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PERFORMANCE, COST AND MARKET PROSPECTS OF TECHNOLOGIES USED FOR THE PRODUCTION, TRANSFORMATION AND EFFICIENT USE OF BIOMETHANOL

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Abstract

Energy and, in particular, the clean energy, is an important scientific topic that needs special attention by the scientific community World-wide and, more so, in the context of the developing countries. Amongst different kind of renewable energy sources, bioenergy has to play an important role in the future energy supply scenario. It is in this context that ENEA, in the framework of a project financed by the Italian Ministry for the Economic Development, has focused its attention on the performance, costs and market prospects of technologies used for the production, transformation and final efficient use of bioenergy. The work is addressed basically to the energy experts, stakeholders and decision makers as well as consumers who have to make choices on energy technologies.
Keywords: Bioenergy, Biomethanol, Energy technologies for production of bioethanol from biomass, Technical-economic performance, Potential and barriers, Environmental impact of the use of biomass.

Introduction

Methanol is a basic product of the chemical industry, used in the production of other basic products, such as, formaldehyde, acetic acid, ethylene, propylene. From these latter, it is possible to obtain consumer products such as polymers, synthetic fibers, adhesives, paints and more. It is also used in the production of biodiesel, anti-knockers (MTBE, TAME), mixed with gasoline (M10, M15, M85), as a solvent and antifreeze. Research is currently focused on the use of methanol as fuel for road and sea transport, as such or in the form of dimethyl ether (DME).

There's been striking technical advance and now countries are waking up to the potential for a meaningful supply of methanol to meet transportation fuel mandates, or even to pursue green chemistry. Worldwide, over 90 methanol plants have a combined production capacity of about 110 million metric tons. Methanol is currently produced largely from natural gas (80%) and other fossil sources, but production from biomass (bio-methanol) is gaining increasing interest from sustainability point of view. Bio-methanol can be produced from virgin or residual biomass of an agricultural or industrial type (e.g. glycerol), but also from the CO_2 produced by the combustion of fossils [1-9]

The production of bioethanol from biomass is based on the gasification of the raw material from which a gas (syngas) is obtained comprising mainly of CO and hydrogen (H_2). After purification and enrichment in H_2, the syngas can be converted into bio-methanol. The hydrogen for enrichment can be obtained through water-shift processes of the syngas itself or from external inputs (e.g. electrolytic H_2). The first method has a limited overall efficiency whereas the latter one is associated with higher costs.

Bio-methanol, being in the constant increasing phase of production is around 200,000 t / y (250 million litres) produced mostly in the Netherlands. However, there is a strong planning to produce more than 1 Mt /year, over the next couple of years.

Italy with an overall methanol consumption of approx. 450-500 Kt / year (almost 90% produced from natural gas and imported from non-EU countries) is used in the production of formaldehyde (70%), acetic acid, MTBE and biodiesel.

Performance, current and expected costs

The technology used for the production of bio-methanol is still in the evolution stage where the technical-economic performance depends on the type of plant, process, raw material and eventual co-productions. Several studies available in the literature suggest that the production of bio-methanol, under appropriate hypotheses, can reduce GHG emissions by 25-40% compared to methanol from fossil sources. On the economic level, the most favorable conditions occur in the poly-generation plants, enhancing the co-products (other chemicals, heat, electricity), using industrial organic waste available locally or gasification plants using mixed feed, e.g. biogas / natural gas or biomass / coal with significant potential and considerable interest as an intermediate stage towards more and more sustainable productions of bioethanol.

Currently, the production cost of methanol from natural gas is between € 100 and € 200 / t whereas, as reported in the literature, the cost/t for bio-methanol production is nearly 1.5 to 4 times higher, varying in the range of € 160 to € 940 from wood residues that, in fact, fall short to 200-500 € / t in case of residues of other processes. The most expensive process (€ 500-900 / t) is the one that uses CO_2 as raw material. Many of the projects in progress or in the start-up phase make use of industrial residues (e.g. glycerol) that offer process economies, wood waste and urban waste. The conversion of CO_2 into methanol can be convenient for niche productions, when low-cost electricity is available that reduces the cost of producing hydrogen from electrolysis.

Potential and barriers

The development of bio-methanol production on the commercial scale is for the moment limited by both the high production and investment costs. Better prospects can be expected from development of the gasification processes and their economies evolution in view of their constant increasing demand. Bio-methanol is currently used for the production of biodiesel, but there are prospects for its use in mixtures with gasoline (M10, M15, M85) to reduce emissions in the road transport, as well as in maritime transportation to reduce the sulfur content of the fuels (Directive (EU) 2016/802, May 2016), and for the use of pure methanol in vehicles with fuel cells. In perspective, the (bio) methanol has also been proposed as an alternative energy carrier to hydrogen (Methanol Economy) with respect to which it offers ease of use, transport, storage and distribution. The economic competitiveness of bio-methanol also depends on the prices of natural gas (from which methanol is produced today), the cost attributed to $_{CO2}$ emissions associated to the environmental and social impacts of fossils, and, hence to the economic value attributed to the reduction of emissions (carbon credits). This accounting, already introduced in the energy policies for biofuels, though partly, has not yet been adopted for basic chemicals.

Technologies and market aspects

Methanol is an important basic product for the chemical industry. It is produced from fossil fuels such as: natural gas, coal and oil fractions (e.g. heavy refinery residues, naphtha, etc.) and is used in the production of a wide range of products. In 2014, about 80% of the methanol produced was used in the chemical and petrochemical industry for the preparation of chemical products [10] amongst which mainly the formaldehyde and acetic acid, in turn, used for the production of polymers such as polyethylene terephthalate (PET) and polyurethane (PUR). Methanol is also used as a solvent and antifreeze. Great attention is given to the conversion of methanol into other basic chemicals (e.g. ethylene, propylene). This process, known as methanol-to-olefins (MTO), is being implemented mainly in China, a country with large coal deposits and low availability of natural gas and oil.

In the transport sector, methanol is used for the preparation of anti-methylantants (MTBE and TAME) and biodiesel from fats and oils. More recently, being characterized by lower emissions of SOx, NOx and particulate [11], it is also considered as fuel for motor vehicles, both in mixture with conventional fuels (e.g. M10, M20, M35 and M85) and converted into methyl ether (DME). In China, the mixtures of both M10 and M85, are currently in use to run approximately 470,000 vehicles [12-19].

Thanks to the initiatives of the International Maritime Organization (IMO) and the adoption of regulations on the reduction of marine emissions in the ECA areas (Emission Control Area, marine areas affected by the convention MARPOL 73/78) and the consequent directives, also, strong interest has been shown in the use of both methanol and DME in the maritime transport sector.

Moreover, it was in May 2016 when The European Parliament approved the Directive (EU) 2016/802 thus limiting among other things, the sulfur content allowed in marine fuels, i.e. below 0.1% by weight [20]. The use of methanol in the transport sector increased from around 20 million tonnes in 2010 to around 27 million tonnes in 2014 [21].

The production of methanol on the global level was estimated to be around 65 million tonnes (Table 1). Consumer assessments during the year 2015, on the other hand, indicated a growth in demand of 70 million tonnes [23, 24]. The main producers with high capacity plants (up to 5,000-6,750 t / day) are China, Middle East, Russia and Trinidad and Tobago [25]. Approximately 80% of methanol production is from natural gas, while the remainder is from coal (17%) and small amounts from oil [16]. In particular, in China, where large coal reserves are available, the capacity of methanol production from 9 Mt / year in the year 2009 [27] to around 22 Mt / year in 2014 (about 63% of total production) [28], has undergone a very rapid growth.

Table 1 : Production of methanol Worldwide [22]

Geographical area	Millions of Ton
China	35
Medio Oriente	14
South America	10
South-East Asia	4,8
United State of America	2,8
Europe	2,6
Total	65

The main uses are the use as fuel for transport and, as previously mentioned, the production of ethylene and propylene through MTO process (methanol-to-olefins) from which the corresponding polymers are then obtained. The rising prices of oil and natural gas in the recent years as well as the need to contain greenhouse gas (GHG) emissions have aroused increasing interest in alternative processes for the production of methanol from renewable sources that, in fact, chemically identical to methanol from fossil fuels but, with much lower greenhouse gas emissions over the entire life cycle, including production and possible combustion. Besides the reduction of GHG, the different uses of bio-methanol can lead to a reduction in imports of fossil fuels and stimulate local economies, as well. Raw materials for bio-methanol are in fact biomasses, landfill biogas, waste raw glycerol from biodiesel production, wastewater and black liquor, the liquid fraction rich in lignin and hemicellulose produced in the paper industry.

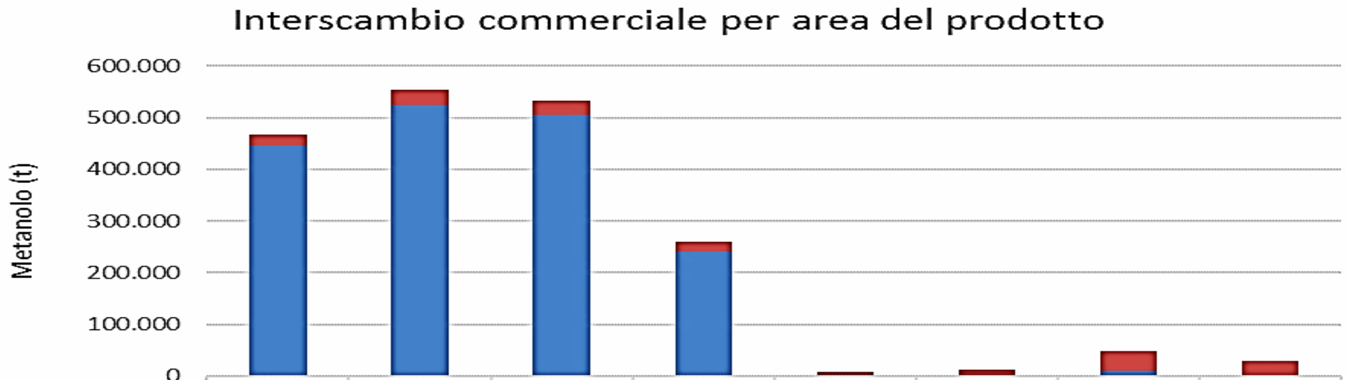
Performance

In Italy, since 1930s, methanol was produced using local coal as raw material. At the time there were active companies such as SIRI (Terni), Methanol and Derivate (in Sardinia) and others. After World War II, mainly because of the economic reasons combined with government policy to import methanol to meet the national demand, production of methanol recorded a negative trend. However, some of the production plants remained operational until 1970s (Filago and Castellanza), a period after which the government also started importing methanol from Libya and Algeria, as well.

With the assertion of producing methanol from natural gas, imports from non-EU countries, mainly North Africa and the Middle East, became dominant. In more recent times, these imports have been joined by those from the United

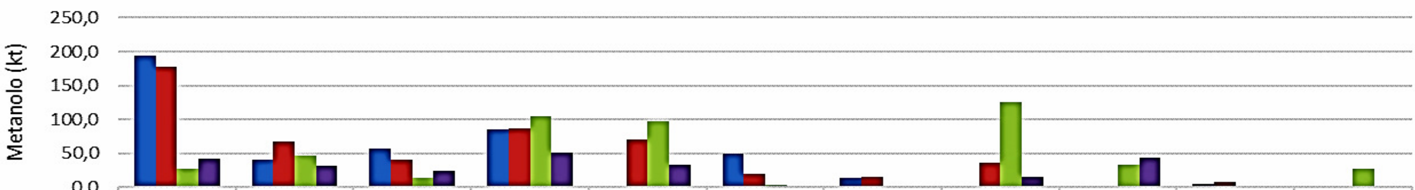
States and Trinidad and Tobago. For about a decade, imports have been decreased to around 500,000 tons compared to the previous period (over 700,000 tons).

The reasons for this decline are the decline in demand in the chemical sector, deindustrialization, transition of some plants from the production of MTBE to that of ETBE thus consuming ethanol instead of methanol and in the failure to take off the production of biodiesel, with much unexpressed production capacity due to lower allowances for tax exemption and import of the finished product. Given the lack of methanol production facilities, most of the Italian companies in the sector (tar the major Methachem [29] and ENI Ecofuel [30]) deal exclusively with marketing. The Istat import / export data of methanol (Figure 1) for the three-year period 2014-2016 indicate a sharp increase in quantities in the last year (data updated to May 2016) [31]. Imports from non-EU areas, mainly North Africa, the Middle East (Figure 2), the United States and Trinidad and Tobago covered over 90% of the demand.



	IMP2013	IMP2014	IMP2015	IMP2016	EXP2013	EXP2014	EXP2015	EXP2016
[UE 28]	22.363	29.280	27.761	18.674	7.591	11.188	38.076	28.262
[Extra UE 28]	445.913	524.335	505.300	241.725	607	486	9.403	235

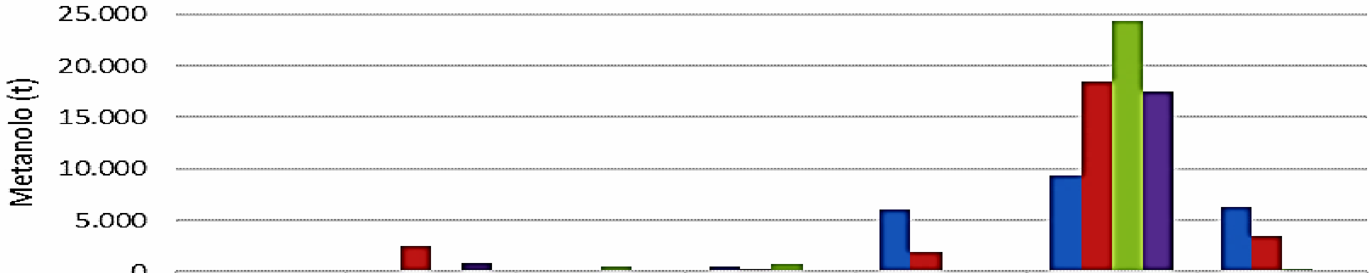
Fig. 1 : Import/export of methanol in Italy [31]



	Egitto	Algeria	Libia	Arabia Saudita	Repubblica islamica dell'Iran	Oman	Bahrein	Trinidad e Tobago	Stati Uniti	Russia	Azerbaigian
IMP2013	194,8	40,6	56,7	85,8	0,0	49,6	13,5	0,0	0,0	5,0	0,0
IMP2014	178,2	67,0	40,7	86,6	71,2	20,1	15,6	36,4	0,0	8,5	0,0
IMP2015	27,1	46,8	14,6	104,5	96,8	3,5	0,0	126,2	33,2	0,0	27,5
IMP2016	41,8	31,5	24,5	50,8	33,3	0,0	0,0	16,1	43,7	0,0	0,0

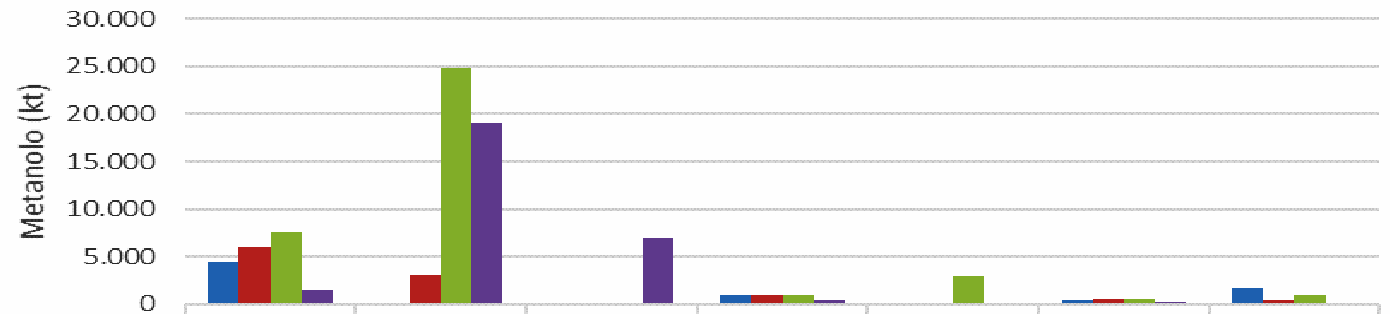
Fig. 2 : Imports from main non-European countries during 2014-2016 [31]

Within the European Union, Italy imports methanol mainly from the Netherlands, Malta and Slovenia (Figure 3) and exports it mostly to Austria, Belgium, France and Greece (Figure 4). The comparison of the data reveals that over 90% of the imported methanol remains in Italy to cover the domestic needs (over 460 kt / year in the three-year period 2014-2015) for the production of formaldehyde and derivatives (about 70% of total consumption), acid acetic, MTBE and biodiesel [32, 33].



	Austria	Belgio	Francia	Germania	Malta	Paesi Bassi	Slovenia
IMP2013	0	11	91	562	6.029	9.391	6.272
IMP2014	0	2.506	96	296	1.990	18.458	3.429
IMP2015	25	6	520	737	0	24.384	314
IMP2016	0	843	33	56	0	17.543	192

Fig. 3 : Main European countries supplier of methanol [31]



	Austria	Belgio	Francia	Germania	Grecia	Malta	Slovenia
EXP2013	4.428	0	0	935	0	423	1.706
EXP2014	6.032	3.001	24	956	8	568	420
EXP2015	7.532	24.846	137	975	2.941	489	933
EXP2016	1.458	19.113	6.956	456	0	247	0

Fig. 4 : Main countries importer of methanol from Italy [31]

Production processes

Biomass can be converted to MeOH via thermochemical and biotechnological pathways. Biomethanol can be produced from a wide range of biomass feedstocks via a thermochemical route similar to the Fisher-Tropsch process for BtL. It can be blended in petrol at 10-20%. Methanol has also been investigated for use as a fuel in shipping.

Figure 5, presents a summary of the production steps based on the starting raw material including natural gas, coal, biomass, waste / by-products and carbon dioxide (CO_2) [34, 35].

In general, the plant configurations for the production of bio-methanol follow those adopted for the production of methanol from fossil fuels: the gasification of solid biomasses recalls the gasification of coal as well as the process of steam reforming of the biogas recalls that of natural gas .

The most recent path is the synthesis of bio-methanol starting from CO_2, a process able to reduce the consumption of fossil fuels, CO_2 emissions and possibility of using excess electricity produced from discontinuous renewable sources such as photovoltaic and wind power, at low cost [36, 37].

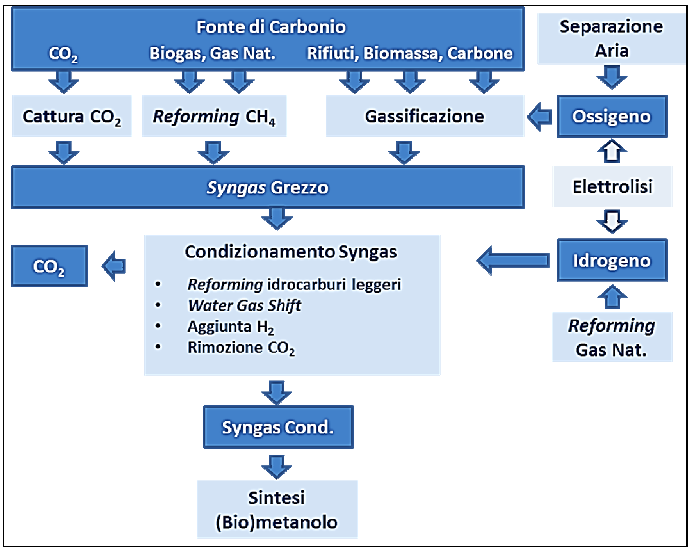


Fig. 5 : Principal processes for production of methanol based upon the starting raw material [35]

Under extreme assumptions, in the case of solid raw material (e.g. coal, biomass) or liquid, the main steps of the methanol production process are gasification and subsequent purification of gas, while in the case of raw gas (natural gas, biogas)) the first phase is reforming. Both processes produce a synthesis gas (crude syngas) which in the subsequent phases is purified and subjected to further treatments aimed essentially at the hydrogen enrichment of the syngas and its preparation for the synthesis of methanol [38].

More specifically, if the production starts from biomass, the operations listed above are preceded by the pre-treatment of the biomass, for example chipping and drying in the case of woody biomass, or purification in the case of liquid raw material (e.g. raw glycerol, black liquor). In gasification, biomass is converted into crude syngas comprising of CO, H_2, CO_2, H_2O and to a lesser extent by light hydrocarbons (CH_4 and C_{2+}). Gasification can be carried out by using oxygen or air as gasification agents [39]. It is true that use of air as gasifying agent is quite cheap compared to oxygen but in such cases, presence of nitrogen in the air (when compared to the use of oxygen) results into a significant increase in the flow of gas through the gasifier and the downstream equipment [40] thus requiring larger equipment and increased investment costs [41]. On the other hand, the use of oxygen, no doubt, reduces the overall investment costs due to smaller plant sizes, but it certainly entails higher operating costs due to the need for oxygen. To reduce the production costs of bio-methanol it is therefore necessary to find the right compromise between investment costs and operating costs.

For removal of contaminants such as: tar (tar), powders and inorganic substances (ash, H_2S, HCl, NH_3, etc.), moving in the direction of the crude syngas produced in the gasification chamber, it is subjected to the purification. Further, it is subjected to the conditioning processes that optimize the composition of the gas for the purposes of methanol synthesis (Figure 5) thus attaining at least twice the contents of H_2 compared to that of CO, the main carbon monoxide involved in the hydrogenation reaction [42].

The initial composition of crude syngas depends on the carbon source and the gasification method used [43, 44]. In the conditioning phase, the concentrations of CO and H_2 can be modified in various ways: for example by means of catalytic steam reforming or auto thermal reforming of the light hydrocarbons present in the gas which can be converted into further CO and H_2 [40]. To increase the concentration of hydrogen, the gas stream is then subjected to a water gas shift (WGS) reaction in which part of the CO reacts with H_2O, producing H_2 and CO_2. It is followed by the removal of CO_2, whose content can be reduced by chemical absorption with amines or other washing liquids, cryogenic separation or permeation through membranes [45].

The content of H_2 in the syngas can also be increased by addition from the outside. Hydrogen is produced at the industrial scale by steam reforming of methane or water electrolysis. Electrolysis is quite expensive, but if associated with a gasification process it can offer important synergies, for example, if the co-produced oxygen is used as a gasifying agent (Figure 5). On the environmental side, electrolysis makes sense only if the electricity used comes from renewable sources [46, 47]. It should also be noted that, if the electrolyser device is sized to supply the necessary oxygen for gasification, the relative production of hydrogen is not sufficient to satisfy the optimal stoichiometric requirement for a complete conversion of both CO and the CO_2 present in the syngas, into methanol. Therefore, in this configuration, if the conversion of carbon to methanol is to be maximized, an over-sizing of the electrolyser, is a must; if, on the other hand, conversion is to be optimized, a partial removal of CO_2 [45] must be envisaged.

After conditioning, the syngas is converted into methanol by a process employing catalysts based on copper and zinc oxide (Cu / ZnO / Al_2O_3) or zinc oxides and chromium (ZnO / Cr_2O_3) [41, 47]. To remove the water generated during the methanol synthesis, the product is finally subjected to distillation. Biomass gasification technologies are similar to the well-known coal gasification technologies, but one of the greatest challenges remains economic competitiveness.

Table 2 provides an overview of the plants for the production of bio-methanol in operation or of upcoming start-up, updated at the date of writing of this document. Tables 3 and 4 show a list of projects carried out in Europe, financed by national as well as Community resources (Horizon 2020, 7 FP, NER 300) and, aimed at the production of bio-methanol, and possibly other chemical products, and its use as an energy carrier, e.g. fuel for fuel cell systems, one of the most promising future applications, especially in the transport sector [49].

Still in the R & D phase, it is the production of bio-methanol from CO_2 through high temperature thermochemical splitting of CO_2, possibly associated with splitting of H_2O, using solar reactors or photochemically [50, 51]. Another option for the production of methanol is provided by biochemical processes analogous to those used for the production of ethanol by fermentation. While ethanol production takes place by fermentation of sugars present in a liquid phase, production of methanol takes place by microorganisms capable of fermenting methane [52-55].

Technically, any carbon source can be converted into syngas and bio-methanol, but ongoing projects mainly focus on the use of raw material as by-products from other industrial processes, as shown in Table 2 and Table 3. Furthermore, integration of the production bio-methanol with other products, from which these by-products derive not only simplify the aspects related to the supply of raw materials and logistics but allows to share some costs and favours the general economy thus giving production flexibility compared to the fluctuations in the prices of one of the products [68].

Sectors of potential plant integration, or at least with important synergies with the production of bio-methanol, are the production of paper [68] generating black liquor as the waste, production of biodiesel [70, 71] generating large quantities of raw glycerol as a by-product, processing of sugar cane which produces bagasse as a by-product [72, 73], and, of course, sector of solid urban waste [47, 74].

All these by-products are convertible into bio-methanol. With the exception of glycerol, other by-products mentioned above can now also be applied in the production of electricity from biomass and waste.

Table 2 : Plants for production of bio-methanol: Operational or ready to be operational

Nation	Company	Starting year	Capacity (kt/a)	Production (kt/anno)	Products	Type of plant	Feeding material	Source
Operational								
Holland	BioMCN	2010	440	200	Methanol	Comm.	Raw glycerol, bio-methane [a)]	BioMCN [56]
Canada	Enerkem	2010	4	-	Methanol (+ethanol since 2012)	Demo	Used telephone wooden poles and urban solid waste	Enerkem [57]
Island	CRI	2011	-	4[b)]	Methanol	Comm.	CO_2 from geothermal plant	CRI [58]
Canada	Enerkem	2015	29	-	Methanol (+ethanol dal 2017)	Comm.	RSU	Enerkem [59]
Canada	Al-Pac	2015		2	Methanol al 99,85%-p [c)]	--	By products from paper production	Al-Pac [60] [61]
To be operational								
Sweden	Varmlands Methanol	2015-17[d)]		92	Methanol	Comm.	Residual biomass	Värmlands Methanol AB [63]

Sweden	Chemrec & Domsjor Fabriker	> 2015[d)]	140 (100)		Methanol (DME)	Demo	Black liquor	Chemrec [64], [65]
Holland	Woodspirit	2016-17[d)]	413	200	Methanol		Biomass	Biofuelstp [66]
USA	Domestic BioSolutions	2016-17		75	Methanol		Biogas	Domestic BioSolutions [67]

a) Until 2013, the plant produced bio-methanol from raw glycerol whereas after that used bio-methane (green gas), or methane introduced into the network and coming from biogas upgrades);
b) Plant became operational in 2011, with initial production of about 1.3 M litres / year. In 2015, it produced 5 M of litters / year, about 4 kt / year (methanol density: 0.79 kg / litre);
c) Methanol with a purity of 99.85% by weight, with sulphur of 60-70 ppm, higher than the limit S <0.5 ppm of the international IMPAC specification. Used for internal consumption [61]
d) Starting date [62]

Performances (Current and expected)

The performance of plants for the production of bio-methanol depends on many factors, such as, plant layout, raw materials used, co-production, specific production technology, etc. A key factor is also the local conditions such as the availability of raw materials and electricity from renewable sources. It is worth to note that mainly because of the limited number and variety of commercial operational plants available, indications on the energy and environmental performance, typical of any plant, are difficult to identify (Table 2). Different models based on different hypotheses used to study different configurations of plants, present at specific sites [76], leads to estimation of efficiency and environmental impact though not easy to compare.

Table 3 : Research and development projects for production of bio-methanol financed in the framework of European communities/ National [75])

Program	Project	Duration	objectives	Output	Type of plant	Input	Website linked to the project
Horizon 2020	MefCO2	2014 - 2018	Methanol from CO_2 using surplus eletric power	MeOH	Comm	CO_2	http://cordis.europa.eu/project/rcn/193453_en.html; http://www.mefco2.eu/
7 FP	SUPER METHANOL	2008 - 2011	Methanol form reforming of raw glycerol in supercritical water, to be used in the production of i biodiesel	MeOH	Pilot	Raw Glycerol	http://cordis.europa.eu/project/rcn/85746_en.html; http://www.supermethanol.eu/
	BioDME	2008 - 2012	DME from biomass to be used in transportation and industries	MeOH, DME	Demo	Black liquor	http://cordis.europa.eu/project/rcn/90341_en.html; http://www.chemrec.se/Page294.aspx
	BIOGO-for-Production	2007 - 2013	Partial catalytic oxidation of biogas and reformation of pyrolytic oil for autothermic synthesis of gas and conversion into fuels	MeOH et al.	Lab	Biogas and Biomass	http://cordis.europa.eu/project/rcn/110962_en.html; http://www.biogo.eu/biogo_home.html
	Eco2CO_2	2012 - 2016	Bio-refinery for chemical products for photo-catalytic reduction of CO_2	MeOH	Lab	CO_2	http://cordis.europa.eu/project/rcn/105900_en.html; http://www.eco2co2.org/
	CEOPS	2013 - 2016	CO_2 for energy storage and methanol conversion after methane production	MeOH	Pilot	CO_2	http://cordis.europa.eu/project/rcn/105903_en.html
NER 300	WOODSPIRIT	2016	Bio-methanol from gasification of cellulosic material	MeOH	Comm	Wood	http://www.biomcn.eu/woodspirit-nominated-for-ner300-program/; http://www.biofuelstp.eu/methanol.html
National	Bio-Comet (Holland)	2011-2015	Bio-methanol from CO_2 through bio-enzymatic processes powered by solar energy	MeOH		CO_2	http://www.biosolarcells.nl/onderzoek/kunstmatige_bladeren/biocomet.html; http://www.wur.nl/en/show/Solar-cells-for-sustainable-production-of-methanol-from-CO2-1.htm
	GLV Prototype (Italy)	2015	Construction of a biomass hub in the Ferrara petrochemical industry	MeOH + ethylene and propylene	Lab	Biomassand residual Waste	http://www.aster.it/green-lab-valley

A favourable option from the economic point of view appears to be the co-feeding of fossil and renewable raw materials. In addition to the economic aspect, this approach is of interest because it could facilitate a gradual transition from the production of methanol to that of bio-methanol while at the same time improving knowledge on biomass production. For example, a plant can be co-fuelled with gas produced from biomass gasification together with gas produced by steam reforming of natural gas.

Since the steam reforming gas has a ratio H_2/CO (3: 1) higher than that required by the stoichiometry of methanol synthesis (2: 1), and the biomass gas has instead an insufficient H_2 / CO ratio for direct conversion in methanol, the combination of the two gaseous streams allows to optimize the final gas composition, avoiding the need for enrichment in H_2 or the removal of CO_2, with significant economic advantages [77].

Another co-feeding option is the co-gasification of coal with biomass or waste in an IGCC (integrated gasification combined cycle) plant. This approach was adopted in the past in Germany at a plant of Sustec Schwarze Pumpe GMBH precisely for the production of methanol [78]. A third approach concerns the use of biogas, which, after an upgrading process, can replace natural gas in the current methanol production plants [79].

The conversion of biogas into methanol (biogas-to-methanol) has not yet been carried out on a commercial scale, but does not appear to present excessive difficulties. However, the process requires some technical changes because biogas typically contains a much higher share of CO_2 (25-45% by volume) [80] compared to natural gas (0.1-1.5%), which has an impact on the composition of the product syngas [81], and also contains H_2S hydrogen sulphide in varying degrees (0.1-10 g / m^3 [67]) which must be removed to avoid the deactivation of the catalysts used in the conversion of syngas into methanol.

A further option to improve the economic and environmental performance of bio-methanol production is the co-production of electricity and heat, and of chemical products (hydrogen [83, 84], bio-ethanol [85, 86], urea [87]). Co-generation of electricity [87] and heat for district heating [47] is already often included in plant layouts to increase overall energy efficiency and revenues.

Table 4 : Projects relevant to the use of methanol as fuel [75])

Program	Project	Objectives	Output	Web site linked to the project
Horizon 2020	MetaFuel	Development of high temperature fuel cells fuelled by methanol	DMFC	http://cordis.europa.eu/project/rcn/197967_en.html
	FEDMFC	Development of direct methanol Fuel Cell with flow electrolyte	DMFC	http://cordis.europa.eu/project/rcn/196123_en.html
7 FP	BeingEnergy	Membrane Fuel Cell with a polymeric electrolyte integrated to reforming methanol	PEMFC	http://cordis.europa.eu/project/rcn/104614_en.html
	LiquidPower	Development for marketing of H_2Fuel Cell from reforming of methanol	FC	http://cordis.europa.eu/project/rcn/106155_en.html
	IRMFC	Fuel Cell with polymeric membranes with internal reforming of methanol at high T	PEMFC	http://cordis.europa.eu/project/rcn/108673_en.html
	ARTEMIS	Fuel Cell with polymer membranes coupled with methanol reforming for automotive application	PEMFC	http://cordis.europa.eu/project/rcn/105438_en.html
	DURAMET	Development of durable and economical components for direct methanol Fuel Cell and solid polymeric electrolyte	DMFC	http://cordis.europa.eu/project/rcn/101147_en.html
	ISH2SUP	Development of micro Fuel Cell for portable H_2 devices from methanol electrolysis	FC	http://cordis.europa.eu/project/rcn/94281_en.html
	IRAFC	Fuel Cell with high temperature polymer membranes for internal reforming of alcohols	PEMFC	http://cordis.europa.eu/project/rcn/94277_en.html

Efficiency and emissions

The production of bio-methanol can contribute to reducing the consumption of fossil fuels and greenhouse gas emissions. The savings achievable in this sense are indicators for assessing the environmental impact of the use of biomass. The data on the production of bio-methanol are actually quite small and not always comparable due to the reduced industrial practice and the variety of technical solutions. The energy efficiency of the natural gas methanol production process is around 60-70% [88-90]. For the production of methanol from natural gas, petroleum products and coal, the process energy is in the range 29-37 (GJ) per tonne [91]. For the production of methanol from biomass and coal, energy efficiency is lower, around 50-60% [88, 74] due to the lower H / C ratio of the raw material and the higher production of ash and char. In general, the overall energy efficiency of a bio-methanol plant depends on which phases of the process are included, whether or not the co-production of electricity and heat, and the size of the plant [34].

Estimates of the consumption of renewable and non-renewable energy for the production of bio-methanol are available in the literature as a result of several hypotheses on the production process. For example, some studies assume that the necessary process energy (heat and electricity) is produced using biomass [68]. In this case, therefore, no conventional energy is used in the production of bio-methanol. In other studies, conventional energy sources are used to cover the electricity needs. This clarification is useful for correctly interpreting the emission data of the methanol and bio-methanol production processes. For the production of methanol from coal and natural gas, 3.8 and 1.6 kg CO_2 per kg of methanol is used respectively while for the bio-methanol from woody biomass, values of 0.2 kg CO_2 / kg of methanol, are reported. For methanol produced from CO_2 exhaust gas emissions of about 0.8 kg CO_2 / kg are estimated, a value that is higher than that from biomass due to the energy consumption for the separation of CO_2 from the other gas components [88, 92-98].

Finally, some studies explore the benefits of poly-generation including the possibility of CO_2 capture [99], particularly in the case of production of methanol from fossil fuels. If Polygeneration generally allows a reduction in production costs for the synergies already discussed, CO_2 capture obviously involves an increase in cost. In the case of coal methanol, for example, the integration into the CO_2 capture process leads to an increase in production costs of around 25% [100].

Costs : Actual and expected

Production costs

Important factors influencing the estimates currently available on the production costs of bio-methanol are the local conditions, the type of raw material and the relative cost, the mix and the costs of the process's energy inputs (fuels, electricity, heat), the scale of production, production technology, the degree of final purity of the product. Local conditions and raw material influence the choice of technology for a new plant and have a significant impact on production costs.

For example, if the hydrogen necessary for production is produced by electrolysis, the electrical energy required may account for between 23% and 65% of the cost of producing bio-methanol, depending on the plant configuration [47]. The upper limit of this range refers to bio-methanol production plants that use CO_2 as a carbon source and electrolyte hydrogen for its reduction. This configuration finds application in an Icelandic plant that produces methanol from CO_2 using electricity of geothermal origin (Table 2). Electrolysis actually requires a lot of electricity, but if the price of electricity is low, such a plant configuration can be economically interesting.

This is the case in Iceland where 80% of the electricity is of geothermal and hydroelectric origin at low cost and with small emissions of greenhouse gases. The Eurostat data indicate in EU-28 an average cost of kWh for domestic use in 2015 equal to € 0.211 compared to € 0.127 in Iceland [101].

This situation, although rather exceptional, demonstrates the importance of local conditions and provides evidence of how opportunities for bio-methanol production at favourable cost-benefit ratios may already be current.

The variability and the number of factors listed above translate into a wide range of production cost estimates. Figure 6 shows a comparison of methanol production costs from various raw materials: woods, residues, process by-products (e.g. glycerol), CO_2, natural gas and coal (literature data). These estimates reflect the assumptions made in relation to energy prices, technology, services and revenues originating from possible co-products. However, it should be noted that the differences between the various options and in general the average cost of production are significantly reduced as the size of the plant increases.

The costs of producing natural gas and coal methanol (respectively points in red and black) range from € 75 to € 250 / t for the former, and from € 150 to € 300 per tonne for the latter. The global weighted average (IRENA bottom-up estimate) is around € 160 / t, with a production capacity of around 830 kt per year. However, it should be noted that for small-scale coal production (up to 200 kt / year) production costs can increase significantly up to € 470 / t. The costs of production from wood (points in orange) range from about € 160 / t [41] to € 940 / t [117], wide range mainly determined by the different plant solutions and local conditions. However, the distribution in Figure 6 suggests a very significant impact of production capacity (kt / year) and economies of scale for wood production.

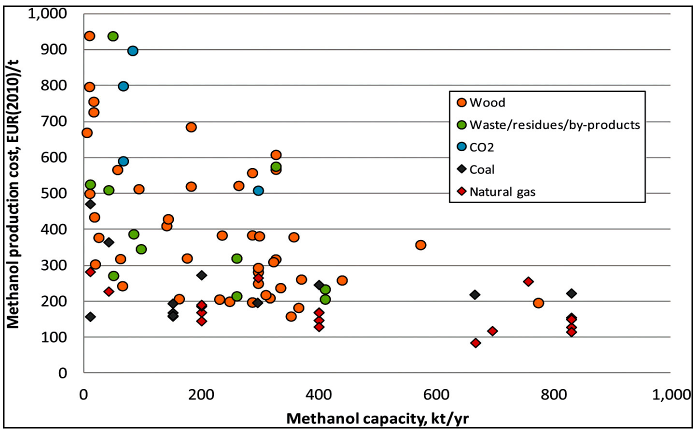


Fig. 6 : Production costs of bio-methanol from different raw materials as a function of capacity of the plant[1] [35]

Neglecting the outlier points (€ 940 / t and € 580 / t), waste production is slightly cheaper (€ 200- € 500 / t) compared to wood, with the usual effect of economies of scale. CO_2 production is the most expensive process (€ 510-900 / t). The cheapest production is natural gas, while wood and waste production can be competitive with coal production in the most favourable cases. Overall, the analysis shows that compared to the production of fossil fuels, bio-methanol is always more expensive than natural gas, whereas in comparison with coal production costs are 4.0 to 1.5 times higher. Higher up to be almost comparable in large capacity plants. It follows that in the short term the production of bio-methanol for biomass gasification could become economically competitive in plants integrated with other industrial processes such as the production of paper, bio-diesel, bio-ethanol, from which residual currents arise. (black liquor, crude glycerol and lignin) that can be used as raw materials for the production of bio-methanol (Table 2).

Investment costs

Information on the investment costs of bio-methanol production plants currently under construction is summarized in Table 5. The data reported show that the capital cost per production unit in the case of bio-methanol from residual currents is at least 4.9 times higher than the capital cost for natural gas plants. As expected, this ratio is reduced in the case of mixed feed where, according to an evaluation carried out by referring to the BioMCN process [124] in which the production of methanol from raw glycerol and natural gas is considered, the capital costs are range of those for production from natural gas alone [125].

Table 5 : Estimated investment costs of plants for generation of bio-methanol

Company	Feed Materials	Cost of investment (M USD)	Productive capacity (kt/year)	Capital costs (USD/t/anno)	Source
Chemrec	Black liquor	440	100	4.400	Chemrec 2009 [120]
Varmlands-Methanol	Waste from forest	540	100	5.400	Varmlands-Methanol 2011 [121]
Enerkem	RSU	100	29	3.500	Enerkem 2015 [102]
CRI	CO_2	15	1,6	9.500	CRI 2011 [123]
BioMCN	Glycerol and natural gas	340	450	800	Van der Ham 2013 [124]
--	Natural gas	880 - 1710	1600 - 1900	550 - 900	MMSA 2015 [125]

In the case of bio-methanol form CO_2, such as the Icelandic CRI plant (Table 3), the capital cost is about 17 times higher than the cheaper natural gas plant. In the latter case, however, it should be noted that these costs refer to a plant of 1.6 kt per year whereas for plant of higher sizes (30-40 kt / year), the estimated and / or expected costs are considerably lower. Finally, in comparison with plants for the production of bio-ethanol from corn (first-generation technology), bio-methanol plants have a plant cost that is 1.8 times higher than the same energy output [68].

Development potential and barriers

Supply of raw material and demand for methanol

From the point of view of the availability of raw material for the production of bio-methanol, energy content of waste and by-products (black liquor, glycerol) is about 3,550 and 39 PJ / year, respectively [126]. In principle, this means a production of bio-methanol of 72 Mt / year from the black liquor [68] and 1.4-2.1 Mt / year from glycerol [127, 128]. These production potentials must be compared with the current production of methanol from fossil fuels, which for 2015 was around 70 Mt/year [129, 130].

The glycerol market is currently falling as the ever increasing bio-diesel production has led to a considerable oversupply, with raw material prices varying from 290 – 130 € / ton between the year 2011-2013 [131]. With the prices nearly half, resulted bio-methanol production to be cheaper.

The current global gasification capacity from coal corresponds to a methanol production potential of nearly 9.0 Mt / year, with always increasing trend, especially in China [17]. This gasification capacity could, in principle, also be co-fed with biomass with significant share of bio-methanol production. However, in reality, these potentialities are difficult to exploit because the different types of biomasses of interest for the production of bio-methanol, are already used in other applications. For example, black liquor is currently used in paper mill boilers to cover indoor thermal needs [68] thus forcing bio-methanol production to compete with the current use of residues.

A similar situation is in the case of Glycerin with a wide range of uses [52, 132-123]. Possibility of its use in a new application, such as the production of methanol, could therefore lead to an increase market prices.

In terms of demand, bio-methanol would be used in the substitution of methanol from fossil sources, but also in the conversion (through the MTO process, methanol-to-olefines) into ethylene and propylene whose world production in 2011 were respectively 120 and 65 Mt / year [134]. Thanks to the development of the sector in China where 6 commercial scale systems 300 ÷ 800 kt / year [135] are already operating and others ready to be operation [136], consumption of methanol in the MTO process amounting to nearly 10 Mt during the year 2014, is surely destined to increase. Also, methanol can be used as a substitute for petrol and diesel for which global consumption is estimated to be around 970 and 720 Mt / year, respectively [137].

To replace ethylene and propylene from fossil sources through the MTO process, based on the data available in 2011, it is predicted that a bio-methanol requirement of around 650 Mt / year is needed [138].

For gasoline and diesel, the demand would be about 2,150 and 1,500 Mt / year of bio-methanol (based on the energy value of fuels). The potential for great demand in this sector (the methanol economy, as suggested by Nobel Prize winner George Andrew Olah [45] would obviously make the current gasification capacity largely insufficient. This prospect would require not only the availability of gasification capacity, but also the broad availability of all types of biomass, a possibility that at present is quite distant [139, 140].

Conclusion

Research is currently focused on improving the production of bio-methanol and biomass gasification to reduce the environmental impact of the chemical industry and ensure optimal product quality. However, the possibilities of a more widespread production are hampered by various aspects. From a technical point of view, gasification is the most critical stage with various types of gasifiers based on different principles that offer different performances, some of which have achieved sufficient technological maturity for the transition to the commercial scale in the fields of combined electricity production and heat

(CHP) or in the production of BioSNG. However, much remains to be done to improve plant performance and availability, as well as the sustainability of the related processes [43, 141]. The improvement of the gasifiers would certainly bring important benefits also for the production of bio-methanol.

For the conversion phase of the syngas in methanol, the expectations of process improvement are limited, since they are consolidated processes with long experience at a global level and in various technological fields. Improvement could originate from microchannel reactor technology, of which the US company Velocys [141] is a world leader. This technology could bring benefits in terms of process intensification, with a consequent reduction in investment and operating costs [141, 142]. A further obstacle to the commercialization of bio-methanol is the relatively high investment cost required for the construction of a plant.

This is partly due to the fact that the raw syngas produced from biomass is more contaminated than natural gas and therefore requires additional [74] purification technologies. However, it should be borne in mind that the increase in syngas purification capabilities in bio-methanol plants makes the plant potentially more flexible than using a wider range of feed raw materials. This can make plants for bio-methanol also suitable for the gasification of solid urban waste [74] with possible additional environmental benefits to be assessed also in economic terms taking into account the income generated by recycling activities that could offset the high costs capital. In this sense, one example is the Enerkem bio-methanol production plant in Edmonton (Canada), whose reference power is precisely originated by the MSW (Table 3).

The price of natural gas could also have an impact on the growth of bio-methanol production. In this direction, the removal of fossil fuel subsidies, as also recommended by the OECD [127], could help to bridge the price gap between natural gas methanol and bio-methanol. It should however also be noted that natural gas methanol is always produced in large plants (more than 1 Mt / year), which offer significant economies of scale and reduced production costs, while the production of bio-methanol takes place in capacity plants, reduced due to technical and logistical problems of supply and handling of large quantities of biomass [74]. Plants with biomass co-feeding and by-products that are not affected by seasonal variation, as well as co-feeding with fossil sources, could contribute to overcoming this problem. The development of the bio-methanol market will obviously also depend on the demand for biomass for other uses such as the production of electricity and heat, and bio-fuels such as bio-ethanol and biodiesel.

The optimal use of biomass is an aspect that also involves energy policy measures: while for the electricity sector and transport are available various sustainable alternatives (e.g. photovoltaic, electric mobility), the chemical industry will always require a carbon source whereas as an alternative to fossils it can only be supplied sustainably from biomass, agricultural and industrial waste and recycling. The promotion of bio-based materials in the chemical sector requires the consideration of emissions throughout the life cycle. On the other hand, current policies tend to consider only direct emissions of chemical processes. A new regulatory framework is therefore needed to give credit to the environmental benefits of bio-based materials. Measures based on the carbon taxation of the whole life cycle and on the ecological labelling of chemical products could be more effective than the current ones in promoting the production of bio-based materials [143]

Table A : Summary of the main data – Worldwide

Technical Performance		**Actual typical values**		
Technological variants		**BioMeOH from glycerol (BioMCN)**	**BioMeOH from waste (Enerkem)**	**BioMeOH from CO_2 (CRI)**
		min/max	min/max	min/max
Technological development, TRL		9	9	9
Energy efficiency	%			60
Operational life				
Capacity factor	kt/year	450		4
Typical plant size	kt/year	200	29	4
Construction time	year	2 (2007-2009)		2 (2009-2011)
CO2 emissions	kg CO_2/tMeOH			143 Rif [124]
Emissions of GHGs				
Polluting emissions				
Solid / liquid waste report	t/tMeOH			0,59 (distilled water)

Costs				
"Overnight" capital cost	M USD	340	100	15
FOM (fixed operating and maintenance) costs				
VOM costs (variable operating and maintenance)				
Cost of absorbed energy				
Decommissioning cost				

Cost for GHG emissions				
Cost for waste management				
Final production cost	€/t	475-525 Rif [125] (Groei, p. 50)	200-500	600

NB: Detailed data at the national level is not available.

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