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### Citation for published version:

Sanna, A 2014, 'Advanced Biofuels from Thermochemical Processing of Sustainable Biomass in Europe', *Bioenergy Research*, vol. 7, no. 1, pp. 36-47. <https://doi.org/10.1007/s12155-013-9378-4>

### Digital Object Identifier (DOI):

[10.1007/s12155-013-9378-4](https://doi.org/10.1007/s12155-013-9378-4)

### Link:

[Link to publication record in Heriot-Watt Research Portal](#)

### Document Version:

Early version, also known as pre-print

### Published In:

Bioenergy Research

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# Advanced bio-fuels from thermo-chemical processing of sustainable biomass in Europe

**Aimaro Sanna**<sup>a\*</sup>

<sup>a</sup> Centre for Innovation in Carbon Capture and Storage (CICCS), School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh, EH14 4AS, UK

**Corresponding author:** Aimaro Sanna, School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh, EH14 4AS, UK. Tel: +44(0)1314513299, [A.Sanna@hw.ac.uk](mailto:A.Sanna@hw.ac.uk)

## Abstract

Bio-fuels can play an important role in decreasing the use of fossil fuels, in particular in the transport sector, which absorbs about 30% of the EU energy requirements. This review illustrates the motivations behind bio-fuels development, the government incentives and regulations and the current approaches on sustainable biomass conversion in Europe, and provides an overview on the major steps involved in thermo-chemical processes and on the issues challenging their deployment at large scale, with particular emphasis on the pyrolysis of biomass and bio-oil upgrading using conventional oil refinery settings. Distribution of sustainable bio-fuels in Europe and future prospects towards achieving success of transport bio-fuels were also addressed. The literature suggests that importing bio-fuels and increasing the cost of CO<sub>2</sub> to at least € 60/tCO<sub>2</sub> will be necessary to meet the renewable obligation targets in the EU. Algae represent the future feedstock for bio-fuels but currently are limited by their high production costs and high N content. Pyrolysis is cost competitive compared to other technologies such as fermentation and gasification, but the quality of bio-oils requires upgrading mainly to lower its oxygen content and enhance its thermal stability. The recent advances in bio-oil upgrading using catalytic cracking and hydro-treating are very promising for the future deployment advanced bio-fuels in the coming decades. However, significant investments in applied research and demonstration are still required to meet the 2020/2030 bio-fuels targets.

**Keywords:** Biomass, pyrolysis, bio-oil, bio-fuels

## 1. Introduction

Bio-fuels derived from local biomass and biomass waste materials offer the prospective to reduce the dependence on fossil fuels, help to mitigate the global warming issue, address the fuel security issues and at the same time favour the growth of a sustainable economy and related jobs [1]. As a result, there has been a strong drive towards bio-fuels, such as bio-derived liquids that can be processed into existing refinery settings, especially in Europe.

The energy sector is one of the most important in the European economy and will become of increasing strategic importance in the near future because of its vitality for its competitiveness and energy security. Although new oil reserves have been discovered, in the medium-to long term there will be several factors affecting the supply of energy, such as geopolitical instability, increased costs of extracting unconventional reserves and finally, long term reserves shortage [2-3]. Under these conditions, the energy security issue is becoming central to the European policy to

guarantee stable fuels price in the long term. Europe has to face in the coming years a dramatic dependency of petrol and gas import from foreign countries and at the same time, the crude-oil price is \$100 or more per barrel [4-7]. Moreover, high levels of greenhouse gases emissions due to the massive fossil fuels usage is linked to the global climate change. In response to these driving forces, the Kyoto protocol and the “new Copenhagen accord” set compulsory emission limits for the reduction of greenhouse gases. Therefore, the EU goal for 2020 is to reduce the CO<sub>2</sub> emissions to 20% below the 1990 level [2]. Biomass is becoming a strategic source of renewable energy and commodity chemicals due to the necessity to substitute fossil fuels with carbon neutral energy sources. However, the complex structure of biomass currently represents a substantial technology barrier for the conversion of biomass into bio-fuels and chemicals. Bio- and Thermo-route approaches are currently investigated to address the “recalcitrance” of biomass [8-10]. Moreover, existing crude oil refinery settings may represent the best platform to upgrade intermediate liquids produced by the conversion of biomasses at a large scale [1,6].

This paper illustrates the perspective of producing bio-fuels for the transport sector in Europe using thermo-chemical processes towards the integration of biomass in existing crude-oil facilities. The objectives are to examine the current state of technological development with emphasis on bio-oils upgrading, evaluate and compare the different conversion techniques and identify the future challenges and perspectives towards 2<sup>nd</sup> and 3<sup>rd</sup> generation bio-fuels. The review starts with the driving forces and motivations behind the need for bio-fuels, continues with an overview of the development of biorefineries and sustainable biomasses, government incentives, regulations and bio-fuels potential in Europe. Then, a description of the technologies involved on the production of 2<sup>nd</sup> generation bio-fuels and an analysis of the potential production of advanced bio-fuels in Europe is provided. Finally, the conversion of densified biomass by catalytic cracking, hydro-processing and constraints to be overcome are discussed.

## **2. Motivation for Sustainable Bio-fuels Development**

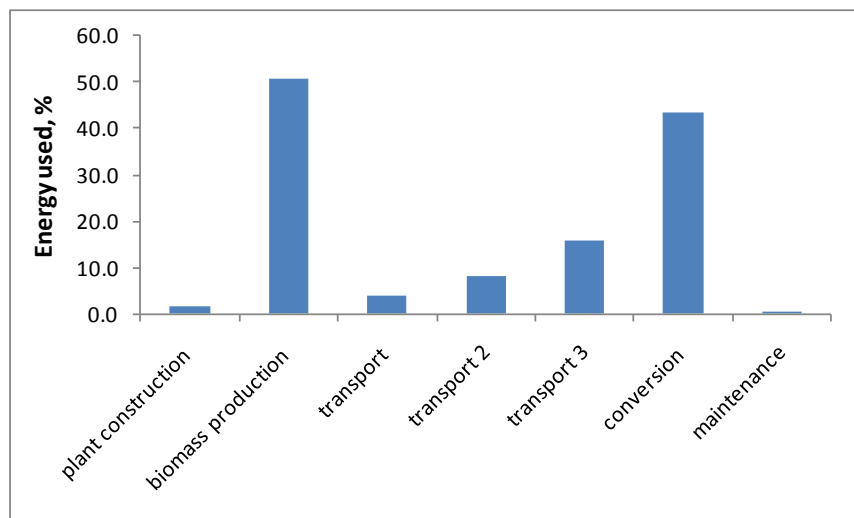
Sustainability is intended as the capacity to satisfy the necessity of the present without compromise the capacity to satisfy the needs of the future generations [11-12]. Advances have been made in R&D on biomass cultivation and conversion technologies in order to promote the use of sustainable bio-fuels, which represent a significant opportunity in terms of development and

jobs in rural areas. For example, marginal or degraded lands not adapt to grow food crops can be used to grow energy crops helping reducing the dramatic problem of land erosion and restoring degraded soils [13-14]. Change in land use primarily affects Greenhouse Gases (GHG) emissions due to carbon stocks variation. For instance, temperate energy crops (e.g. wheat and rapeseed) present lower GHG emissions (from direct and indirect land uses) than diesel/gasoline emissions when grown in arable land, while emissions increase about 20% if they are grown on converted pasture [15]. Similarly, tropical energy crops (e.g. palm oil plantation) show emission much higher than fossil fuels if grown on tropical rainforest soils, while emissions are lower than fossil fuels if grown in degraded soils [15].

Bio-fuels, which are among the range of renewable resources currently being investigated for the production of sustainable energy in the EU [16], are the most suitable to substitute crude oil as a transport fuel. However, it is estimated that the production costs of bio-fuels still are 2-3 times higher than that of petroleum fuels. Cost of the feedstock, conversion efficiency, the scale of the process and the value of the products are among the factors that influence the cost of the biomass technology [16-17]. Therefore, the transition to a bio-refinery economy would involve large investments due to the different properties of the feedstocks and may take several decades. Costs of bio-fuels production vary as a function of the location and the type of products and greatly affect their final costs. To evaluate the energy involved to transform biomass into bio-fuels, the cultivation of plants including use of fertilizers, fuels for machines and water through the harvest steps, transport from the field to a temporary stock and to the processing place, storage, drying and crushing of biomass, and finally the conversion into transportable fuel have to be taken into account. Of great relevance is the feedstock cost, which accounts for 75-80% of bio-diesel production and about 65% for bio-ethanol production [17].

The distribution of the energy used through a bio-refinery system (Figure 1) highlights that the production of biomass is one of the most important energy consuming steps together with the biomass conversion, including biomass crushing and drying, absorbing about 50% and 43%, of the energy in the integrated biomass gasification cycle taken as example, respectively. Also, the transport of biomass gives an important contribution on energy consumption with the value ranging from 4% to 16%. In terms of costs, it was assessed that the production of a dry metric tonne of biomass with a transportation distance of 60 km can ranges from €47 to €72 (the

exchange rate used to convert the \$ in € throughout the article was 0.747€//\$ ,18/06/13), with low price associated to corn stover and high price related to switchgrass, where the key parameter for estimating transport costs was the number of round trips/day a truck could make rather than the distance covered [18]. The possibility to reduce transport costs by producing bio-oil from wood chips and miscanthus near to the crops and transporting the bio-oil to a central plant was investigated and it was found that this would only be cost effective (max 30% reduction) for large generation plants (20 PJ/year) [19].



**Figure 1** LCA of an integrated biomass gasification cycle [20]. Also, transport of biomass from different works is reported for comparison. Transport-2 typical % of energy used for transport biomass in a bio-energy system referred to the final energy delivered [21]; Transport-3 energy used in transport during pellets production [22].

If the biomass is transformed into a liquid intermediate with properties similar to those of crude-oil close to the production site, it would be possible to transport the densified biomass to an oil refinery and co-process it with oil, thus decreasing the overall costs of the final bio-fuels.

### 3. Bio-fuels and Bio-refineries development

It has been suggested that biomass can be converted into a range of bio-products, bio-fuels and bio-chemicals at an integrated bio-refinery to maximize the value of the biomass, taking as example the pulp and paper industry [23-24]. Currently, biomass is mainly used for power generation, such as co-firing with coal and also to produce biodiesel and bioethanol in Phase I biorefineries; representing about two-thirds of renewable energy consumption in Europe [25]. Phase I biorefineries process vegetable oil, grains, using conventional technologies (e.g.

esterification plant using plant oils). Therefore, these 'primitive' biorefineries do not possess the flexibility needed to face future changes of products required in the market and also, do not own the essential capacity to accommodate the diversity of biomass feedstocks. Phase II biorefineries can process lignocellulosic materials (e.g. non-food crops, wheat straw, wood) using advanced technologies such as bio-Fischer-Tropsch-diesel. Finally, Phase III biorefineries are flexible both on feedstocks (e.g. non-food materials, algae) and end products (e.g. fuels, chemicals, materials) using a range of different technologies. The 1<sup>st</sup> example of a non-food and lignocellulosic biorefinery in the world is the Chemopolis platform in Finland, which produces a wide range of products (cellulosic bioethanol, glucose, lignin, acetic acid, fertilizer, furfural, wood pulp etc) using an integrated set of processes (Cooking, Washing, Bleaching, Hydrolysis, Fermentation, Evaporation, Distillation, Drying) [26]. However, these advanced biorefineries characterized by a number of new technologies necessitate the building of new facilities and are expensive in comparison to traditional fossil-fuels settings [24]. Therefore, integrating biomass conversion into existing oil refineries may be the most viable option to produce liquid bio-fuels and bio-chemicals from renewable resource.

First generation biomasses are edible feedstock from the agricultural sector such as corn, wheat, sugarcane, and rapeseed and can be divided in function of their products: starch (corn, wheat, barley, sorghum), sugar (sugarcane) and oil (rapeseed, canola, palm, soybean) [27]. The main advantage of these feedstocks is the fact that they are harvested in large quantities as animal and human feed, but they consistently affect food prices and are considered not sustainable. The main feedstock for the production of bio-fuels in the EU is represented by 1<sup>st</sup> generation crops such as rapeseed for bio-diesel and wheat and barley grains for bioethanol production, which will dominate the market up to 2020 [28]. Nevertheless, in the long-term, it is suggested that 2<sup>nd</sup> gen. bio-fuels (lignocellulosic materials, residues) and 3<sup>rd</sup> generation biomasses (algae) will represent the main feedstock for bio-fuel production, with a forecasted share close to 75% by 2050 by the IEA [28]. These advanced bio-fuels avoid the food vs fuel competition. 2<sup>nd</sup> generation feedstocks such corn stover, wheat straw, rice hulls, cane bagasse and energy crops (miscanthus, willow, poplars, eucalyptus) are far more versatile than conventional energy crops since they can be cultivated in a much wider range of soils, present fast growth rates and high tolerance to environmental stresses. It has been forecast that 44-53 million hectares of cultivated land could be

used for bio-energy feedstock production by 2030 in EU with available land mostly in Eastern Europe [29]. Also, about 250Mt agricultural residues may be available for bio-fuel production, which is comparable to feedstock plantations of some 15–20 million hectares (taking into account that ~ 40 tonnes per hectare of lignocellulosic residues are produced and underutilized each year and assuming 50% of it used for bio-fuels) [27,29].

Finally, 3<sup>rd</sup> gen. biomass is represented by algae. Microalgae use solar energy, water and CO<sub>2</sub> to produce biomass as the higher plants, but present efficiency 30 times higher than plants in terms of mass produced per unit of land [30]. Their main advantages are the non-competition with food crops, since they can be grown in degraded lands (e.g. abandoned industrial sites), they do not require herbicides or pesticides and can produce a wide range of products (e.g. methanol/methane, proteins for animal feed, pharmaceutical products). However, the conversion processes investigated so far are more expensive compared to other biomass resources [30]. The main environmental advantages of 2<sup>nd</sup> and 3<sup>rd</sup> gen. biomasses compared to conventional energy crops are presented in Table 1, where the GHG emissions are also reported.

**Table 1.** Environmental impact of different biomasses to bio-fuels [modified from 30].

	<b>Corn</b>	<b>Sugar cane</b>	<b>Soybeans</b>	<b>Rapeseed</b>	<b>Switch grass</b>	<b>Wood residue</b>	<b>Algae</b>
<b>Water</b>	high	high	high	high	med-low	low	med
<b>Fertilizer</b>	high	high	med	med	low	low	low
<b>Pesticide</b>	high	med	med	med	low	low	low
<b>Food competition</b>	high	high	high	high	med-low	med-low	low
<b>Energy</b>	high	med	med-low	med-low	low	low	high
<b>GHG emissions * (kg CO<sub>2</sub>/MJ)</b>	81-85	4-12	49	37	-24	n/a	-183

\*GHG fossil fuels (kg CO<sub>2</sub>/MJ): Gasoline 94, Diesel 83

Large investments in R&D are needed to provide effective solutions for logistic, technology and economic issues for the success of 2<sup>nd</sup> and 3<sup>rd</sup> generation biorefineries. Also, innovative feedstocks (e.g. algae, microorganisms) require a larger time horizon (e.g. after 2030) to become competitive [31-33].

#### **4. Bio-fuels towards the reduction of CO<sub>2</sub> emissions in Europe**

Renewable energy sources contribute for a small fraction (~8%) to the EU overall gross inland energy consumption representing the 3<sup>rd</sup> largest global consumer with 15%, after the USA (19.5%) and China (16.4%) [34]. Moreover, the EU imports about 53% of the energy requirements and is

expected to import even more reaching 70% by 2020 [35]. The potential of bio-energy in Europe is summarised in Table 2. Forestry & forestry residue and agricultural & organic residues could supply ~8 EJ by 2020, with their contribute expected to decrease in the following decades due to uses competition (e.g. animal feed). Instead, energy crops are expected to be the larger suppliers of bio-energy at about 20 EJ by 2020, with land available for energy crops in the European Union (EU27) to be close to 100Mha [36].

**Table 2.** Summary of bio-energy potential at EU27 [36].

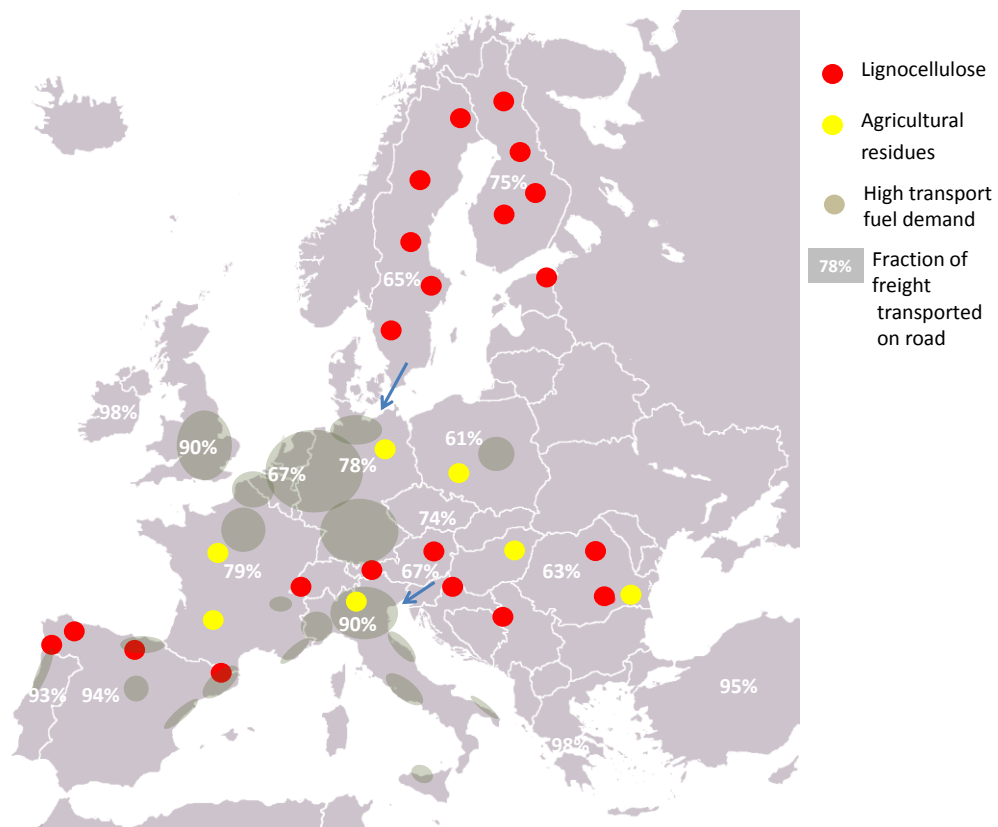
<b>Europe</b>	<b>EJ/y</b>		
	<b>2020</b>	<b>2030</b>	<b>&gt; 2050</b>
Energy Crops	0.5-14.7	2.18.4	15.4-19.9
Forestry & Forestry residues	0.8-4.2	1.6-3.7	1.7-2.2
Agricultural residues & organic wastes	1.5-4.4	1.1-3.1	0.7
<b>Total</b>	<b>2.8-23.3</b>	<b>4.8-25.2</b>	<b>17.8-22.2</b>

The EU-27 consumed about 90 EJ of energy in 2012 (15% of 600 EJ) of which about 33% (30 EJ) was required by the transport sector, with some of the countries such as the UK (38%) and Spain (42%) consuming an higher share of energy in transport and some others less than EU average (Germany 30% and Poland 24%) [34, 37]. The transport sector represents the natural target for the bio-fuels and it has been estimated that about 1/3<sup>rd</sup> of energy required by the transport sector in the EU-27 by 2030 could be produced in EU without being in competition with food crops [25], as can be seen in Table 2. However, currently less than 4.7% of the transport sector's energy in EU consists of renewable energy, which is lower than the obligation set for 2010 (5.75%) indicating that is it unlikely that the 2020 target will be met [38]. Also, the statistics clearly indicate that import of bio-fuels will be required to meet the fixed targets.

The reduction of fossil CO<sub>2</sub> emissions is the main motivations behind policies and targets promoting a transition towards bio-fuels in the transport sector, followed by oil price and energy security issues [38]. Interestingly, a recent study indicates that a CO<sub>2</sub> cost about €60/t CO<sub>2</sub> would be required to generate 3% of 2<sup>nd</sup> generation bio-fuels to meet the 10% bio-fuels obligation target by 2020 without interfere with other goals (e.g. 20% greenhouse gases emissions reductions by 2020) [38-40]. However, the carbon prices are stable below €10/t CO<sub>2</sub> in 2012, supporting the idea that a strong policy support is now required to facilitate the success of bio-fuels (renewable in



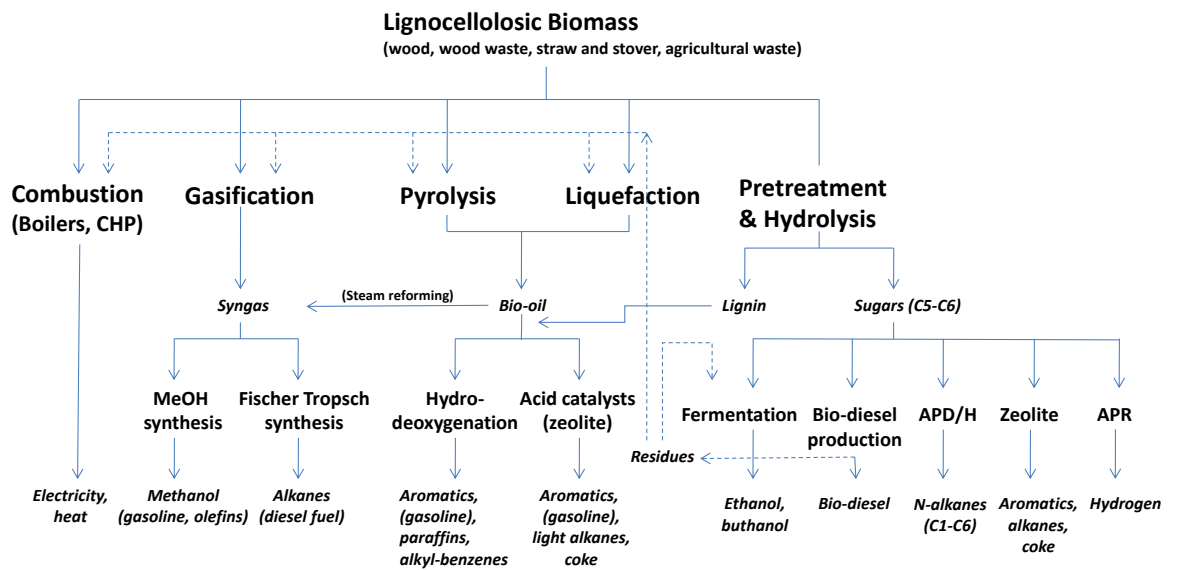
general) in 2020-2030, otherwise unlikely to happen in the required scale [3]. The analysis of the potential bio-fuels productions from lignocellulose and agriculture wastes (Figure 2) in the various European geographical areas found that North Europe (excluding UK and Ireland), Austria, the Atlantic coast of Spain, France, Germany and East Europe can become the key 2<sup>nd</sup> generation fuels production area due to high feedstock availability and demand for co-produced heat [38]. Also, Figure 2 shows that most of the goods are transported over the road network, with Germany (by far), France, UK, Italy and Spain being the countries with the highest freight volumes [41]. The lignocellulosic biomass produced in Scandinavia can be transported to Holland, Belgium and North Germany to cover the high demand of fuels in those areas, without losing its environmental benefits if modern carriers are used [21].



**Figure 2** Potential biomass for bio-fuels production in Europe and larger areas for transport fuel demand [38, 41].

## 5. Biomass conversion technologies comparison

The commercial development and deployment of bio-fuel technologies will require significant progress in a number of areas to overcome the technological and cost barriers they currently face. Figure 3 shows the technologies currently available for biomass conversion. Overall, there are two main routes to convert 2<sup>nd</sup> generation biomasses into bio-fuels: the biochemical and the thermo-chemical pathways. Both routes, which are under continuous development present a biomass/bio-fuel conversion of ~35% and remain unproven at the fully commercial scale [42].



**Figure 3** Current and future strategies to produce fuels and energy from biomass [adapted from 60].

Unlike the thermo-chemical route, biochemical conversions require a pre-treatment stage (physical, thermo-chemical, biological pretreatment) to reduce the polymeric degree and enhance the accessibility to cellulases. The pretreatment is followed by enzymatic or acidic hydrolysis of hemicellulose/cellulose to monomeric free sugars (saccharification) subsequent to biological fermentation where sugars are fermented into ethanol and then purified via distillation [43]. Hydrolysis in presence of acids is common, but it leads to dehydration reactions with formation of undesired products such as aldehydes. This has driven the development of enzymatic hydrolysis using enzymes such as *Trichoderma reesei*, which are deactivated by presence of lignin and result expensive in comparison to the former hydrolysis method [44]. Therefore, the development of pre-treatments able to remove lignin, are fundamental for the success of the biochemical route to ethanol. Genetic engineering has been investigated to modify the conventional yeast's capability

to ferment all sugars simultaneously and combine the hydrolysis and fermentation in one single vessel [43]. However, since this process requires high temperature, thermophilic anaerobic bacteria and yeasts such as *T. saccharolyticum* and *Thermoanaerobacter ethanolicus* are being developed for their potential to utilize a wide range of feedstocks at temperatures above 65°C. For example, companies such as DuPont Danisco Cellulosic Ethanol and Butalco prefer this approach for their higher alcohol tolerance and yield [43].

The undergoing development to reduce the costs of the biochemical conversion of cellulosic feedstock are centred on improving the pre-treatment processes, the efficacy of enzymes and the overall process integration [42]. However, lignocellulosic material (including residues from bioethanol and biodiesel production) thermo-chemical conversion is still preferred [45]. Present thermo-chemical conversion technologies include: (I) combustion, (II) gasification, (III) pyrolysis and (IV) liquefaction.

Combustion is an exothermic reaction between a fuel and an oxidant; it is already used in processes such as co-firing with coal reducing the emissions of greenhouse gases compared to using fossil fuels alone. Due to the difference in biomass and coal properties, co-firing is generally limited to about 20 wt% biomass [46]. Co-firing 10% biomass in a power plant trial indicated that the plant performance can be managed by the plant's control system. Also, co-firing showed emissions higher in particulate rich in carbon (> 200µm) and CO [47].

Gasification, which has been strongly investigated in Europe, is a process used to produce a gas mixture called syngas at temperatures >800°C, which is rich in CO<sub>2</sub>, H<sub>2</sub>, CO, CH<sub>4</sub> and other impurities such as nitrogen, sulfur, alkali compounds and tars. Gasification is possible by using oxygen, air, steam or mixtures of these as the gasifying agent [48]. The syngas is clean from the impurities (particulates, tar, and sulphur content) and then converted in long chain liquid hydrocarbons by Fischer–Tropsch's (FT) synthesis using transition metal-based catalysts (mainly Co and Fe). Filters (ceramic or metal-based filters), sorbents and catalytic steam reforming are used in the gas cleaning step [48]. Gasification presents a series of technical and economic obstacles such as cost of hot-gas cleaning, micro-pollutants present in biomass, corrosion and fouling in hot gas heat exchangers, tendency of ash for sintering and tar removal issue. In particular, cracking-tar tends to condense into downstream equipment. Novel catalysts have been also proposed to reduce the tars and coke formation. For example, nickel cerium modified olivine

resulted in significant improvement in carbon- and hydrogen based yields and substantial reduction in tars and char [49]. Increased production on hydrogen (~50%) and reduced coke deposition was found during gasification in presence of novel bi-functional Ni–Mg–Al–CaO catalyst [50].

In order to enhance the production of bio-fuels from gasification, the process integration and optimisation tools will play a primary role. Both the materials and heat streams can be integrated to improve the economic viability of the overall process. For example, the waxy material remaining from the FT synthesis can be recovered by hydrocracking in presence of Pt, Pd or bimetallic catalysts into gasoline, kerosene and other liquid fuels enhancing the quality of the final liquid bio-fuels [48]. Also, the tar is being exploited as a separate feedstock to produce value-added chemicals by bio-fuel companies such as Choren and Ensyn [42]. Recently, a promising one-stage production of high purity hydrogen (99% pure, 90 yield%) from lignocellulosic biomass by sorption enhanced catalytic steam gasification in presence of Pd/Co–Ni catalyst has been reported [51]. The single step was obtained by combining the gasification/steam reforming, water-gas shift and H<sub>2</sub> separation by CO<sub>2</sub> capture steps.

An alternative for the production of bio-fuels from biomass may be its densification into a liquid hydrocarbon with characteristics similar to those of petroleum towards its further upgrading into a crude-oil refinery. Pyrolysis is the thermal decomposition of organic substances in an oxygen free atmosphere and it is a well-established technique for the production of a liquid called bio-oil [53]. Pre-treatments such as hydrolysis have been also employed to enhance the pyrolysis conversion [54]. Bio-oil contains 25-75% of the starting biomass compounds depending on the conditions applied, but is instable due to the large oxygenates content and low in energy content [55]. Higher protein containing biomass seems to produce a less acidic and higher energy content bio-oil [56]. Bio-char is the solid by-product of biomass pyrolysis, which can be used with a broad field of industrial applications, including gasification, metallurgical applications and the chemical industry [55]. Several companies have been involved in fast pyrolysis technology developing different reactor types. The most used is the bubbling fluid bed with examples in Spain (200 kg/h pilot unit at Union Fenosa), the UK (250 kg/h pilot unit and Wellman and Biomass Engineering Ltd) and Finland (500 kg/h plant at Fortum). Currently, UPM and VTT are operating a 4MWth unit in Finland [57]. Instead, other companies have developed other reactors types such as circulating

beds (650 kg/h ENEL plant in Italy built by Ensyn) and ablative reactors (6t/day pilot unit at PyTec, Germany) [57].

Liquefaction involves solvent extraction at high pressure (120-200atm) at mild temperatures (300-400°C) with or without catalysts. This technique is able to remove higher amount of oxygen in comparison with fast pyrolysis, due to strong decarboxylation reactions and use of hydrogen. For example, hydrothermal liquefaction of swine manure produced 70% of oil and a solid fertiliser rich in nitrogen [58]. However, the high viscosity of liquefaction bio-oil, about 15000 cP at 61°C, limits its use without upgrading. Also, liquefaction presents capital and operational costs 15-20% higher than pyrolysis because it works at high pressures and generally has low efficiency [59].

Production of liquid fuel by fast pyrolysis presents economic advantage because this technology can be built on small scale and used directly where the biomass is generated. This allows smaller capital costs in comparison with biological technologies such as fermentation, which needs longer reaction time leading to higher capital costs and gasification followed by Fischer-Tropsch synthesis, which is uneconomic due to the large investment costs associated with its commercial application.

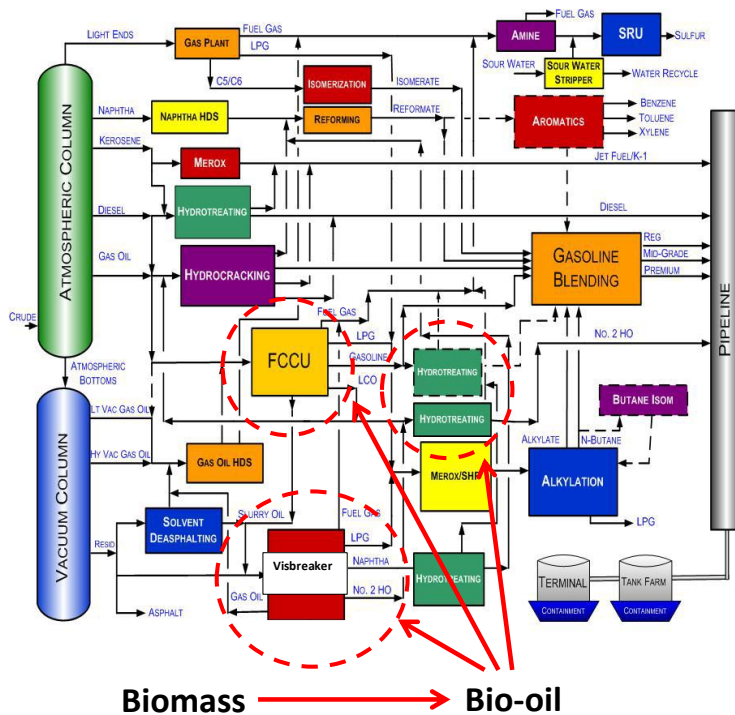
Capital and operating cost of three leading biomass conversion platforms such as 1) pyrolysis followed by hydroprocessing, 2) gasification followed by Fischer-Tropsch synthesis and hydroprocessing, and 3) biochemical conversions using dilute acid pre-treatment with simultaneous saccharification and co-fermentation were compared using corn stover as feedstock and a plant capacity of 2000 t/day. Pyrolysis was found to be the cheapest technology with lower capital costs (€ 149M) and biomass-to-liquid fuel plants are expected to produce fuels with a product value of € 0.40 per litre of gasoline equivalent, while bio-chemical products value resulted in € 1.08 per litre gasoline equivalent. Gasification presented the higher capital costs (€ 448M) [61]. Pyrolysis energy efficiency ranged from 77% (including char produced) to 54% (without char) while net efficiency was 42-52% for gasification and 44% for bio-chemical conversion [61].

A recent work compared several bio-oil production techno-economic assessments taking into account sales of bio-char, which is a co-product of pyrolysis and the electricity consumption of the pyrolysis plant and biomass pre-processing plants. The findings indicate that bio-oil production cost is comparable with those of mineral oils where woodchips and miscanthus are used in large plants (> 800t/day) [62]. This strengthens the idea that biomass pyrolysis is a promising technology

to convert biomass into a densified bio-oil. However, bio-oil needs to be upgraded to be mixable with crude oil based fuels, since its quality is poor.

### 6. Bio-oil upgrading using crude-oil refinery techniques

Crude oil settings can be used to reduce the tar and oxygen content of pyrolytic bio-oil, rendering its properties similar to those of petroleum derived fuels [63]. There are three general methods, as shown in Figure 4, based on crude-oil processing that can be used to convert low quality pyrolytic bio-oils namely: catalytic cracking, carbon-coke elimination and hydrogen addition. The first method is Visbreaking which is low in costs because it involves the formation of a low quality coke fraction that allows the production of high quality oil without the use of expensive external hydrogen.



**Figure 4** Crude oil refinery’s flow chart. Rounded in red is visible the visbreaking unit used to reduce the viscosity of vacuum distillation residues, in order to meet specification of heavy fuel oil. Visbreaking process is mostly applied in Europe while Coking is preferred in USA [99].

A list of activities in bio-oil upgrading is reported in Table 3, together with the type of upgrading and the catalyst used. A comprehensive list of the activities around the world is available in a recent work [57].

**Table 3.** Bio-oil upgrading activities in Europe, modified from [57].

Organisation	Upgrading method	Catalysts used	Ref.
University of Nottingham, UK	Thermotreatment		[70]
Groningen University, Netherlands	Hydroprocessing	Ru and homogeneous Ru	[100]
IRCELYON CNRS Université Lyon 1, France	Hydroprocessing	Ru on C	[89]
Technical U. of Munich, Germany	Hydroprocessing	Pd on C	[93]
U. Twente, Netherlands	Hydroprocessing	precious metals	[91]
U. Twente, Netherlands, IRCELYON, UMR-CNRS, France	Hydroprocessing	Ru on C	[98]
Aston U. UK	Catalytic cracking	ZSM-5	[57]
CPERI, Geece	Catalytic cracking	ReUSY catalysts with a Re <sub>2</sub> O <sub>3</sub>	[75]
CPERI, Geece, Sintef (Norway), Norwegian Uni. Sci. & Technol.	Catalytic cracking	Al-MCM-41, SBA-15	[77]
U. of the Basque Country, Spain	Catalytic cracking	H ZSM-5, Ni-HZSM-5	[101]
Groningen U. Netherlands	Reactive distillation and acid catalyst		[102]
Helsinki U. Technology, Finland		Zinc oxide	[103]
University of Nottingham, UK		Ni/olivine/serpentine	[78]

Catalytic cracking is widely used to convert the high-boiling, high-molecular weight hydrocarbon fractions of petroleum crude oils to more valuable gasoline, olefinic gases, and other products.

Finally, the 3<sup>rd</sup> method involves the consumption of external hydrogen to enhance the molar H/C ratio and it is able to upgrade the whole feedstock, but the costs are much higher. Visbreaking is becoming an attractive part of the refineries, since it improves operative margins challenges by high crude oil price and the depleting oil reserves. Visbreaking or thermal cracking is sometimes preferred in EU compared to catalytic cracking since the heavy oil residues contains high metals content and aromatic compounds such as asphaltene and resins that deactivate the catalyst [64-65]. Visbreaking under mild conditions (470-500 °C and low residence time of 1-3 minutes) enhances the viscosity of residues maximizing the yield of liquid hydrocarbons and minimises coke production. Low residence time and presence of additives such as H-donors (e.g. tetralin) avoids coke deposition [66-68]. This technology has been applied in laboratory scale to the bio-oil upgrading producing low volumes of bio-crude and solid bio-coke with properties similar to crude-oil and coal, respectively [69-70].

Direct catalytic deoxygenation during pyrolysis has been proposed since the beginning of the 80s [71]. The in-situ decarboxylation seems to be the most economically viable route since it does not involved the use of hydrogen and can be carried out using a relatively simple fluidised bed reactor [60]. Fluid catalytic cracking using acid zeolites radically affects the bio-oil characteristics, resulting in higher hydrocarbons content and less heavy oxygenated compounds compared to the thermal bio-oil. However, the deoxygenating reactions lead mainly to water, reducing the bio-oil caloric value [72]. Zeolites catalysts (predominantly ZSM-5) have been widely used to produce valuable aromatics that can be mixed with gasoline or used as building blocks for chemicals

production [73-74]. Other materials that have been investigated including catalytic cracking catalyst [75], aluminas [76] and mesoporous materials [77]. Also, minerals such as olivine previously considered for tar-removing in steam reforming of biomass syngas in gasification process have been recently investigated in catalytic pyrolysis of biomass [49,78-79].

In particular, several studies have been focusing on modifying zeolites as catalyst for converting both lignocelluloses and algae into fuels and chemicals. For example, addition of Ga to ZSM-5 increases the rate of aromatics production during CFP by enhancing the rate of decarbonylation and olefin aromatization. This suggests that more selective bifunctional catalysts represent a promising option to converting biomass into useable fuels [80]. Pore size narrowing in zeolite (ZSM-5) has been used to increase p-xylene selectivity in the products from biomass CFP, where the para selectivity increased from 32% to 96%. This opens a door to the inexpensive production of renewable p-xylene from biomass [81]. One of the main limits of zeolites is the fact that large oxygenates produced from pyrolysis cannot enter their pores and form coke on their surfaces, decreasing the hydrocarbon yield and deactivating the catalyst. Recently, a mixture of mesoporous, macroporous ( $\text{Gamma-Al}_2\text{O}_3$ , CaO and MCM-41) and microporous (LOSA-1) catalysts have been proposed to reduce this drawback [82]. The proposed catalysts cracked the large oxygenates into small oxygenates (macro/mesoporous fraction), while converted these latter into olefins and aromatics (microporous fraction). The aromatic + olefin yield was 40% higher compared to presence of only LOSA-1.

Since algae are considered as the ultimate biomass resource, numerous researchers are evaluating their catalytic pyrolysis. The major difference between lignocellulose and algae is their high content in proteins and virtual absent content in lignin. Recent studies suggest that algae-proteins are difficult to convert into aromatics with HZSM-5 [83-84]. Also, the fate of the nitrogen derived from the proteins depends to the pyrolysis temperature employed, with most N released as ammonia at 800°C or found in the biochar at 400-500°C [84].

Catalytic hydro-deoxygenation (HDO) is an important technique to decrease the oxygen in fuels derived from biomass or other non-conventional feedstock [85]. Traditionally, HDO has attracted minor attention in the oil industry, since oxygen level in crude-oils is rarely higher than 0.5 wt%. Usually, the oxygen content in the conventional fuels is very low, about 1-2wt%, while the pyrolytic oil produced from biomass presents 45-50 wt% of oxygen. The HDO mechanism



involves the reaction of bio-oil's oxygen with hydrogen to form water and saturated C-C bonds and generally, the energy needed to break the C-O bonds is higher for the aromatics than the aliphatic compounds [60]. Hydro-deoxygenation can be an important method to transform bio-oil into a more stable and high energy density feedstock that could be used to partially replace petroleum derivative feedstock. HDO of real feedstock has been successfully done in numerous studies and generally the oxygen level were decreased from 50-40 wt% to 1-9 wt% after two stages using NiMo, Ru, CoMo, NiWO, NiW-Al<sub>2</sub>O<sub>3</sub>, Pt-SiO<sub>2</sub>-AlO<sub>3</sub> and Ru/C catalysts [86-88]. The process conditions include temperature between 300-400°C, hydrogen pressure between 35 and 180 bar (1500-2600 psi) and space velocities (LHSVs) between 0.2 and 10 h<sup>-1</sup> [86]. However, in traditional HDO, the catalyst deactivation is high with the deposition of coke on the catalyst surface and limits its application. Recently, it has been demonstrated that partial deoxygenation of bio-oils is able to produce a product that present sufficient stability to be introduced in FCC and HDO units in crude-oil refineries [89-91]. At least two routes occurring in parallel in HDO, one involving decarboxylation (-CO<sub>2</sub>) and the other the HDO of carboxylic group to methyl group (-2H<sub>2</sub>O). The latter route requires the presence of at least six atoms of active surface hydrogen in the proximity of carboxylic group compared with one hydrogen atom consumed during decarboxylation. Therefore, the availability of active surface hydrogen may be crucial for the former route. Also, formation of CO confirmed the coexistence of decarboxylation and decarbonylation reactions [92]. Most of the HDO studies have been focused on lignocelluloses while hydro-processing of 3<sup>rd</sup> gen. biomass (algae), which is particularly challenging, has received little attention. This is due to its high nitrogen content (up to 10 wt%), which can deactivate conventional catalysts and noble metals based catalysts. Therefore, future work on HDO should focus on the development of entirely different catalysts able to maintain stability in the presence of basic reactants [92].

Aqueous Phase Process (APP) has also been suggested as a route to avoid hydrotreating problems, such as high level of coke that deactivates the catalysts sensitivity to sulphur and finally poisoning in the presence of small amount of water [93-95]. Hydrogenation of C-O bonds without breakage of C-O and C-C bonds at low temperature allows minimizing the formation of light gas species like methane [96]. APP produces alcohols, which can be used as precursors of chemicals (e.g. ethylene and propylene glycols) or further upgraded by catalytic cracking into gasoline cuts using

zeolites [90]. The polyalcohols produced during APP hydrogenation can be also deoxydehydrated by oxorhenium producing linear polyene products, possible feedstock for polymers and fuels [97]. Recently, it has been demonstrated that partial deoxygenation of bio-oils is able to produce a product that present sufficient stability to be introduced in FCC and HDT units in crude-oil refineries [91,98]. The co-processing of bio-oils from lignocellulosic biomass pyrolysis in small pilot-scale refining processes such as fluid catalytic cracking (FCC) and hydro-treating units it is technically viable and depends on the concentration of the bio-oils in the mixture [72]. Instead, hydro-treating in presence of conventional catalysts achieved very high de-oxygenation of the bio-oil (85 wt%) but was seriously limited by operating problems (e.g. plugging of the catalyst bed). The upgraded bio-oil was also separated by distillation in a light fraction (gasoline and diesel range compounds) and a heavy fraction with properties similar to that of vacuum gas oil [72]. The co-processing of up to 20% upgrade bio-oils with Vacuum Gas Oil (VGO) in large-scale units, such as Fluid Catalytic Cracking (FCC) or Hydro-Treating (HDT) has been proved without plugging the reactor and producing same level of coke (5%) of VGO [89,98]. Despite the fact that refining processes such as methanol synthesis, trans-esterification and Fischer-Tropsch are technically mature, other conversion processes and the integration of biomass using existing crude-oil technologies still need major investments in applied research and demonstration to overcome the technical bottlenecks by 2030 [3,33]. A commercial example of bio-fuels is the Neste Oil Corporation (formerly Fortum Oil) in Finland, which runs since 2007 a biomass to liquid technology NExBTL with capacity of 170,000 t/y. The plant processes vegetable oils into commercial bio-fuels (biodiesel). This process can be integrated with conventional petroleum refinery and employs proprietary catalysts that are stable in the presence of water [104]. Also UOP/Eni Ecofining process developed by Honeywell's UOP is commercialising green diesel and jet fuel produced from vegetable oils coming from a variety of biomasses, including algae. The multistage process catalytically converts and blends the biofeeds with petroleum feeds obtaining commercial fuels [105].

## **7. Concluding Remarks**

Advanced bio-fuels assessments indicate that between 3 and 25 EJ of energy could be produced in Europe in the next decades, which could represent 5-50% share of transport energy. At the current

state, bio-fuels from agricultural and forestry wastes are more economic compared to promising 3<sup>rd</sup> generation algae, while 1<sup>st</sup> generation bio-fuels, the most diffuse, present relevant sustainability issues that may limit their future expansion. Biomass does not present a homogeneous distribution among the EU, where the Scandinavian countries represent the main producer of lignocelluloses, while Germany, France and East Europe are rich in agriculture residues.

There is no agreement about the biomass conversion technologies that might emerge at an industrial scale over the next decades. However, it is likely that a range of different advanced technologies able to use wastes, biomass residues and 2<sup>nd</sup>/3<sup>rd</sup> generation biomasses will become established. Both biochemical and thermo-chemical conversion routes are being promoted around the world with the thermo-chemical option preferred in EU. Currently, there is not a clear advantage (in terms of commercial deployment) between the two pathways and both will be driven by the carbon price, which at the current level (€5-10/tCO<sub>2</sub>) is not supporting the diffusion of advanced bio-fuels. The biochemical route is currently limited by the high costs of the required pre-treatments, while the large success of gasification/Fischer-Tropsch route is limited by its high capital costs. Instead, the densification of biomass by liquefaction/pyrolysis and the further upgrading of the bio-liquids using well established technologies such as catalytic cracking and hydro-treating could represent the cheapest and most flexible option for the production of chemicals and advanced fuels. The development of more efficient catalysts is the key factor for the success of bio-fuels at global scale. In future, major work will need to focus on cracking and hydro-treating of algae feedstock, which received minor attention so far and present important challenges such as their high N content. Overall, there is still a lack of cost effective technologies to produce advanced bio-fuels from biomass feedstock in comparison with the well-established fossil fuels technologies.

### **Acknowledgements**

The author thanks the Centre for Innovation in Carbon Capture and Storage, Heriot-Watt University (EPSRC Grant No. EP/F012098/2).

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