important element for decision. For a modern society, it is very important to create the conditions for a true competition to avoid monopolization of the market, which will increase the costs. It is thus important for biofuels to incentive the conditions and solutions favoring a large number of investors. In other words, solutions should be promoted (between the many possible) which can be efficient on a small-medium scale, and which do not require very large investments [22].

From a sustainable perspective (a main driver for biofuels is to reduce the carbon footprint), large investments in an energy market (where it is difficult to make an exact forecast) will be limited and will take long time for the decision. Thus technologies requiring smaller investments and with a broader base of possible investors will be introduced much faster on the market. In other words, society will have in a shorter term a benefit from the introduction of the new technologies. The field of biofuels, due to the many relevant socio-economic implications, cannot be thus evaluated with the conventional techno-economic parameters, and the societal implications and return in terms of sustainability and competitiveness has to be included. This is the perspective to assess the second-generation biofuels.

Assessing the eco-impact of biofuels is also an important element for the analysis of the different routes. There are manifold effects on the environment related to an expanding biomass usage. There are direct impacts on the environment through the biofuel production and usage itself. Sustainability criteria by which assess the different biofuels are related to preserving biodiversity, conservation of ecosystems, avoiding negative impacts of fertilizer, avoiding water pollution and soil erosion. These aspects are usually considered by life cycle assessment (LCA) [23–25]. A LCA considers the full life cycle of a product from resource extraction to waste disposal (i.e. from “cradle” to “grave”), in order to give a complete view of the environmental impacts of products or process. The assessment should include the production of biomass, its harvesting and transport, the production of the biofuel, and the distribution and use of the biofuel. It may also include other aspects, which are relevant, such as the land use change (for example, from forest to plantation), the usage of the fuel in motor engines, waste disposal and so on. By-products should be considered along the life cycle of the production of the fuel, but are not always included. Often contrasting results are obtained by LCA analyses, because the boundary limits of the analysis are different. In addition, the impacts are dependent on the global or regional system, where the production takes place or whose resources are used. It is thus necessary in principle to have a precise knowledge of the specific localization, while often general-purpose database are used. This is a further element of discordance between the published LCA analyses. LCA is thus a very powerful methodology, but it is often necessary to have a closer inspection on the specific method applied and of its limits.

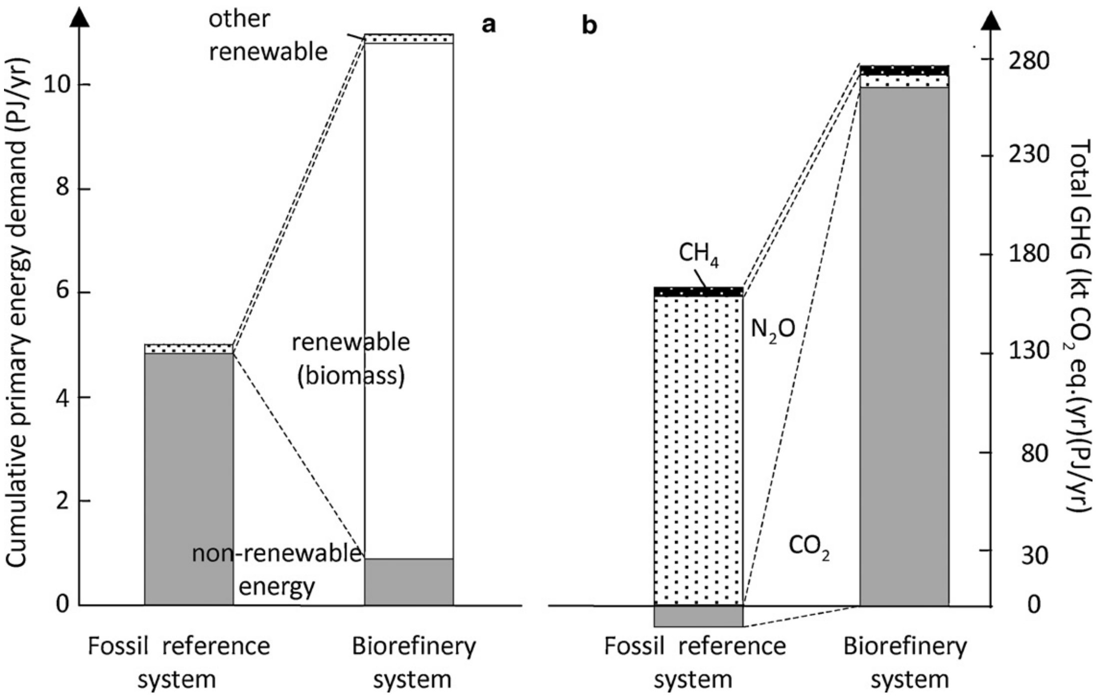

Fig. 3. (a) Cumulative primary energy demand of the biorefinery and fossil reference systems. (b) Total GHG emissions of the biorefinery system using an average N_2O emission factor from land with respect to fossil reference systems.
Adapted from Ref. [25].

An interesting example of LCA analysis is given in the evaluation of a biorefinery concept producing bioethanol, bioenergy, and chemicals (phenols) from switchgrass [25]. The LCA starts at the top with carbon fixation from the atmosphere via photosynthesis, which results in crop growth. At the end, the biorefinery system supplies, products, and services: bioethanol, phenols, electricity, and heat. The LCA accounts for all input and output flows occurring along this chain, from planting and harvesting the crops, processing the feedstock into biofuel, transporting and storing of feedstocks, distributing, etc. to the final use of biofuels. The fossil fuel case starts with consumption of non-renewable sources (i.e., fossil oil and natural gas), and includes the main stages in the process: extraction and transport of raw materials, production of the fuel, refining, storage, distribution, and combustion.

The results of this LCA analysis [25] are summarized in Fig. 3. The cumulative primary energy demand of the bio- and fossil-fuel chains (Fig. 3a) reveals that the biorefinery system needs a higher cumulative primary energy demand than the fossil reference system (10.9 against 4.7 PJ), but it is mainly based on renewable energy (i.e., the energy content of the feedstock itself). There is thus about a twice higher energy consumption, but a saving of non-renewable energy. The intensified land use due to agriculture for growing the biomass leads to an increase of N_2O emissions, a greenhouse gas (GHG) having an effect around 300 times higher than CO_2 (on a time span of 100 years). The N_2O emissions from agriculture derive from many sources: (i) direct soil emissions, (ii) volatilization of part of nitrogen present in fertilizers as NH_3 which is then in part converted to N_2O, and (iii) and leaching to groundwater as nitrate which also in part are then converted to N_2O. There are discordances on the estimation of these different factors. On the average, 0.13 g N_2O are emitted per g N present in the synthetic fertilizer. The results are summarized in Fig. 3b. It can be observed that even if the impact of biofuels is still positive in terms of reduced emissions of GHG, the inclusion of N_2O due to intensive agriculture causes a drastic reduction of the effective benefit. The effect is depending on the amount of fertilizers necessary to grow the biomass, the type of soil, etc. For example, fast growing biomass, i.e. the energy-crops considered for ligno-cellulosic ethanol, need typically large amounts of fertilizers.

The GHG emissions also depend largely on the type of biofuels, the raw biomass used, and the process technology. Fig. 4 reports a summary of selected estimations on the GHG potential (kg CO_2 equivalent per unit energy of the fuel) for different biofuels and raw materials, based on LCA assessment well-to wheel (WTW), in comparison to conventional fossil fuels. The range reported in Fig. 4 corresponds to the bandwidth of the results reported in literature by different studies [18]. This derives from the fact that different LCA studies for biofuels are carried out under different assumptions made in the phase of the goal and scope definitions, e.g. with regard to system boundaries, cut-off criteria, allocation of by-products, etc.

While current biofuel options do not promise high GHG mitigation potential (in some cases for biodiesel and bioethanol their GHG are even higher than for reference fossil fuels), results for advanced and future biofuels show the tendency to increasing GHG mitigation potentials. However, these results have been calculated for theoretical biofuel production concepts, since these options need to be demonstrated at commercial scale.

There are many other aspects relevant in the assessment of the sustainability and eco-impact of biofuels. Other environmental impact categories sometimes included in LCA analysis are abiotic depletion, ozone layer depletion, human toxicity and aquatic ecotoxicity, acidification and eutrophication. The use of biofuels has a negative impact on acidification and eutrophication with respect to fossil fuels. Acidification is due to biomass production (related to fertilizers) and biomass combustion for heat and power production to sustain the higher energy demand (Fig. 3a). Eutrophication is mostly given by fertilization. Emissions induced by fertilizer application also influence other environmental categories, like terrestrial and fresh water ecotoxicityand human toxicity.

Oil refineries have a significant impact on water system, due to the large amount of wastewater (nearly in a ratio 1:1 with respect to inlet petroleum) containing waste oil and toxic by-products from

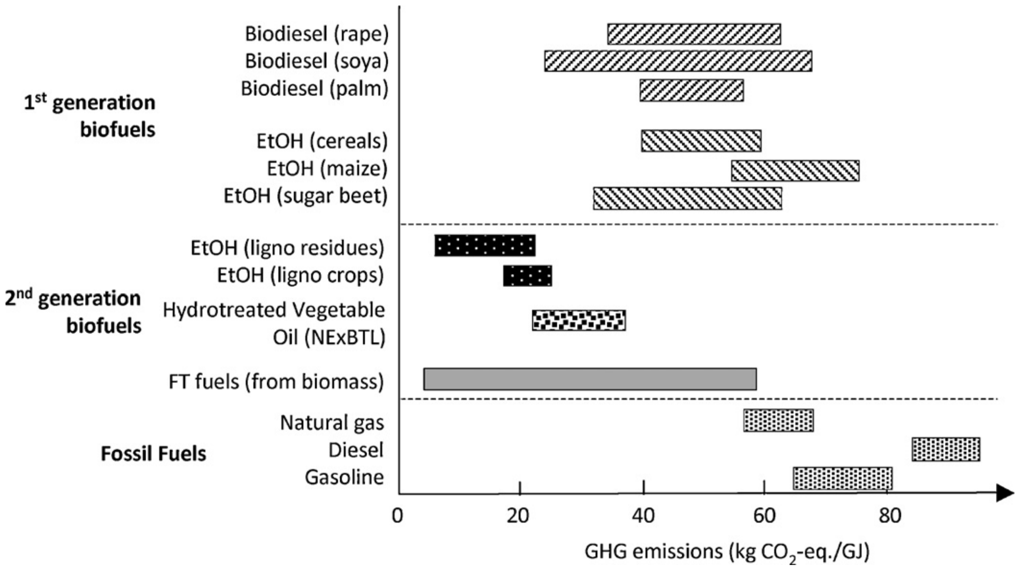

Fig. 4. Estimated GHG emissions per unit of energy content by LCA WTW assessment for fossil fuels and selected cases of 1st and 2nd generation biofuels. Adapted from Ref. [18].

the refinery process. Some impurities such as heavy metals, sulphide, and phenols are in the crude oil. Toxic compounds such as cyanide, dioxins and furans are generated during the refining process. Refineries also discharge large amounts of pollutants to the air and generate hazardous solid waste. Most of the oil refinery sites groundwater is contaminated with refinery toxic chemicals as phenols, cyanide, dioxins, furans, etc.

In principle, biorefineries have a much lower impact on the local environment, due to the lower amount of toxic byproducts. However, biorefineries have large water consumption. For example, in ethanol produced from corn kernels water is required for the slurry operation with whole corn, followed by saccharification to produce sugars from starch via hydrolysis. This is followed by fermentation and distillation operations. An estimation of the consumptive water use from these facilities indicates an amount of wastewater produced about four times the amount of ethanol produced [26], e.g. about three-four times higher than the case for oil. By considering the impact on water associated to also biomass production, values even larger are obtained. The wastewater contains high amounts of organics and nutrients, and thus alters the eco-system, with an increase of algae in water, which lead to a lowering of the oxygen level and thus negative effects on the aquatic life.

Producing ethanol from cellulosic materials such as grasses, crop residues, and wood requires a different process than for corn because they are not rich in starch or sugar. The total water requirements for lignocellulosic ethanol are larger, about a factor 9–10 with respect to the bioethanol produced, even if this value may be probably reduced in the future. Thermochemical conversion of cellulosic materials, one of the technologies considered for the 2ndgeneration biofuel plants from lignocellulosic raw materials, has also a significant impact on wastewater, estimated in a ratio 4–6 with respect to biofuels. The wastewater also contains much larger amounts of toxic chemicals such as phenols.

There are thus increasing environmental policy concerns more than just emissions of air pollutants (odors and volatile organic compounds due to fermentation of biomass) and greenhouse gases. In respect of soils and water, the expansion of crops for biofuels has various negative effects. The rapid growth in demand for biofuel feedstocks is changing cropping patterns, with various negative effects, and has a negative impact on water system, due both to growth of biomass and its transformation. Large volumes of wastewater effluents and of fertilizers are increasing the level of nutrients in the aquatic systems, with a significant alteration of the eco-system.

Therefore, despite a rapid worldwide expansion of the biofuel industry, there is a lack of consensus about the potential of biofuels to decrease greenhouse gas (GHG) emissions and the preferable technologies for their production. It is necessary to give more attention to the issue of the sustainability of biofuels, and the twin relationship with the socio-economic context. The market growth has caused in the tropics a change in land use of natural areas (for example, reduction of tropical forests in Malaysia to increase palm plantations to produce palm oil for biodiesel use). This caused a negative effect instead of a positive one on CO_2 emissions (due to land use change), and on the local ecosystems (for example, reducing the territory for wild animals). When marginal land is available, or when biomass residues can be used (the actual amount can cover about one third of the forecast biofuel production), the carbon footprint is positive (e.g. they allow a net saving on energy, considering the full life cycle assessment – LCA), but the case is different when forests are substituted by plantations as in tropical countries.

The assessment of biofuels cannot be thus based on only techno-economic evaluations due to both the fact that the biofuels are and will be subsidized by public and the impact they have on the eco-system. Therefore, the social dimension (in terms of sustainability and impact on the eco-system) is an important component for the selection of the optimal strategies for bio-energy and bio-economy development, and next generation biofuels. We have discussed here some aspects, although the complexity of the problem prevented to be exhaustive.

The size necessary for efficient biofuel processes is another key element for evaluation. In fact, it will determine the distance from which it is necessary to transport the biomass to allow the constant feed of the plant (e.g. the penalty in CO_2 emissions due to transport of the feedstock to the plant), and other relevant aspects for sustainability such as the investment costs, the possibility of location and so on. Flexibility in feed, e.g. the possibility to use multiple types of raw materials, is another key parameter. The possibility to use different lignocellulosic sources (agro-food and wood production residues, sorted municipal solid wastes, herbaceous energy crops) makes possible to:

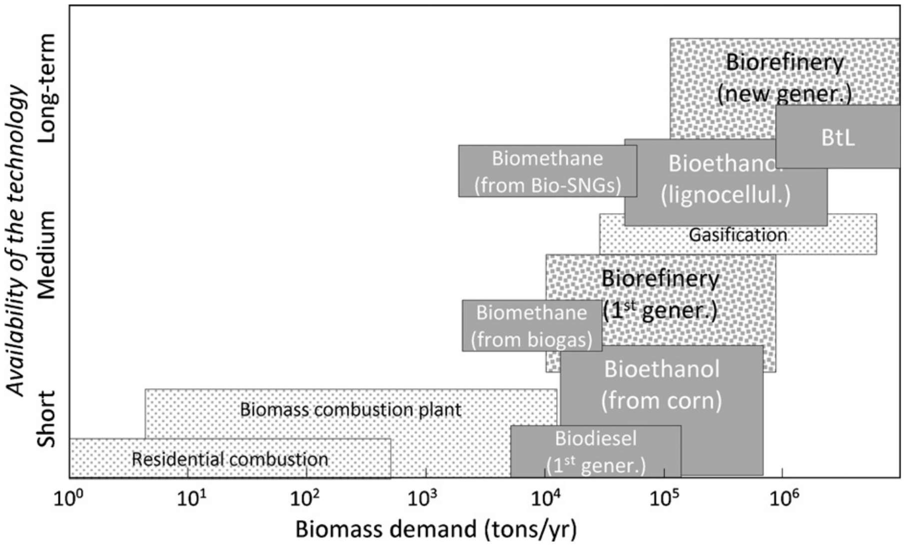

Fig. 5. Biomass demand of some of the current and of the future biomass applications.

Adapted from Ref. [27].

(i) Limit the distance from which the raw materials are transported.
(ii) Guarantee the more constant use through the year avoiding the storage of large volumes of biomass (and related problems of fermentation, emission of odors and wastewater, etc.).
(iii) Integrate better and more efficiently in agro-food districts.

Biomass is a limited resource in most of the developed countries. There are two main options: (i) regional biomass supply to increase the local added-value and (ii) trans regional supply of biomass and bioenergy. The first case, is the preferable from the social perspective for the motivations discussed before, but many of the concepts for biofuels and bio-based chemicals production are subject of the system inherent trade-off between preferably medium to large-scale plants with regard to "economy of scale"–and thus a high biomass demand and a relatively small catchment area for the supply of this feedstock demand [27]. This is particularly true for so far not matured concepts that are designed for large-scale conversion of biomass (e.g. energy crops, straw and forestry wood). Fig. 5 illustrates this concept of the biomass demand for present and some of the future process technologies for biofuels.

A rule of thumb is that the transport distance of biomass production and biomass demand should be lower than about 100–150 km, in order to limit CO_2 penality due to the transport of biomass itself. It should be also considered that a plant should be feed all over the year, while biomass collection is typically discontinuous. There are many aspects determining the biomass logistics: (i) the area or region specific potential (i.e. the technical biomass potential per ha total area land of a region or country; in other words the density of biomass potentials), (ii) the biomass assortment and their treatment, (iii) the plant site and local infrastructure (e.g. detour factors, connection points, available land), (iv) the means of transport (e.g. semitrailer, train or navigation vessel) and depending on the potential density and local infrastructure the transport distance, and (v) storage technology and storage demand according to the specific annual biomass demand of the biofuel production plant.

On the average, for countries such as those in Europe, this rule of thumb translates to biomass demand of about 10^4–10^5 tons per year, although the many factors outlined above influence this value. Nevertheless, this estimation indicates that some of the 2nd generation biofuel processes, particularly those based on thermochemical routes, e.g. BTL processes via syngas formation, have biomass demands higher than this indicative value.

There are thus several parameters determining the optimal choice and these are significantly dependent on local conditions. An optimum technology for a country may not necessarily valid in a different country. Due to the presence of multiple aspects, advanced analytical techniques such as LCA, though necessary, are not sufficient. Each country should develop its own preferable mix of technologies, or at least invest significantly in research and development to enable the optimal choices that best suit the country needs.

3. How to utilize the biomass in a sustainable perspective

The previous section has discussed some of the aspects to consider, from a sustainable perspective, when evaluating the different possible routes in converting biomass. We can summarize these factors determining the strategic choices for future energy scenarios as follows:

- The push to biofuels derives from a mix of factors (different from country to country), but in Europe*GHG reduction* is a key factor and a main motivation for subsidies that determine significantly the future of biofuels. Also in other countries this starts to become a critical factor. However, GHG account should consider all the well-to wheel production chain of biofuel.
- The target is *liquid fuels* which can well *integrate into the existing energy infrastructure* to store and transport energy, and to use biofuels. This would reduce significantly the heavy investments otherwise necessary. Many are the important parameters to consider for commercial use, from specific properties (viscosity, flash and pour point, water and sediment content, carbon residue and ash, distillation temperature range, specific gravity, heating value, carbon-hydrogen and carbon-oxygen content) to fuel properties (octane or cetane number, boiling and solidification point, lubrification properties, smoke properties, etc.).
- Hydrocarbons have a *higher energy density* than oxygenated, and thus using flex fuel the km per liter of fuel decrease of about 30%(for E85). This is in contrast with the regulation in various countries to decrease the fuel consumption in the cars. In US, for example, there is the need to increase average gas mileage from

25 to 35 MPG (mileage per gallon) to reduce CO_2 emissions, while this value decreases from 25 MPG to 18 MPG using flex fuel. Flex fuel is a mixture of conventional gasoline and ethanol. Up to 10% in ethanol – E10 – no major changes are requested in engines, but higher concentration – E85 used in Brazil – request to adapt the engine, due mainly to the poor lubrification properties and higher corrosion character of ethanol.
- *Chemicals* from biomass are an *added-value bonus* to realize better economics in biorefineries producing higher added-value products (monomers for polymers, intermediate or fine chemicals). However, it is important that the same type of platform molecules could either go to fuels or chemicals, in order to give to biorefinery the flexibility to fast adapt to a changing market. One of the elements of success of bioethanol in Brazil was the possibility to switch the production from bioethanol to sugar, following better the market and minimizing the risks.
- In Europe, *diesel* components are *better than gasoline*. In the choice of the preferable route it may be thus important to have the flexibility to produce components both for gasoline or diesel, minimizing as much as possible the number of different processes steps, and thus ideally starting from the same platform molecules. It is indicated "component for", because the estimation for 2030 by IEA [4] is that biofuels will cover in Europe, for example, only 14% of the market for transport fuel, while 84% will be by fossil fuels, the difference being electric and natural gas fuelled cars. Due to the lower fuel consumption of diesel with respect to gasoline cars (on the average 20% less), the market in Europe for diesel will account more than 60% of transport fuel.
- *C-efficiency* of the biofuel production is a key element. It is necessary to avoid as much as possible the loss of carbon in the processing, in order to increase the intrinsic energy of the fuel and to reduce GHG emissions associated to biofuel production. CO_2 is produced by fermentation. From a glucose unit, two ethanol molecules and two CO_2 molecules are formed. When H_2 is required in producing biofuels, the CO_2 associated to H_2 production (either from biomass or from fossil fuels) should be considered. Although only a full LCA study could define precisely the GHG impact of the different biofuels, the C-efficiency of biofuels, defined as the number of carbon atoms in the biofuel with respect to the loss of CO_2 during the process, is a good indication. From glucose, the theoretical C-efficiency of ethanol is 0.75, while that of methylfuran and γ-valerolactone (two possible components for gasoline) is 0.83. Dimethylfuran, another possible gasoline octane booster (see later), has a C-efficiency of 0.5 as ethanol, but higher energy density (half the oxygen content).
- The use of biofuels is a *short-medium scenario*, highly depending on the investments costs and biomass transport costs. There is the need of "smart and small" (distributed) technologies and of a high flexibility in the type of feed.

In US, as the result of a large discussion involving many academic, companies, representatives from US national labs and program managers (NSF, DOE, USDA) a research roadmap for making lignocellulosic biofuels a practical reality was published [28] and then presented in various meeting [29]. A conclusion of this activity was that the production of hydrocarbon fuels from biomass has many advantages:

- "*Green*" *hydrocarbon fuels* are essentially the same as those currently derived from petroleum and thus it will not be necessary to modify existing infrastructure (e.g. pipelines, engines) and hydrocarbon biorefining processes can be tied into the fuel production systems of existing petroleum refineries.
- Biomass-based hydrocarbon fuels are energy equivalent to fuels derived from petroleum. In contrast to the lower energy density of E85 flex fuel, there will be no penalty in gas mileage with biomass-based hydrocarbon fuels. In addition, hydrocarbons produced from lignocellulosic biomass are immiscible in water; they self-separate, which eliminates the need for an expensive, energy-consuming distillation step.
- Biomass-based hydrocarbon fuels are produced at high temperatures, which allows for faster conversion reactions in smaller reactors. Thus, processing units can be placed close to the biomass source or even transported on truck trailers. The amount of water needed for processing hydrocarbon fuels from biomass can be greatly reduced, compared with the dilute sugar solutions to which enzymes are constrained. This is because heterogeneous catalysts work well in concentrated water solutions or alternative solvents (ionic liquids, for example). Furthermore, heterogeneous catalysts allow continuous operations reducing costs of separation with respect to bio-catalysts. The elimination of energy-intensive distillation, the higher reaction rates, and the much smaller process footprints can also lead to lower biofuel costs than are possible using currently available biological pathways for producing cellulosic ethanol.

The conclusion from this US roadmap [28] are thus in very good agreement with the sustainability criteria discussed before, and pointed out also the role of catalysis and process intensification as one of the key aspects. This is in well agreement with the "smart and small" concept presented above.

A synthetic overview of the main pathways for the production of liquid transportation fuels from biomass is presented in Fig. 6. On the top are reported examples of the various types of feedstock, according to 1st and 2nd generation raw materials. Sugar and starch are used to produce bioethanol by fermentation via saccharification in the case of starch. Various vegetable oils could be used to prepare biodiesel by catalytic transesterification. A recent alternative for "green diesel" is based on the hydrotreating, which could be used not only to convert plant-derived oils such as soybean, rapeseed, and palm, but also non-edible oils, such as Jatropha and algal oils as well as animal fats [30]. Since 2005, UOP and eni have developed the Ecofining^{TM} process based on conventional hydroprocessing technology to produce diesel-fuel ("green diesel")[31] or jet-fuel [32]. Analogous technologies have been developed by Neste Oil (NExBTL Renewable Diesel) [33] and Petrobras (H-Bio process) [34].

While algae and non-food seed oils can be grown on marginal lands, the expansion of the market of vegetable oils to produce renewable diesel from poses serious questions. Fargione et al. [35] first questioned about land clearing and the biofuel carbon debt. Converting rainforests, peat lands, savannas, or grasslands to produce crop- or oil-based biofuels creates a "biofuel carbon debt" by releasing 17–420 times more CO_2 than the annual greenhouse gas (GHG) reductions that these biofuels would provide by displacing fossil fuels. In contrast, biofuels made from waste biomass or from biomass grown on degraded and abandoned agricultural lands planted with perennials incur little or no carbon debt and can offer immediate and sustained GHG advantages.

Together with the competition with food and related social aspects, this issue of avoiding land use change penalty is one of the motivations to shift to 2nd generation biofuels. For biodiesel, non-edible oils, such as Jatropha and algal oils will be used in the future, taking advantage that the process is very flexible in terms of feed. These non-edible oils are a potential resource for developing countries such as Africa, but there are many logistic aspects limiting the expansion of this route. In addition, one of the motivations for biofuel subsidies is to incentive the local agriculture (in developed countries such as Europe). It is probably that in the future the structure of subsidies for biofuels will change to favor the latter aspect, and thus productions out of the country (as the case for these non-edible oils) could be penalized and not economically competitive.

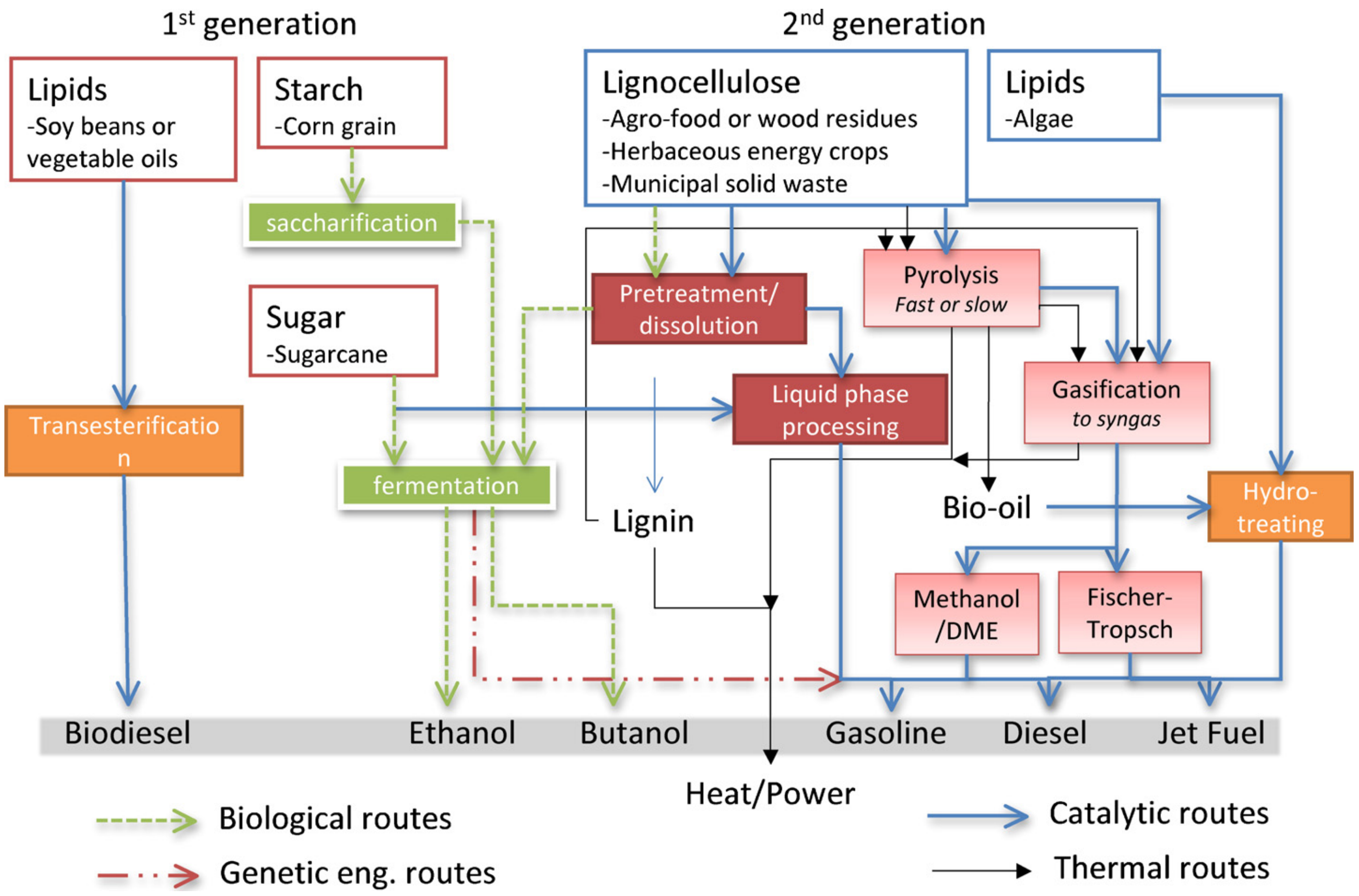

Fig. 6. Main routes to biofuels.

Adapted from Ref. [16].

This is the reason why in developed countries various energy-companies are instead pushing the algal oil as the route for 2nd generation biodiesel. The attractive aspects of this route are that algal fuels not affect fresh water resources, can be produced using ocean and wastewater, are biodegradable and relatively harmless to the environment, use land that is not suitable for agriculture, and the growing of algae can be stimulated from waste CO_2. However, there are also a number of problems: (i) harvesting/processing algae is difficult, costly and energy intensive, (ii) random natural algae tend to start taking over from artificially seeded algae fairly rapidly unless the pond is covered, (iii) ponds often have to be lined to meet groundwater regulatory requirements, (iv) algae grown in only the few first centimeters in ponds, because light do not penetrates more in depth, while photoreactors are too expensive, and (v) biodiesel fuels derived from algae have poor properties at lower temperatures (‘cold flow’) and they degrade more easily than other biofuels. Therefore, the cost of producing biodiesel from algae is still too high, and it is unclear whether it could be significantly reduced. In addition, there are a number of other technical problems to solve. Massive investment by private investors and the federal government have spurred interest in algae, but there are still a multitude of complex technical and financial issues to solve. The potential, however, is great, considering for example that soybeans may produce 5–6 l ha^{-1} per year, while algae could potentially yield somewhere between 450 and 650 l ha^{-1} per year.

Various types of lignocellulosic feedstock can be used, from forest and agricultural to energy crops such as switch grass and also solid municipal wastes (the bio-organic part). There are three main routes for converting lignocellulosic biomass: (i) thermo-chemical, (ii) bio-chemical and (iii) chemo-catalytic. The thermo-chemical approach consists in the pyrolytic treatment processes of biomass to produce solid, liquid or gaseous products that can be subsequently upgraded to fuels (synthetic biofuels). Depending on the reaction conditions, different types of pyrolysis, gasification, and torrefaction are used to produce gaseous, liquid or solid fuels [36]. Temperatures in the 600–800 °C range are used. These primary treatment methods produce intermediates that should be first purified, often in multiple steps, and then be further upgraded to fuels through catalytic treatments, e.g. hydroprocessing, cracking, steam reforming, methanation, Fischer–Tropsch (FT), etc. In principle, all types of biomass can be used for the thermo-chemical treatment. Thermochemical processes require a larger capital investment in process equipment than other routes. This appears the main limit according to the criteria previously discussed.

Another issue in conversion of biomass to energy is an inconsistency of compositions and physical properties of different types of biomass, which makes hard to process a mixture of various types of biomass as a feedstock for a gasification/pyrolysis process [37]. To better utilize biomass wastes, the gasification/pyrolysis systems should be able to handle the inconsistency of feedstock to maintain the stable product yields and properties. The high capital costs for building a gasification system is addressed by new solutions, such as plasma gasification [38] or microwave-induced pyrolysis to produce bio-oil [39] or bio-syngas [40], for example, but still there are a number of problems regarding quality of the products obtained and their purification.

The first FT pilot plant based on bio-syngas was set in Freiberg (Germany) in 1998 by CHOREN using woodchips and straw, for a capacity of 1 MW. In 2003–2005 started the construction of the world's first commercial 45 MW BTL Plant in Freiberg/Saxony. The plant has a production capacity of 15,000 tons of BTL fuel per year and the next generation 600 MW BTL-plant is planned to be operative in 2012–2013. A three-stage gasification process is used: (i) low temperature gasification, (ii) high temperature gasification and (iii) endothermic entrained bed gasification. Using this process it is possible to obtain diesel that has some advantages over the conventional diesel [41]: (i) higher cetane number and therefore much better ignition performance, (ii) absence of aromatics and sulphur that significantly reduces pollutants in exhaust emissions and (iii) no need of any adjustment to existing infrastructure or engine systems.

There are few other BTL pilot/demonstration units in operation worldwide. For example, the 8 MW CHP (Combined Heat and Power) demonstration plant in Gussing (Austria) is producing FT liquids since 2005 in a smaller scale and commissioning of their 30 MW plant to produce 4200 tons/a diesel demonstration plant is underway. An IGCC (Integrated Gasification Combined Cycle) facility plant to produce bio-DME, bio-methanol and FT-diesel is now under construction in Varnamo, Sweden [42].

In the bio-chemical approach, a physicochemical pre-treatment of lignocellulosic biomass is necessary, due to a slow rate of the direct enzymatic conversion of lignocellulose. Lignin is not converted by enzymes and can be combusted, but its conversion using new advanced biochemical methods is also possible [43]. The conversion of lignocelluloses into ethanol is based on the following principal steps: (i) pre-treatment of lignocellulose (some more aspects will be discussed in the following section), (ii) hydrolysis/saccharification of the carbohydrate polymers to produce fermentable sugars like hexoses (C6 sugars) and pentoses (C5 sugars), and (iii) fermentation of hexose and pentose to produce ethanol. Using different enzymes, products other than ethanol (butanol, for example) can be also synthesized.

In the chemical or chemo-catalytic approach, the cellulosic biomass undergoes catalytic hydrolysis, using acids either in aqueous solution (commercial method, for example, using diluted sulphuric acid) or heterogeneous phase (using solid catalysts or ionic liquids) to lower the impact on the environment [44,45]. Chemo-catalytic routes are then necessary also for the conversion of the intermediates (platform molecules) formed in the primary treatments to synthetic fuels and bioH_2, or chemicals. The following section will discuss in a more details some of the alternative possibilities.

Sugars can be catalytically converted to liquid alkanes, allowing thus to produce liquid fuels equivalent to those currently derived from petroleum (e.g., gasoline, diesel, jet fuel) [7–10,15,46]. Liquid phase catalytic processing of sugars is typically carried out at lower temperatures (e.g., 230 °C) compared to biomass pyrolysis, liquefaction, or gasification. However, whereas these latter process can operate with complex biomass feedstock (e.g., containing cellulose, hemicellulose, and lignin components), liquid-phase catalytic processing typically involves feedstock containing specific biomass-derived compounds, such as sugars or polyols. The biomass must be thus pretreated to prepare a feed solution for the subsequent liquid-phase catalytic processing. The alkanes are easily separated from the aqueous feed, significantly improving the process thermal efficiency. Virent Energy Systems has developed, based on these concepts, the process known as Bioforming®, from which water soluble sugars are converted into green gasoline, diesel, and jet fuel via aqueous phase processing. In March 2010, Virent and Shell announced the demonstration plant based on Virent's Bio Forming® process. The demonstration plant in Madison, WI can produce up to 38,000 l per year, which will be used for engine and fleet testing. In June 2010, Virent announced that it has secured $46.4m from Cargill and Shell to accelerate biofuel scale-up.

Therefore, not only ethanol and biodiesel, even if from 2nd generation processes, can be produced as liquid biofuel. There are increasing possibilities to produce liquid hydrocarbons from biomass [47]. Hydrocarbons can be made from the sugars of woody biomass through microbial fermentation or liquid-phase catalysis, or directly from woody biomass through pyrolysis or gasification. However, the latter possibility involves large investments, and do not fit the sustainable criteria previously discussed. Lipids from nonfood crops as well as algae can be also converted to hydrocarbons. The resulting hydrocarbon biofuels will be, in principle, drop-in replacements for gasoline, diesel, and jet fuel (although there various problems, as commented before), will allow to reduce CO_2 emissions per km instead that increasing them as the case of ethanol, and will work in existing engines and distribution networks. However, these routes are not equivalent in terms of the various criteria discussed before, although a full systematic analysis is missing. Another important difference regards the possibility to realize an optimal integration with the production of added-value chemicals. Some aspects will be discussed in the following section.

4. Converting lignocellulosic raw materials in an integrated chemo-catalytic biorefinery

The discussion in the previous sections has highlighted some of the sustainability criteria to consider in evaluating the different routes in transforming biomass not in competition with food (2nd generation processes). The field of energy is so complex and pervasive that it should be avoided to indicate that one route is definitively preferred over the others, also because this decision depends on so many aspects that differ from case to case. As a matter of fact, all the routes schematically outlined in Fig. 6 are currently investigated by different companies [16,28]. For example: (i) Amyris and LS9 the microbial processing, (ii) Virent the liquid phase processing, (iii) Choren/Shell the BTL, (iv) Sapphire and ExxonMobil the algael fuel, and (v) Envergent and KioR the pyrolysis. There are more companies developing these and some other alternative routes, for example based on the direct biofuel production by genetic engineering of micro-organisms [48].

Nevertheless, it is useful to shortly comment the alternative routes previously discussed, with reference to the specific situation in Europe, where the marginal lands for an intensive cultivation of energy crops are limited, and where the political sensitivity to the issue of GHG emissions is high. For Europe, the use of waste residues from agro-food production, in order to realize agro-energy districts preserving agriculture, is one of the preferable choices, due to the politics of subsidies previously shortly discussed. The technology to produce biofuels should be thus flexible to adapt to a large variety of raw lignocellulosic biomass, but at the same time efficient on a small-medium scale to avoid transport from long distances, and storage of large volumes of biomass with related problems of odors and VOC. Producing bio-oils by fast pyrolysis, and then transporting these bio-oils to a central gasification unit is one possibility, but energy-intensive, because the bio-oils must be stabilized for transport. The oxygen content of the bio-oil is high (in the 14–17% range). It is thus necessary to have, together with the fast pyrolysis unit, a hydrodeoxygenation (HDO) unit, i.e. a catalytic selective high pressure hydrogenation unit not easy to realize in a distributed model. New alternative technologies for producing bio-oil from biomass, based for example on hot-compressed or supercritical water [49], are interesting, although their commercial development has still to be verified. Licella Energy Resources (www.licella.com) has developed a Super Critical Water (SCW) reactor technology for converting biomass, able to produce a bio-oil with low oxygen content (7–9%) which should be thus stable. They have planned the passage from pilot to the first demo plant.

These bio-oils, however, are very complex in composition and cannot be adapted to an integrated production of chemicals and fuels, one important element for the future sustainability, as commented before. Also the gasification of biomass to produce syngas has similar problems. A development in this area is the short-contact time catalytic gasification of biomass [50] to produce syngas. The gasification conducted over a catalyst bed combines the three reactions of thermal gasification, catalytic tar cleanup, and catalytic water–gas shift into a single, small reactor. Therefore, this technology allows to realize small and efficient gasifiers for biomass, which could be integrated with recent development in microreactor technology for FT synthesis [51] to develop compact systems to produce even at the farmer level fuels from biomass. However, there are still a number of problems to solve, from the poisoning of the catalyst by the inorganic components, to the purification of the syngas, to the energy-effectiveness of the system. It is thus a challenging possible option for the future. Also in this case, this solution is not suited for an integrated chemical-energy production. Although syngas could be transformed to methanol/dimethylether or FT products by established routes, and then these products could be further converted to chemicals, in practical this is not feasible at an agro-energy district level.

The best route from this perspective is thus the selective deconstruction of the components of lignocellulose to obtain suitable platform molecules which can be the converted to either chemicals or fuels. It is useful to briefly recall some aspects of the lignocellulose and of its conversion before to discuss these aspects,.

Lignocellulose is the key structural element of the plants and is found in roots, stalks and leaves. It is composed of three major components: cellulose (38–50%), lignin (15–30%), and hemicellulose (23–32%). Cellulose is a linear polymer of glucose linked by β-1,4 bonds. It is similar to starch, which is a polymer of glucose linked by α-1,4 bonds, but the minor different type of bonding causes a major difference in the reactivity, For example, for the same enzyme loading, amylase hydrolyses starch about 100 times faster than cellulose hydrolyses cellulose. In fact, the hydrogen bonds between adjacent cellulose polymers determine a crystalline structure giving the structural strength to the plants, but making them particularly difficult to attack by enzymes.

Lignin is a polymer of phenyl propane units linked primarily by ether bonds and acts as glue for cellulose. A plant can be visualized as a fiberglass. The cellulose is like the glass fibers with the lignin serving as the epoxy resin. Hemicellulose is a highly branched polymer composed primarily of five-carbon sugars (mostly xylose). It is chemically bonded to lignin and serves as an interface between the lignin and cellulose. Hemicellulose is randomly acetylated, which reduces its enzymatic reactivity.

Due to these characteristics, there are several aspects which influence the rate of deconstruction of lignocellulose by bio- or chemo-catalysts [52,53]:

- *Content of lignin*: Due to the close interaction with cellulose microfibrils, lignin prevents enzyme access to the carbohydrate fraction of biomass. Therefore, it is necessary a physical or chemical treatment able to remove or alter the lignin. In enzymatic hydrolysis, it is necessary to reduce lignin content below at least about 12%.
- *Content of hemicellulose*: Hemicellulose and lignin are covalently linked and therefore acid hydrolysis of hemicellulose can open biomass structure. A hemicellulose removal higher than about 50% is necessary to significantly increase cellulose rate of enzymatic conversion.
- *Degree of cellulose crystallinity and polymerization*: In general, a higher degree of crystallinity reduces the rate of enzymatic attack, as well the rate of acid hydrolysis. Acidic pretreatments hydrolyze cellulose internally to create reactive ends, whereas alkaline pretreatments tend to protect internal cellulose bonds. A pretreatment making internal reactive ends increases the rate of enzyme (cellulose) attack. Some enzymes that convert cellulose into sugars (endocellulases) cleave internal cellulose bonds, thereby creating reactive ends that can be attacked by other enzymes (exocellulases).

Other important parameters are the surface area and porosity (physical pretreatments often change these aspects) and the acetyl content. In hemicellulose, approximately 70% of the xylan is randomly acetylated (CH_3COO-), which sterically hinders enzymatic attack. Other non-structural components of plant tissues, including compounds that are extractable with solvents such as phenols, tannins, fats and sterols, water-soluble compounds such as sugars and starch, as well as proteins and ashes, usually represent less than 5% of the dry weight. These can be a good resource for added-value chemicals in an integrated biorefinery.

In nature, a battery of enzymes (hydrolytic and oxidative) produced by a variety of fungi and bacteria work in synergy to perform lignocellulose degradation [54]. Fungi are able to degrade cellulose and hemicellulose and lignin in decaying plants by a complex set of excreted hydrolytic and oxidative enzymes, while the filamentous bacteria of the genus Streptomyces, among others, are able to degrade lignocellulose found in soil and composts also via the activity of excreted cellulases, hemicellulases and peroxidases. These bacterial enzymes, contrary to the biocatalysts produced by fungi, are more stable towards temperature and are able to perform in an alkaline pH.

However, the rate is too low for industrial processes and thus other types of pretreatments are required. The goal of pretreatment is to alter the physical features and chemical composition of the lignocelluloses to make its reactivity and solubility as well. The different pretreatment have a different effectiveness on the above parameters, i.e. on (i) removing or altering lignin, (ii) removing hemicellulose, (iii) decrystallizing cellulose, (iv) removing acetyl groups from hemicellulose, (v) reducing the degree of polymerization in cellulose and (vi) expanding the structure to increase pore volume and internal surface area. Typically, a combination of physical and chemical pretreatment is required. Process and operative conditions have to be typically optimized to avoid the formation of byproducts such as weak acids, furan derivates and phenolics which inhibit the later fermentation processes, leading to lower yields and productivities. This is a main relevant difference between the biological and chemo-catalytic routes in lignocellulose conversion. In the latter, it may be operate the first step of lignocellulose conversion under harsh conditions making faster and less costly the process, but which cannot be applied when a subsequent fermentation process is present.

Some of the common pretreatment technologies are the following:

- *Acid hydrolysis*: This is the oldest known method. Acid hydrolysis can be divided in two general approaches, based on concentrated acid/low temperature, or dilute acid/high temperature. Concentrated acid-based processes are not more typically used, being expensive, causing significant operational problems related to corrosion and high salt content after neutralization, and being environmentally not acceptable. Dilute sulphuric acid process (acid concentration 0.5–1.5%, temperature 120–180 °C, residence time 5–30 min, pressure 5–15 atm) is widely used industrially. Alternative acids could be also used. Compared to concentrated acid hydrolysis, this pretreatment generates lower degradation products as well much less corrosion problems in hydrolysis

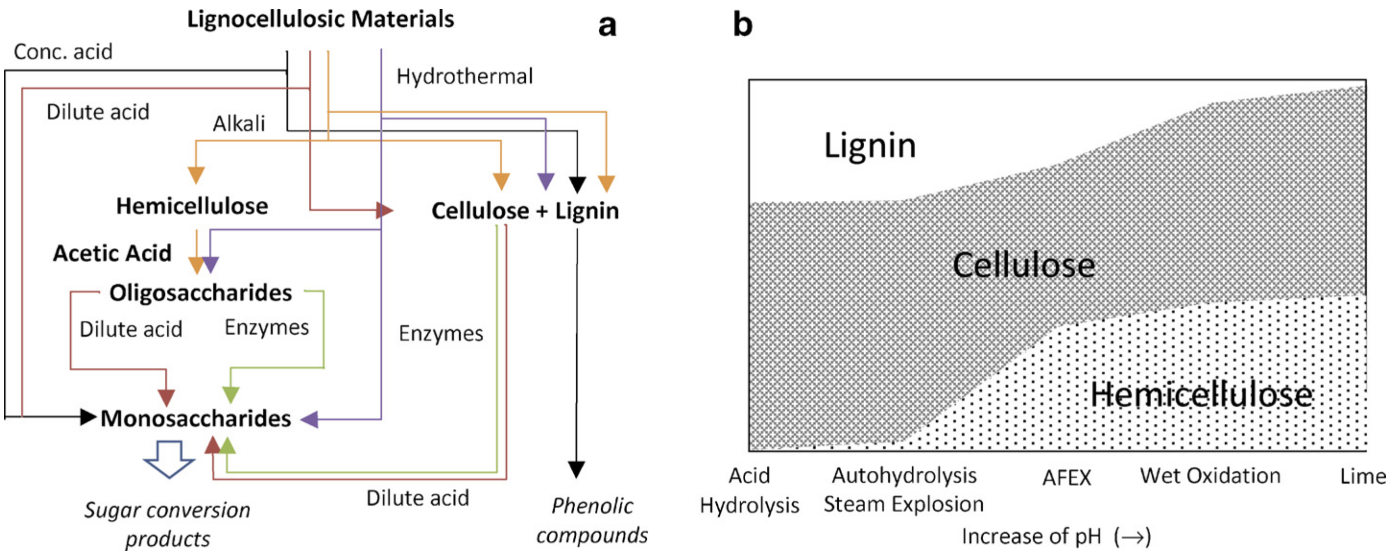

Fig. 7. (a) Main options for hydrolysis processes in biomass fractionation. (b) Typical polymeric solids composition after biomass pretreatment as a function of pH and pretreatment.
Adapted from Ref. [55].

tanks, pipes, etc. Addition of CO_2 to aqueous solutions forms carbonic acid as an alternative of acid addition.

- *Hydrothermal pretreatments*: There is a variety of technologies. The autohydrolysis is based on the fact that when biomass is heated in the presence of steam-saturated water, acids are generated. This removes some of the hemicellulose and alters the lignin structure, but the effectiveness is limited. Liquid hot water is similar to autohydrolysis, except that larger amounts of water are employed and the pressure is elevated to ensure that the water remains liquid. For temperatures below 100 °C, there is no hydrolytic effect on material, whereas above 220 °C some cellulose degradation takes place. Between 240 and 250°C, pyrolysis reactions become important. In relation with temperature, reaction time of hydrothermal treatments varies from seconds to hours. Steam explosion, an often used technology particularly for lignocellulosic ethanol, also belong to this category. When autohydrolysis is followed by rapid pressure release, the liquid water inside the biomass explosively vaporizes which shreds the biomass and increases surface area. This approach combines both chemical and physical pretreatments into one step.
- *Alkaline treatments*: Alkali pretreatment increases cellulose digestibility. Depending on catalyst used, alkaline pretreatments can be divided into two major groups: (i) pretreatments that use sodium, potassium, or calcium hydroxide; and (ii) pretreatments that use ammonia. Conversely to acid or hydrothermal processes, alkaline-based methods are more effective for lignin solubilization exhibiting only minor cellulose and hemicellulose solubilization. Lime is the least expensive alkali and allows to solubilize lignin plus some hemicellullose. For low-lignin biomass (12–18% lignin), simply boiling in saturated lime water is enough, but higher lignin contents require more severe conditions. Ammonia fiber explosion can be considered as a combination of steam explosion and alkaline pretreatments processes. In ammonia recycling percolation, aqueous ammonia is used in flow-through mode. Typical conditions are ammonia concentration of 10–15%, reaction time up to 90 min, and temperatures in the 140–170°C. Ammonia decrystallizes cellulose, rendering it more digestible.
- *Wet oxidation*: Lignocellulose is treated with water, oxygen and a base (typically sodium carbonate) at elevated temperatures and pressures, which selectively removes lignin and hemicellulose.
- *Alternative solvents*: Organic solvent (organosolv) approach is based on the use of organic solvents (e.g., ethanol or butanol) able to solubilize lignin. Self-generated acids can catalyze lignin degradation. Alternatively, acid or base catalysts can be added. Once the solvent is removed, the lignin precipitates and can be used for fuel or chemical purposes. Specific solvents able to selectively solubility cellulose (e.g., calcium thiocyanate, lithium perchlorate and cadoxen – a compound of cadmium and ethylene diamine) could be an alternative, but the process is costly. Ionic liquids (see later) also belong to this category. They are able to solubility both cellulose and lignin, depending on the composition, and the catalyst as well, but the recovery of the products is difficult. The use of supercritical carbon dioxide can be also considered in this class of pretreatment. When combined with a fast depressurization, an explosive pressure release fragments the biomass. It may be also combined with ionic liquids to improve the critical step of recovering the products.

In order to schematically summarize these different options, Fig. 7a shows a simple representation of most commonly used processes and their main effects on lignocellulosic material. Fig. 7b shows instead a cartoon of typical polymeric composition after pretreatment biomass as a function of pH characteristic of each pretreatment [55]. Generally, low pH pretreatments tend to solubilize hemicellulose and render it in oligomeric form, conversely to alkaline pretreatments that selectively solubilize lignin.

The pretreatment is the most costly part in producing ethanol from lignocellulosic sources. Table 1 shows the trend in process-

Table 1
Breakdown of processing costs for ethanol production from corn stover in 2005 US$. Numbers in parentheses indicate % of the total cost.

Process	2005	2009	2012
Pretreatment	0.44 (27%)	0.31 (22%)	0.25 (30%)
Enzymes	0.32 (20%)	0.33 (24%)	0.10 (12%)
Saccharification and Fermentation	0.31 (19%)	0.27 (20%)	0.10 (12%)
Distillation	0.18 (11%)	0.17 (13%)	0.15 (18%)
Balance of plant	0.34 (21%)	0.27 (20%)	0.22 (27%)
All processing	1.59	1.35	0.82

Adapted from Ref. [56].

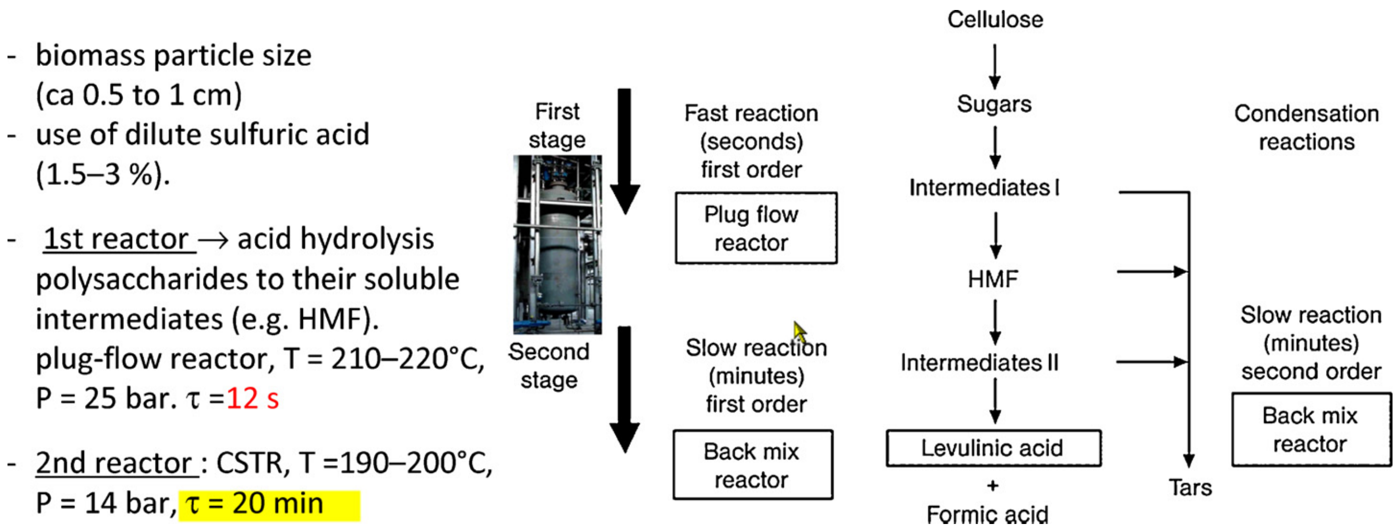
- biomass particle size (ca 0.5 to 1 cm)
- use of dilute sulfuric acid (1.5–3 %).
- 1st reactor → acid hydrolysis polysaccharides to their soluble intermediates (e.g. HMF). plug-flow reactor, T = 210–220°C, P = 25 bar. τ =12 s
- 2nd reactor : CSTR, T =190–200°C, P = 14 bar, τ = 20 min

Fig. 8. Chemical conversion of cellulose to levulinic acid, formic acid, and tars in the two Biofine process reactors, with indication of the reaction conditions. Adapted from Ref. [57].

ing costs of ethanol from corn stover based on US DoE analysis [56].

While development in enzyme and yeast biotechnology in recent years has reduced the cost of enzyme and fermentation cost for biofuel production, and advanced membrane technology will probably reduce in the next decade the cost of separating weak ethanol from fermentation broth, the cost of pretreatment will remain a major issue which is not expected to decline in the foreseeable future (Table 1). In fact, the application of process intensification technologies is not effective in this case, for the drawback of avoiding the further conversion of the monosaccharides to furfurals and acids (see later) which inhibit the fermentation. On the contrary, the chemo-catalytic routes will base their processing scheme on these compounds and thus allows operating more effectively the critical step of lignocellulose conversion to the key intermediates (platform molecules). Dilute acid pretreatment developed is still the dominant process for biomass pretreatment today [52].

An interesting example of commercial use of dilute acid pretreatment applied to the production of chemicals from biomass is the Biofine process [57]. The process uses dilute sulphuric acid in a two-reactor system to form levulinic acid (and formic acid) from hexoses and furfural from pentoses (Fig. 8). The levulinic acid (LA) yields are 70–80% of the theoretical maximum of 71.6% by mass of cellulose, i.e. about 50% of the mass of 6-carbon sugars (typically 35–45% of the biomass) to LA with 20% being converted to formic acid and 30% giving rise to residual “char” material. Various type of biomass can be processes, such as agricultural residues, paper sludge, and the organic fraction of municipal waste. A 50 tons per day commercial facility is operative in Caserta, Italy using a mixed lignocellulosic feedstock: waste paper, municipal wastes and agricultural residues.

The first step in the reaction to form the intermediate hydroxymethylfurfural (HMF) from hexoses and furfural from the pentoses is significantly much faster than the second step which requires much longer contact times (12 s in the first step and 20 min in the second step, although operates at slightly lower temperature (190–200 °C vs. 210–220 °C in the first step). As commented before, these reaction conditions are somewhat a combination between diluted acid hydrolysis and hydrothermal treatment. This temperature range is close to the limit where cellulose degradation takes place as well as side reactions of formation of heavier products become relevant. Operations below 200 °C would be thus preferable, perhaps using a different catalyst than diluted sulphuric acid.

The Biofine process indicates that intensification of the process in the pretreatment step is possible. When the reaction time is in the order of seconds instead of hours such as most of the other pretreatment technologies, fixed bed continuous operations are possible. In Biofine process, a fixed bed reactor is used in the first step, while a slurry discontinuous reactor for the second step due to the longer reaction times. Short contact times thus allow using reactors that are more compact, to decrease the fixed and operative costs, and safer operations. However, due to the higher temperature, the monosaccharides undergo a further dehydration forming furfurals (HMF from hexoses and furfural from pentose). Further slow conversion of HMF gives rise to LA and formic acid. These are valuable products which can be further converted to fuels and chemicals, but the direct conversion of furfurals appears also interesting, because can simplify the reaction steps [58].

Cellulose is hydrolysed in water by attack by the electrophilic hydrogen atoms of the H_2O molecule on the glycosidic oxygen. This is a very slow reaction because of the resistance of the cellulose to hydrolysis. However, this could be overcome using the appropriate catalyst, but cellulose has a crystalline structure (a highly ordered and tightly packed fibrillar architecture of the cellulose microfibrils) that resists to penetration of water [59]. The main motivation of the use of high temperatures (and consequently pressure) in the acid hydrolysis of lignocellulose is thus to overcome this resistance to penetration. On the other hand, solid catalysts have a poor contact with the solid, and thus their effectiveness is essentially dependent on the rate of cellulose dissolution (in water on the average is few % at 150 °C and around 30% at 190 °C, although it is depending on the type of cellulose and eventual pretreatments; often ball milling is use for this reason), and contact with the catalyst.

As an example, Fig. 9 reports the performances of a series of acid catalysts in static conditions in autoclave at 150 °C. Solid acids such as resins (Amberlyst 15), zeolites(Beta and Mordenite) or acid oxides (sulphated zirconia deposited over a mesoporous SBA-15 material) have around half of the activity with respect to diluted sulphuric acid, but in all cases the amount of solubilized products (mainly oligomers of glucose and glucose) is low. At higher temperature (190 °C) and under mixing instead of static conditions, the cellulose conversion is higher, but the rate remains low for practical

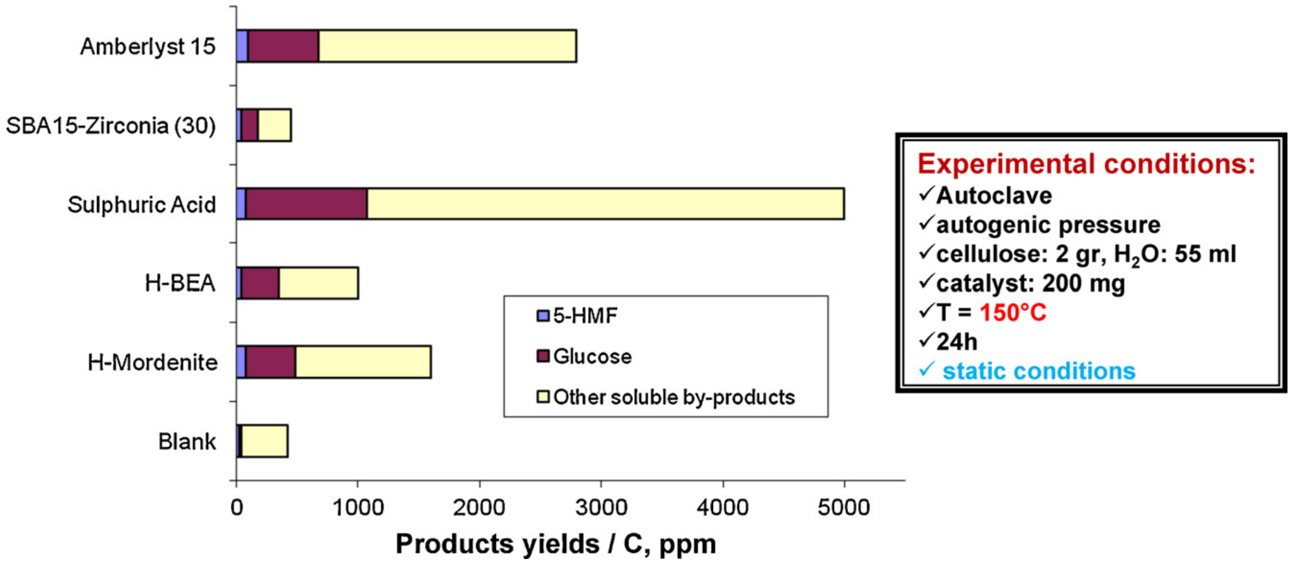

Fig. 9. Products yields in the hydrolysis of crystalline cellulose in water using different acid catalysts.

uses. Using acid materials having an improved contact with the cellulose the performances improve. Suganuma et al. [60] reported for example that SO_3H-bearing amorphous carbon, prepared by partial carbonization of cellulose followed by sulphonation in fuming H_2SO_4, has significantly higher high catalytic activity for the hydrolysis of β-1,4 glycosidic bonds in both cellobiose and crystalline cellulose. They reported that at 100 °C a full conversion of cellulose is obtained with this catalyst, while in the same conditions other acid catalysts (niobic acid, Nafion® NR-50, and Amberlyst-15) have nearly zero conversion and concentrated sulphuric acid is also less active. However, they use a catalyst to cellulose ratio of 12, which is thus unsuitable from the industrial point of view. These data however confirm that the main problem in cellulose hydrolysis is to realize a suitable contact between the catalyst and the β-1,4 glycosidic bond to hydrolize.

Due to these characteristics, the solvent able to dissolve cellulose are polar organic solvents such as DMF, DMAc, DMI or DMSO which could be further promoted with charged compounds such as $[NBu_4][F]$ or LiCl. Ionic liquids (IL) possess good ability to dissolve cellulose and even lignin [61,62]. The first report of dissolution of cellulose in an “IL” dates back from a US patent filed in 1934 [61]. Nevertheless, large R&D interest was raised from the first report that IL containing $CrCl_3$ show high activity at low temperature in the conversion of sugars to HMF. Using a mixture of $CrCl_3$ and $CuCl_2$ and 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl) as ionic liquid it is also possible to obtain a cumulative yield of about 65% in the cellulose conversion at 120 °C (about 38% yield glucose, 13% cellobiose, and 10% HMF, plus minor of other compounds) [63]. Although it is claimed that it is possible by extraction to recover the products, the recover in not full. In addition, the performances strongly depend on the purity of the IL, and thus likely using real lignocellulosic biomass (which contains inorganic elements in traces), the IL cannot be recycled without complex and costly purifications. Depolymerization/hydrolysis of cellulose over solid acids (Amberlyst, Nafion, alumina, sulphonatedzircona, zeolithes) have been also demonstrated to be possible [64]. There are thus various interesting aspects in the use of IL + metal chlorides for lignocellulose conversion, but there are also several question marks about their real applicability: (i) economics of the process, (ii) recovery of the products and (iii) elimination of inorganic byproducts, (iv) stability of operations, (v) eco-impact (IL itself, use of chromium, possible formation of chlorinate compounds).

The interesting aspect is the possibility to selectively form HMF. From fructose, glucose and cellulose 92%, 81% and 54% of HMF could be obtained, respectively, under mild conditions (100–140 °C, 2–5 h of contact time) [65]. The HMF, or furfural from pentose, can be further converted along different possible routes. Even if a mixture of sugars (and small oligomers, such as cellobiose) and these furfurals (furfural and HMF) is obtained, it is possible to separate the products due to their different characteristics and then process separately the sugars for example along the known fermentation routes and the furfurals and other byproducts along a different chemo-catalytic route. It may be thus possible to suggest the simplified scheme reported in Fig. 10 for a chemo-catalytic biorefinery.

The catalytic depolimerization/hydrolysis of lignocellulose converts the cellulose and hemicellulose to small oligomers and sugars, together with furfurals, while lignine is separate from the mixture. Due to the different chemical composition of lignine, it is preferable to process it separately to obtain phenol derivatives, or eventually to use as source of the energy need in the process. Part of the small oligomers can be converted to biofuels or chemicals by selective catalytic hydrodeoxygenation and the C5–C6 sugars are also valuable raw materials itself to produce plastics, levoglucosan, lactic acid, 1,4 butanediol, propanediol and methyl ethyl ketone, 3-hydroxypropionic acid, alkyd resin, itaconic acid, glucaric acid, etc. All these routes are actually explored by various companies in the world (for example, Genomatica, Cargill, Novozyme, Procter & Gamble, Itaconix, Rivertop Renewables, DuPont, BioAmber).

The fermentation of the sugars along the known routes gives ethanol or other alcohols. The company Gevo (in joint venture with Cargil), for examples, uses a genetically alters *Escherichia coli* to produce several higher-chain alcohols from glucose, including isobutanol, 1-butanol, 2-methyl-1-butanol, and 2-phenylethanol. They could be used as biofuels either directly (with respect to ethanol, isobutanol is less volatile and corrosive, does not readily absorb water, and has an octane rating similar to gasoline) or by further conversion to produce biodiesel or jet fuel (see later). In alternative, they are an interesting raw material for chemical products. Isobutanol is the feedstock in the manufacture of isobutyl acetate, which is used in the production of lacquer and similar coatings, and in the food industry as a flavouring agent. Isobutyl esters such as diisobutyl phthalate (DIBP) are used as plasticizer agents in plastics, rubbers, and other dispersions. Isobutanol is a widely used

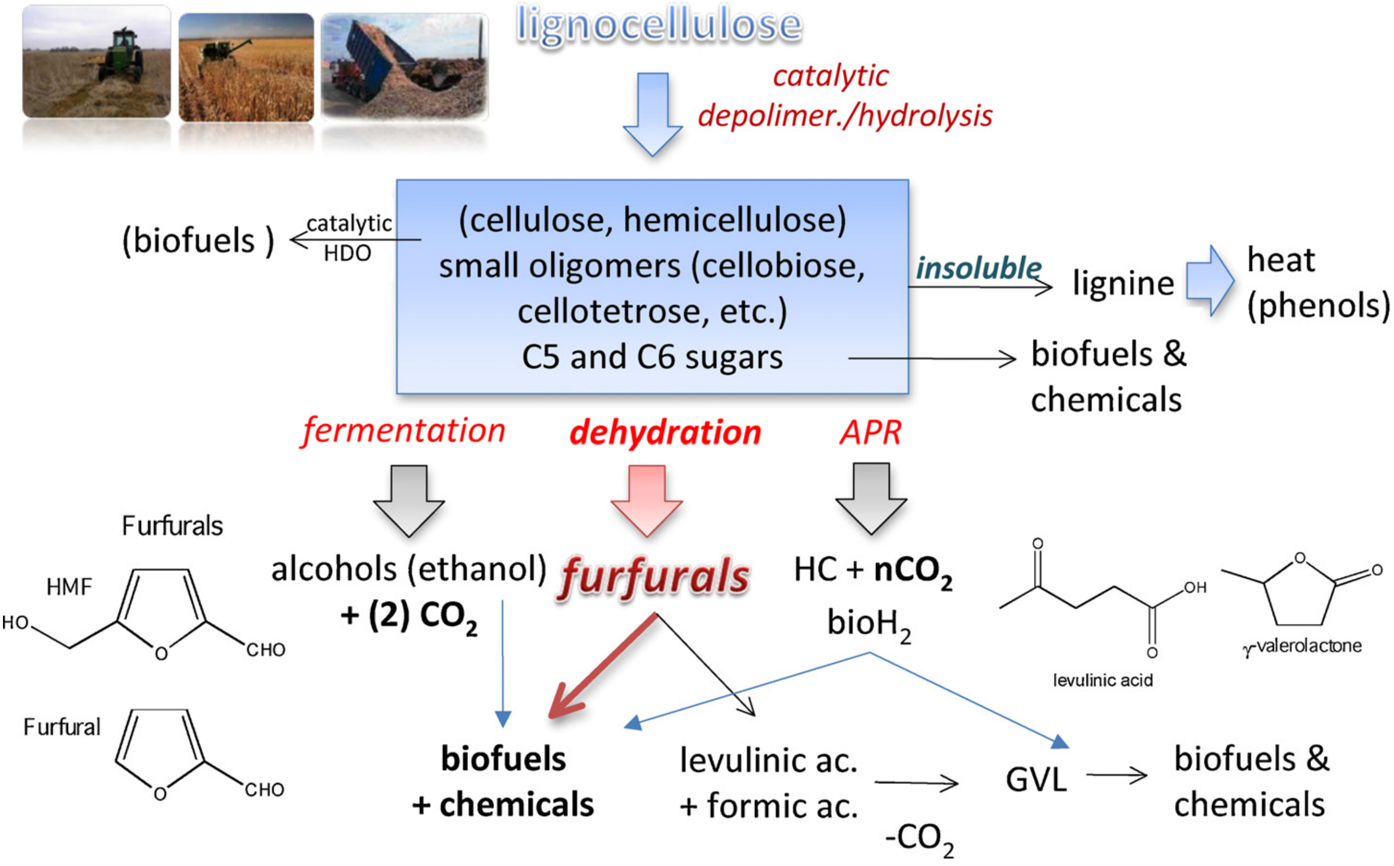

Fig. 10. Lignocellulosic paths: the possible scheme for a chemo-catalytic biorefinery.

paint solvent and varnish remover, and to prepare inks, and so on [66].

Part of the sugars can be also converted to hydrocarbons following the aqueous phase reforming (APR) shortly discussed before, or adapted to produce bio-hydrogen which is needed in various of the steps of upgrading furfurals (see later). Virent Energy Systems is developing the APR process both for hydrocarbons and bio-H_2. A recent study has shown the economic viability of producing hydrogen from biomass using fermentation combined with APR [67].

The furfurals fraction can be instead upgraded along the possible routes outlined in Fig. 11. Before to comment in a more detail these routes, it is useful to highlight that the general reaction scheme outlined in Fig. 10, although apparently complex, has a great flexibility in terms of output to better adapt to market requests, producing different biofuels or biofuel additives, monomers for polymers and intermediates for chemistry. It is based in most of the steps on catalytic technologies which can be intensified and able to realize on small-medium scale efficient processes in continuous mode. One of the key aspects is the need of cost-effective separation of the mixture produce by depolymerization/hydrolysis. There are many advances in the membrane and membrane distillation field indicating that soon this technology could be successful applied to the energy-effective separation of this type of complex mixtures [68,69]. For example, Weng et al. [70] showed recently how nanofiltration could be successfully applied for the separation of the hydrolyzates obtained from dilute acid hydrolysis of rice straw, and in particular the separation of sugars, furans and carboxylic acids.

HMF can be further converted to LA and formic acid, and then LA further converted to biofuels and chemicals, some of which possibilities are summarized in Fig. 11. LA is a valuable platform chemical showing two reactive functional groups that allow various synthetic transformations [57,71]. LA can react as both a carboxylic acid and a ketone. Some of the possible uses are the following:

- To produce diphenolic acid [4,4-bis-(4′-hydroxyphenyl) pentanoic acid] by the reaction of LA with two molecules of phenol. It may be a direct replacement for bisphenol A (BPA) in polycarbonates, epoxy resins, polyarylates and other polymers.
- Oxidation of levulinic acid can lead to the production of succinic acid. Succinic acid can be used to produce tetrahydrofuran (THF), 1,4 butanediol, and gamma butyrolactone (GBL). The latter is used as a chemical intermediate in the manufacture of the pyrrolidone solvents. It can be used in the production of pesticides, herbicides and plant growth regulators.
- The reaction of LA with methanol and Br2 leads (in a multisteps process) to the synthesis of δ-aminolevulinic acid (DALA), an active ingredient in herbicides.
- The dehydration of LA leads to the formation of angelicalactone which reductions form methyltetrahydrofuran (MTHF). MTHF is an interesting blending agent for gasoline, although the research octane number - RON of 87 is not optimal. In “P-Series” fuels, MTHF acts as co-solvent for ethyl alcohol (high-octane) in “pentanes-plus” hydrocarbons obtained from natural gas. MTHF is also an excellent solvent.
- The catalytic hydrogenation of LA leads to γ-valerolactone (GVL). Horváth et al. [72,73] evidence that GVL possess interesting properties for its use as biofuel component and intermediate for chemical. It has low melting (−31 °C), high boiling (207 °C) and high RON of 121.With respect to ethanol, GVL does not form an azeotrope with water. Homogeneous ruthenium catalyst [for example, $Ru(acac)_3/PBu_3/NH_4PF_6$] can be used to hydrogenate LA

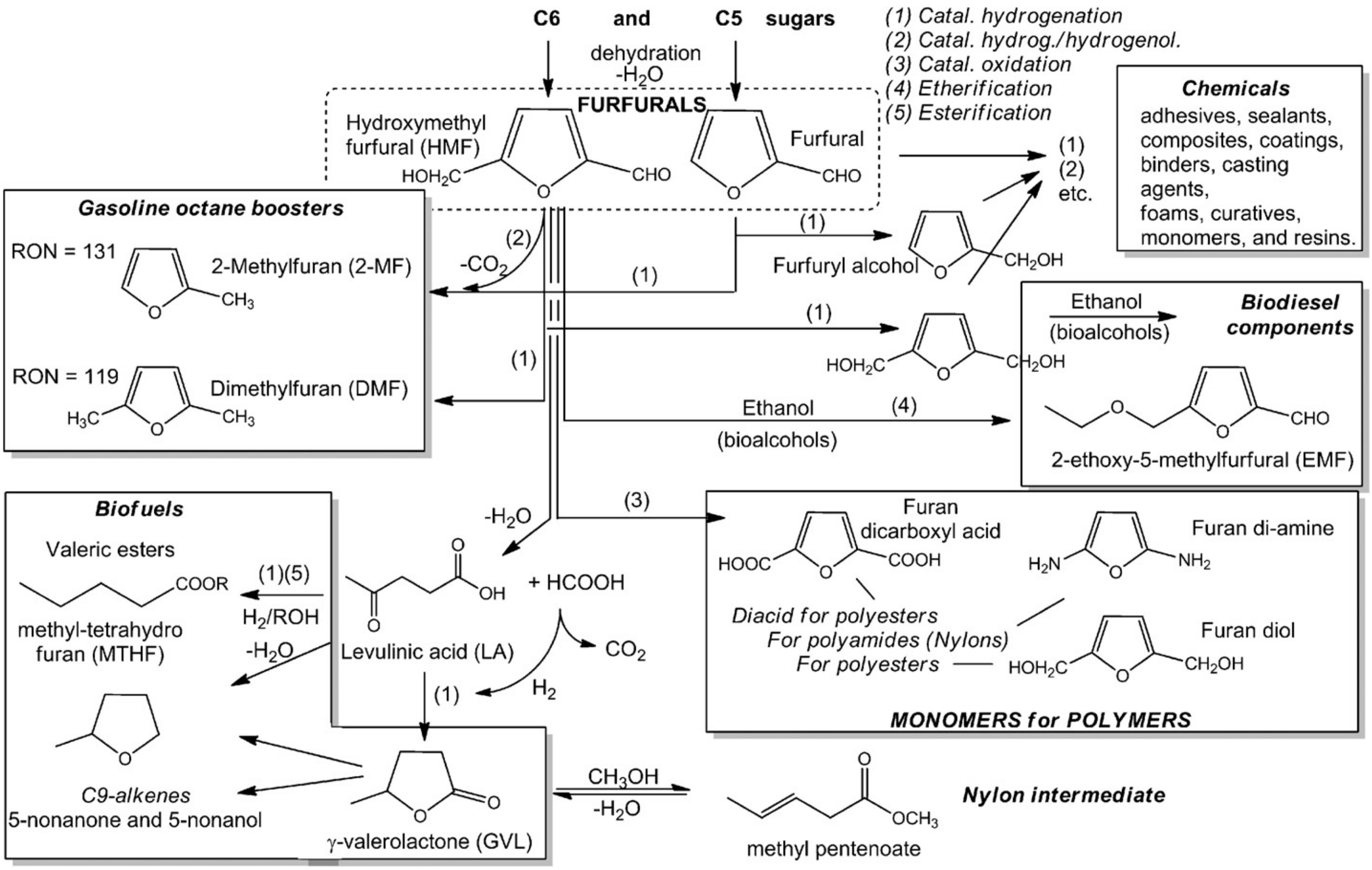

Fig. 11. Selection of the possible reaction pathways in the conversion of furfurals to biofuels and chemicals in a chemo-catalytic biorefinery.

to GVL [73,74], or preferably using heterogeneous catalysts such as Ru/C [75].

- Dumesic et al. [76] indicated that GVL and MTHF suffer from low energy density and have limited applicability for use as jet or diesel fuels. They thus suggested that would be preferable to upgrade GVL to liquid hydrocarbon fuels. The ring-opening and hydrogenation of GVL over a Pd/niobia catalyst produces pentanoic acid, which is subsequently converted via ketonization to 5-nonanone over niobia and/or a ceria–zirconia catalyst [77]. This C9 ketone can then undergo successive hydrogenation and dehydration to produce a mixture of linear C9 alkenes (nonenes), which can be hydrogenated to produce n-nonane for use in diesel fuel. It is also possible to achieve good yields of alkenes in the range of C18–C27 from oligomerization of C9 alkenes. These C18–C27 compounds are in the molecular weight range suitable for jet and diesel fuel applications [76]. Palkovits [78] recently highlighted the value chain based on pentenoic acid obtained by hydrogenation of LA to GVL and subsequent ring opening catalyzed by solid acids (Fig. 12).

Using solid acid such as SiO_2/Al_2O_3, it is possible to convert GVL to an isomeric mixture of pentenoic acids, which are subsequently decarboxylated to n-butenes and an equimolar amount of CO_2 [79]. Both transformations are catalyzed and can be integrated in a single fixed-bed reactor. At 375 °C and 36 bar it is possible to have a complete conversion of a concentrated GVL feed (60%) with a 93% yield of butene. Using Amberlyst-70 it is possible to obtain 77% yield of C8+ alkenes at 170 °C and 17 bar pressure.

The alternative route was developed by Lange [80]. It is based on the use of alkyl-valerate esters as potential biofuels. Hydrogenation of GVL to valeric acid (VA) and its subsequent acid-catalyzed esterification with alcohols leads to alkyl (mono/di)valerate esters. Gasoline blended with 10 and 20% of ethyl valerate (EV) largely comply with the European gasoline specification (EN 228). When compared to the base gasoline, the EV blends shows a favorable increase in octane number (RON and MON) without deterioration of properties such as corrosion and gum formation. EV blending increased the gasoline density and oxygen-content, reduced its volatility (lower RVP and lower E70–E120 numbers) and lowered its content of aromatics, olefins and sulphur. Pt supported on TiO_2 or ZrO_2 are the most suitable catalysts which give 95% selectivity in the LA conversion to GVL (200 °C, 40 bar H_2 pressure). The one-step transformation of GVL to VA is catalyzed by bifunctional catalysts with acid and hydrogenation functions. Over a Pt/ZSM-5 catalyst, the selectivity reaches 90% at 250 °C and 10 bar H_2. The ethyl esters are obtained with >95% selectivity over acidic ion-exchange resins. One-step conversion of GVL into pentylvalerate is possible, but selectivities are in the 20–50% range.

GVL can be also converted to methyl pentenoate (a promising Nylon intermediate) under catalytic distillation conditions [81].

In integration with the LA route, the direct use of furfurals as platform molecules appears interesting for the various possible products: (i) both gasoline and diesel high octane and cetane additives, respectively, (ii) monomers for various polymers and (iii) chemicals for added-value products (Fig. 11). Avantium Furanics is actively involved in the exploitation of this route (indicated as furanics). The advantage of this route is that less steps and more intensified reaction conditions are requested with respect to LA and GVL route, as briefly commented in the case of Biofine process. In addition, less H_2 is necessary and thus lower CO_2 emissions

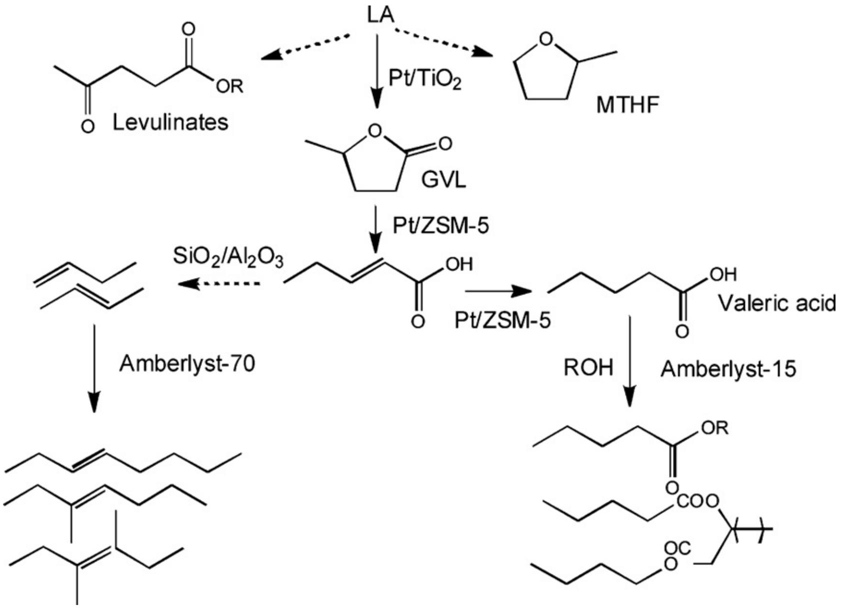

Fig. 12. Potential pathways to biofuels starting from levulinic acid, with a focus on pentenoic acid as a potential platform.
Adapted from Ref. [78].

and higher C-efficiency. Furfurals show higher chemical functionality and reactivity with respect to LA and GVL, and it is thus easier their catalytic upgrading to a variety of added-value products, as well as their conversion to monomers for various type of polymers (Fig. 11).

The catalytic hydrogenation/hydrogenolysis of HMF and furfurals leads to 2,5-dimethylfuran (DMF) and 2-methylfuran (2-MF) both showing high octane number (particularly the latter, see Fig. 11), limited oxygen, content sufficient boiling point (93 °C and 62 °C, respectively) and good miscibility with gasoline. The etherification of HMF with bioethanol leads to 5-(ethoxymethyl)furan-2-carbaldehyde (EMF) which can be obtained with 100% selectivity by tuning the acid-properties of the catalyst [82]. The catalytic hydrogenation of aldehyde groups in HMF and furfural leads to the corresponding alcohols (furfuryl alcohol from furfural, for example) which can be also be etherified with alcohols to produce biodiesel components, or are value intermediates in chemical synthesis (as foundry resins, adhesives, and wetting agents). The energy density of these biodiesel compounds is well comparable with that of fossil fuels, and higher than that of ethanol. The energy density (kWh l^{-1}) of EMF is 8.7, and thus equivalent to gasoline (8.8), although lower than diesel fuel (9.7) and higher than ethanol (6.1) [83].

There is thus a very active research in the valorization of furfurals as platform molecules for biofuels and chemicals, although the preferable route has not been still clearly identified. However, it should be emphasized that it would be impossible to obtain very high selectivities and productivity (particularly in intensified processes) on a single platform molecule. It is thus preferable to develop an eco- and energy-efficient separation processes to separate the different compounds obtained from the chemo-catalytic depolymerization/hydrolysis of lignocellulose, and then use them along the various routes schematically outlined in Fig. 10. This would require, however, to have efficient catalytic processes able to operate on relatively small-scale sizes. On the other hand, this will guarantee a high flexibility in operations of the biorefinery, and its sustainability as well. We believe that these are the necessary characteristics for the future in this field.

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