

Final Report – Bio-Ethanol as an alternative fuel for vessels



Project data

Project number: MIIP 004 -2022

Executed for: Netherlands Maritime Land and Ministry of Economic Affairs

Executed by: Pieter 't Hart, Jeroen Pruyn, Felipe Ferrari

Project title: Bio-Ethanol as an alternative fuel for vessels

Project leader: Maritime Knowledge Centre

Project duration: 01-01-2022 until 31-12-2022

Publication date: 27-01-2023

Status: Final report

Table of contents

1. Preface.....	3
2. The international state of the art	5
2.1. Ethanol.....	5
2.2. Biochemical Route.....	5
2.2.1. First-Generation ethanol	6
2.2.2. Ethanol from sugar-based feedstock - Sugarcane.....	6
2.2.3. Ethanol from sugar-based feedstock – Sugar beet	8
2.2.4. Starchy-based Feedstock – Corn	10
2.2.5. Second-generation ethanol.....	12
2.3. Ethanol from syngas fermentation.....	14
2.4. Ethanol market	16
2.5. Sustainability of Ethanol.....	19
3. Ethanol as a marine fuel	22
3.1. Ethanol as a marine fuel with regard to safety	22
3.2. Ethanol as a marine fuel with regard to engine technology	25
3.2.1. General properties	25
3.2.2. Combustion-related properties.....	25
4. Fuel cost and business case for various alternative fuels	27
4.1. Availability of various alternative marine fuels.....	27
4.2. Production costs of various alternative marine fuels.....	28
4.3. Production costs of fuel blends and associated emissions.	29
4.4. Annual fuel cost based on Thetis MRV- data	32
5. Conclusions and recommendations	33
5.1. Conclusions.....	33
5.2. Recommendations.....	33
6. New projects for bio-ethanol in marine applications.....	35
6.1. Testbed projects	35
6.2. Demonstrator projects	35
References.....	36

1. Preface

There is significant international demand to lower ship emissions of CO₂, NO_x, SO_x, and soot (PM). For larger seagoing vessels, the usage of LNG (Liquefied Natural Gas) presents excellent opportunities, but is not practical for smaller vessels due to the need for additional room on board. Methanol is a fascinating substitute. It is a clean fuel, and even though its NO_x emissions are slightly higher than those of LNG, it is more convenient to store and requires a smaller, more straightforward installation.

Alternatively, bio-ethanol is a good option. It is less dangerous than methanol and it has a higher energy density. The production of bio-methanol is just getting started, whereas more than 100 million tonnes of bio-ethanol is already being supplied. Although bio-ethanol is more expensive than grey methanol and competes with food production as a fuel, it can be an attractive alternative for (smaller) ships with strict safety requirements (passenger ships, government vessels, etc.) and/or where the business case weighs less heavily. Additionally, since it mixes easily with methanol, bio-ethanol can be an interesting and promising intermediate stage in the transition towards green methanol. Several obstacles must be solved for (smaller) vessels to be able to sail on bio-ethanol. The technology is available, but creating integrated technical solutions that are both compliant and economically interesting is challenging. Additionally, a bio-ethanol distribution network needs to be established.

In 2015, EMSA commissioned a study into the applicability of methanol and (bio-)ethanol as alternative fuels for shipping (Ellis, 2015). Both methanol and (bio-)ethanol were good candidates, with the cost of methanol being slightly lower than that of (bio-)ethanol. In the MIIP 2021 project "Inventory of sustainable biobased marine fuels", the feasibility of biomass for methanol, (bio-)ethanol and methane in the EU has also been demonstrated as an alternative to HVO. (Gartland, 2021)

Bio-ethanol outperforms methanol in terms of energy density and passenger and crew safety. Bio-ethanol can therefore be a compelling option across several markets. Additionally, compared to bio-methanol, there is currently sufficient bio-ethanol attainable on a global scale. Whether bio-ethanol is technically, economically, and logistically possible in the Dutch context as well as in (smaller) vessels has not yet been investigated.

With the use of bio-ethanol, hundreds of vessels operating in ports, rivers, coastal areas, and metropolitan areas might significantly reduce their harmful emissions. Ethanol is one of the safest biofuels available, and it has properties that are comparable to those of LNG. In the long run, bio-methanol can effectively replace bio-ethanol, which means that the competition between fuel and food can significantly reduce not only SO_x, NO_x, and PM emissions, but also the CO₂ footprint. This study could serve as the foundation for the use of bioethanol as a transport fuel on an existing or future vessel.

Technology in the field of methanol applications is available for (larger) vessels (Stena Ferry, Maersk container ships, Van Oord offshore wind installation vessels). For bio-ethanol, installation must be adapted and tested. For smaller vessels, solutions that are applied in other modalities (e.g. road transport) can also be researched. The theme is closely related to the theme "clean ships" and secondly to the theme "efficient infrastructure".

This research intends to shed light on the technical, logistical, and economic feasibility of using bio-ethanol as a substitute fuel for smaller vessels. The topic of CO₂ reduction in shipping has been covered in a number of outstanding and thorough reports. These reports served as the foundation for this investigation. However, new opportunities seem to emerge at a steady pace. This report aims to establish a coherent overview of developments and possible solutions for CO₂ reduction in shipping including its strengths and weaknesses, opportunities and threats. These developments and solutions can also provide interesting opportunities for cooperation and further fundamental

research. This report will elaborate on several specific developments, sometimes only a reference will be given to an existing source. We have tried to keep the document concise and challenging for the many stakeholders in the maritime cluster.

This project is executed under the auspices of Netherlands Maritime Land and supported by the Ministry of Economic Affairs.

2. The international state of the art

2.1. Ethanol

Ethanol is a simply 2 carbons alcohol, depicted in Figure 1 liquid at ambient conditions and mostly produced from the fermentation of sugars in their natural occurrences or derived from starch and lignocellulosic feedstocks.

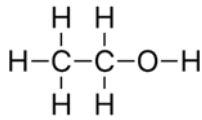


Figure 1: Ethanol Molecule

Also called ethyl alcohol, it has a diverse range of applications, for instance, a disinfectant, solvent and fuel. The hydroxyl group present at the ending carbon confers a polar character to the molecule and is highly miscible in water and with most organic solvents. The main properties of ethanol are summarized in Table 1.

Table 1: Ethanol's main properties and characteristics

Property	
<i>CAS n.</i>	<i>64-17-5</i>
<i>Appearance</i>	<i>Colourless liquid</i>
<i>Molecular weight (g.mol⁻¹)</i>	<i>46.07</i>
<i>Flashpoint (°C)</i>	<i>14</i>
<i>Boiling Point (°C)</i>	<i>78.2</i>
<i>Density (g.cm⁻³ @ 20 °C)</i>	<i>0.78945</i>
<i>Viscosity (mPa.s @ 20 °C)</i>	<i>1.2</i>
<i>Energy Content (MJ.kg⁻¹)</i>	<i>26.8</i>
<i>Cetane Number</i>	<i>< 12</i>
<i>Octane Number</i>	<i>109</i>

Source: (Wyman & Hinman, 1990)

Ethanol can be produced through thermochemical and biochemical routes. Nevertheless, most ethanol consumed globally is formed out of sugar fermented by microorganisms, especially yeast.

2.2. Biochemical Route

Biochemical conversion of carbohydrates to ethanol accounts for the vast majority of global production. Theoretically, any feedstock containing carbohydrates suitable to undergo the saccharification process is a potential raw material for this conversion route (Ferrari, 2021). The

source and nature of carbohydrates considered will reflect on various processes' designing generally classified accordingly as first (1G) and second (2G) generation, obtained from sugar/starch and lignocellulose feedstocks, respectively. Additionally, third (3G) and fourth (4G) generations may apply when addressing microorganism-based carbon, such as algae and genetically modified organisms, respectively (Jambo et al., 2016); however, these are currently at low TRLs, below 6, and, therefore, are not meaningful for today's market.

2.2.1. First-Generation ethanol

First-generation ethanol is produced from biomass with considerable carbohydrate content whether in the form of sugars or starch. The most used feedstocks nowadays based on sugar are sugarcane, sugar beet and sweet sorghum, and, corn, cassava, wheat and rye when considering starchy-based materials. Corn is the most explored feedstock to produce ethanol, especially in USA Cron Belt; however, sugarcane and sugar beet keep the highest crop yields among all feedstocks, as summarized in Table 2. Most of the global production comes from these 3 feedstocks, although their cultivation occurs in opposed climate conditions.

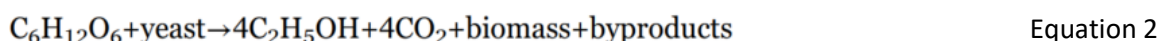
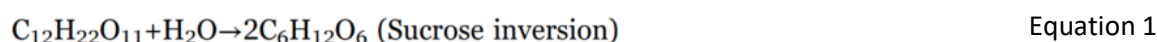
Table 2: Productivity for the most used feedstocks and regions

Feedstock	Biomass Productivity (ton/ ha)	Ethanol conversion efficiency (L/ ton)	Ethanol (m ³ / ha)	Region
Corn	7.5 - 10	360 – 460	2.0 – 4.6	USA, China, Canada, Brazil
Sugarcane	50 - 120	70 -90	5.4 – 10.8	Brazil, Thailand, Argentina, India
Sugar beet	13 – 100	100 - 110	5.0 – 10.0	Europe

Source: (Manochio et al., 2017; Mizik, 2021)

2.2.2. Ethanol from sugar-based feedstock - Sugarcane

Sugarcane is a perennial plant indigenous to tropical and subtropical climates, belonging to the grass family (Lam et al., 2016). Carbohydrates are stored in the stalk in the form of sucrose which is a disaccharide composed of glucose and fructose joined by a glycosidic bond. Sucrose is readily consumed by yeast, as depicted by equations Equation 1 and Equation 2, and, consequently, sucrose-based feedstock does not require the saccharification step, as discussed further in the corn-based process.



The largest producer of sugarcane and sugarcane-based ethanol is Brazil, where industrial production was strongly incentivized during the 70s as a response to the external oil crisis. The industrial process starts with the arrival of sugarcane at the mills, where it is washed and cleaned to remove major

contaminants, such as soil, and headed to sugar extraction. The process is performed in mills, which is normally adopted the soaking process of bagasse with water between the millings to recover the maximum amount of sucrose from the feedstock. The bagasse resulting from the process is harnessed and used in cogeneration systems for heat and electricity, which makes sugar mills energy self-sufficient most of the time. The extracted juice is further treated to remove particulates and other impurities by means of sieving, liming and decanting. The purified juice is then concentrated to improve sugar and, consequently, ethanol concentration. Temperature is adjusted before fermentation and the broth is headed to vat where sugar concentration is adjusted and the microorganisms are added, primarily yeast (unicellular fungi of the species *Saccharomyces cerevisiae*) (Almeida & Colombo, 2021).

The Melle-Boinot process is the most deployed in Brazil, based on yeast recovery from the fermented wine by centrifugation, allowing the reuse of yeast after a treatment to avoid bacterial contamination. The resulting wine proceeds to ethanol purification, in which ethanol is distilled from the wine. Two sequential distillations are needed to reach ethanol with ~95 wt%, namely hydrous ethanol, which can be used as a final product, for instance as a vehicular fuel, or proceed to the dehydration process. Anhydrous ethanol (> 99 wt%) is commonly obtained by distillation using a dehydrating agent, for example, cyclohexane. The addition of cyclohexane leads to a ternary mixture with water and ethanol whose boiling point is lower than the initial binary mixture. After separation, the dehydration is recovered and reused. Alternatively, the system of molecular sieves can be used for the dehydration process. Molecular sieves are composed of a microporous substance, in which water molecules are trapped and adsorbed, whereas the larger ethanol molecules flow around them (Manochio et al., 2017).

Ethanol from the sugarcane process has three main coproducts, namely sugar, electricity and nitrogen-rich material used for feed prevention from the drying of yeasts and residues after fermentation. The simplified process flowchart is depicted in Figure 2.

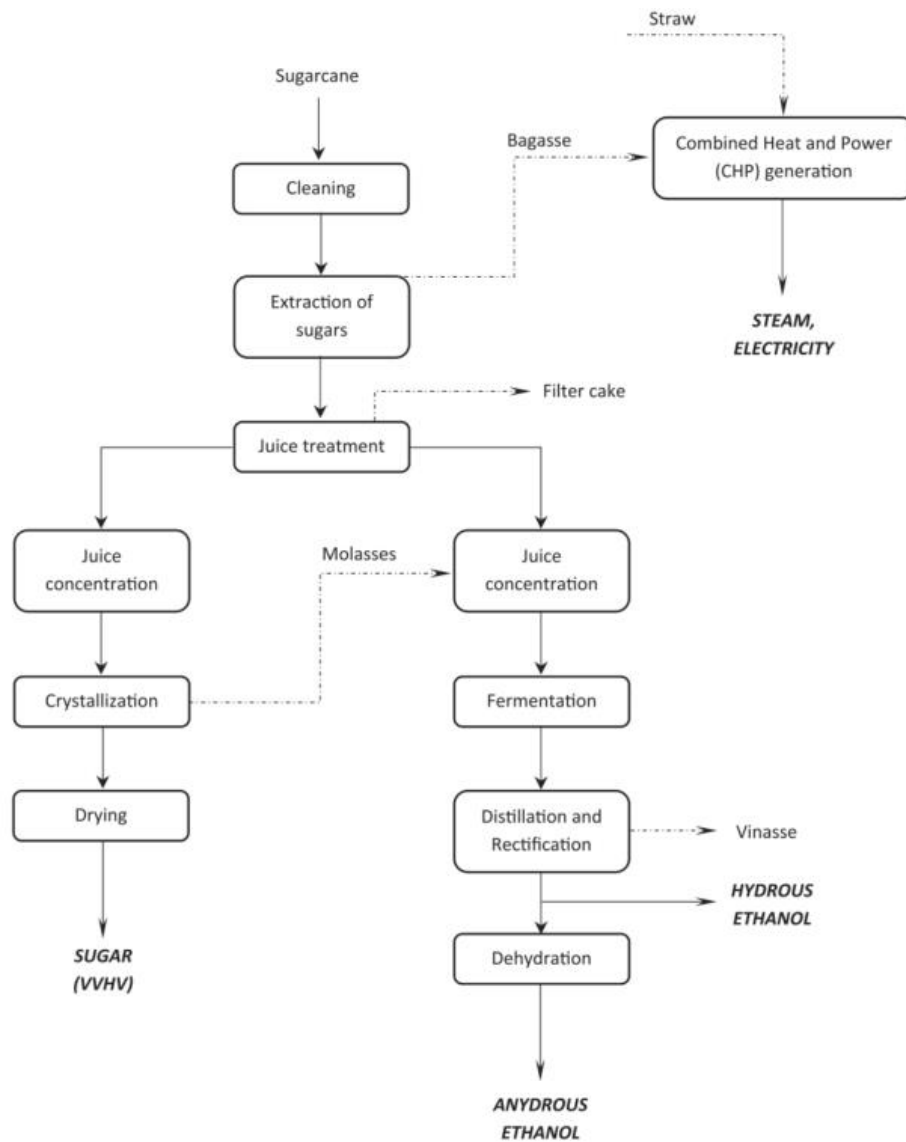


Figure 2: Simplified sugarcane to ethanol process. Extracted from (Manochio et al., 2017)

2.2.3. Ethanol from sugar-based feedstock – Sugar beet

Sugar beet is a root crop originally from Southeastern Europe, adapted to grow in soils with neutral pH, high water retention and aeration, with stable and mature production in Europe (Cruz & Dierig, 2015). The ethanol distillers from sugar beet are usually annexed to the sugar production units due to the costs and supply of the domestic sugar market. Thus, ethanol from sugar beet is usually obtained from beet molasses or beet syrup unless there is a high availability of beets during certain harvest periods. (Manochio et al., 2017).

Sucrose is stored in the roots and the production process of ethanol is similar to that of sugarcane, the major difference happens to be during the sugar extraction step. Sugar beet has a heavily mechanized harvesting process, ending with the reception of the roots without leaves and stems at the industrial unit. Cleaning and washing processes allow the retention of solid contaminants, preparing the beet to be thinly sliced, the cossettes. The cossettes sent to diffusers in which hot water is applied to extract the sugars. The water temperature (70–80 °C) is a fundamental extraction parameter. The fibrous sugar beet pulp is dried and sold for animal feeding. The extracted broth

follows a similar treating process to those found in the sugarcane-based process until ethanol dehydration. The overview of the process is depicted in

Figure 3.

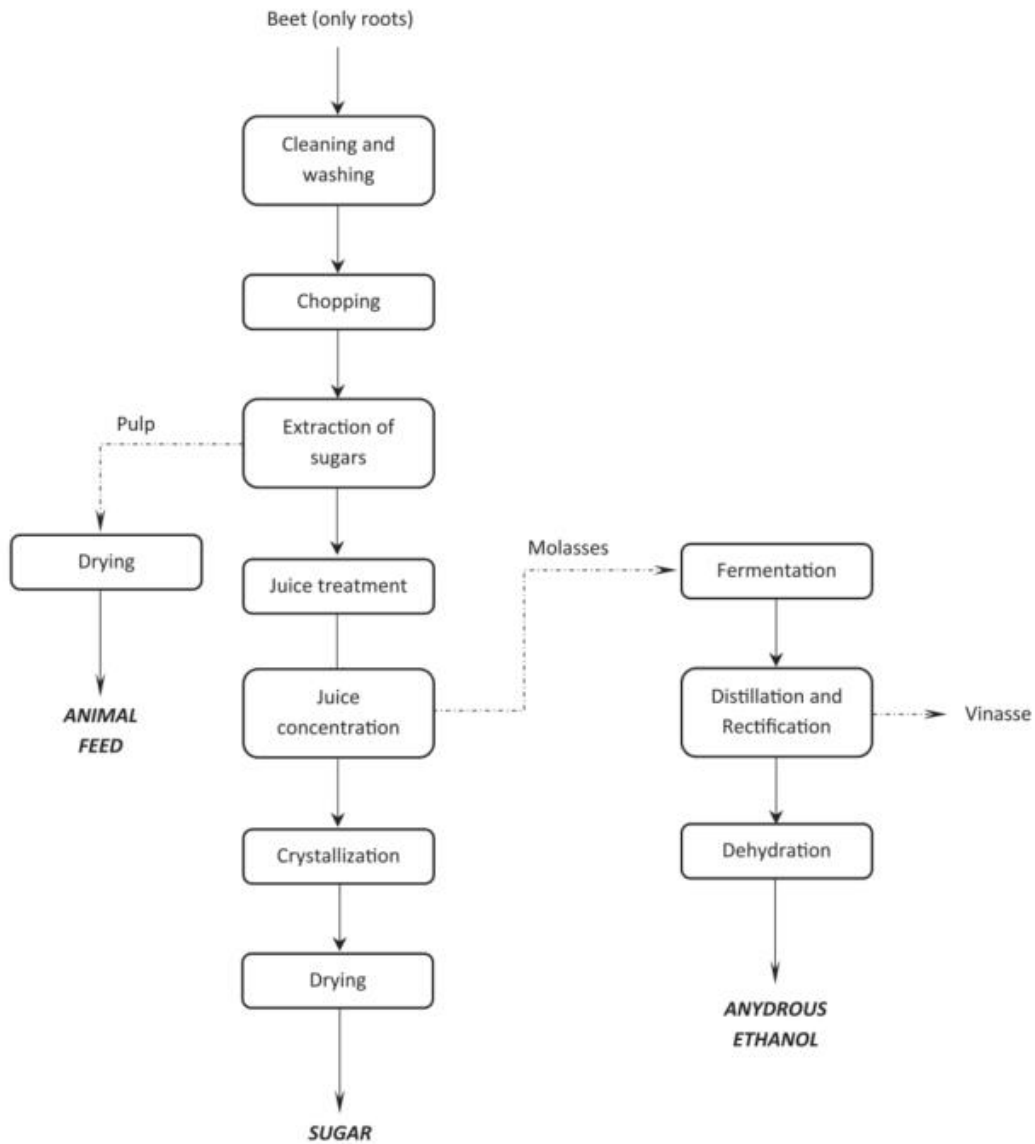


Figure 3: Sugar beet to ethanol simplified process. Extracted from (Manochio et al., 2017)

2.2.4. Starchy-based Feedstock – Corn

Although most of the starchy-based ethanol production comes from corn (~ 95%), it is also possible to find commercial-scale production from cassava and wheat (Bušić et al., 2018). The corn crop originated in Mexico, but today occupies about 150 million ha worldwide, extensively used for food and feed (FAOSTAT, 2015). It is a starch-rich grain whose productivity is negatively affected by water supply, temperature extremes and low solar irradiance. Starch is a mixture of linear and branched polyglucans, amylose and amylopectin. Amylose consists of linear glucose units joined by $\alpha(1-4)$ glycosidic bonds, amylopectin, in turn, is a branched polymer of glucose, which in addition to $\alpha(1-4)$ glycosidic bonds has branches (side chains) connected by $\alpha(1-6)$ glycosidic bonds (Murthy et al., 2011).

Conversely, to what is found in sugarcane and sugar beet processes, starch is not readily metabolized by yeast and, consequently, ethanol production from corn requires an additional conversion step called hydrolysis, or, saccharification. Essentially, the saccharification step breaks down starch into its constituent sugars, namely glucose, by means of enzymatic hydrolysis. There are many naturally occurring enzymes to depolymerize starch into glucose. Endoenzyme α -amylase hydrolyzes $\alpha(1-4)$ glycosidic bonds while glucoamylase is an exoenzyme that hydrolyzes both $\alpha(1-4)$ glycosidic bonds and $\alpha(1-6)$ glycosidic bonds. However, the hydrolysis rate of each type of bond is dependent on individual enzymes (Murthy et al., 2011). Therefore, enzyme production is a vital part of the corn-to-ethanol value chain, the reason why this industry has been growing solid in the USA.

Two strategies are used to process corn into ethanol, namely dry and wet-milling, differing in the initial treatment of the grains. Although the wet-milling process was predominant in the early '90s, dry-milling accounts for 90% of total ethanol production nowadays in the USA (Mueller, 2010). The whole kernel is ground in the dry-milling process and then mixed with water to form a mash which is liquefied by enzymatic hydrolysis. The resulting stream is cooked to prevent bacterial contamination and saccharified to glucose with glucoamylase enzymes. Finally, the cooled stream is destined for the fermentation step where glucose is converted to ethanol.

In the wet-milling process, corn kernel is soaked in water added with diluted sulfuric acid before grinding, facilitating elements segregation. The resulting stream is separated by centrifuge, screen and hydro cyclonic separators into germ, gluten, fibre and starch, where the first may be processed into corn oil (Manochio et al., 2017). Starch-rich liquor is destined for saccharification and the remaining components are dried and sold as feed, or further processed into gluten-based products.

The main difference between processes is that dry-milling has a higher ethanol yield (~15%), and lower CAPEX, but can be higher in OPEX. On the other hand, wet milling delivers high value-added coproducts (Mizik, 2021).

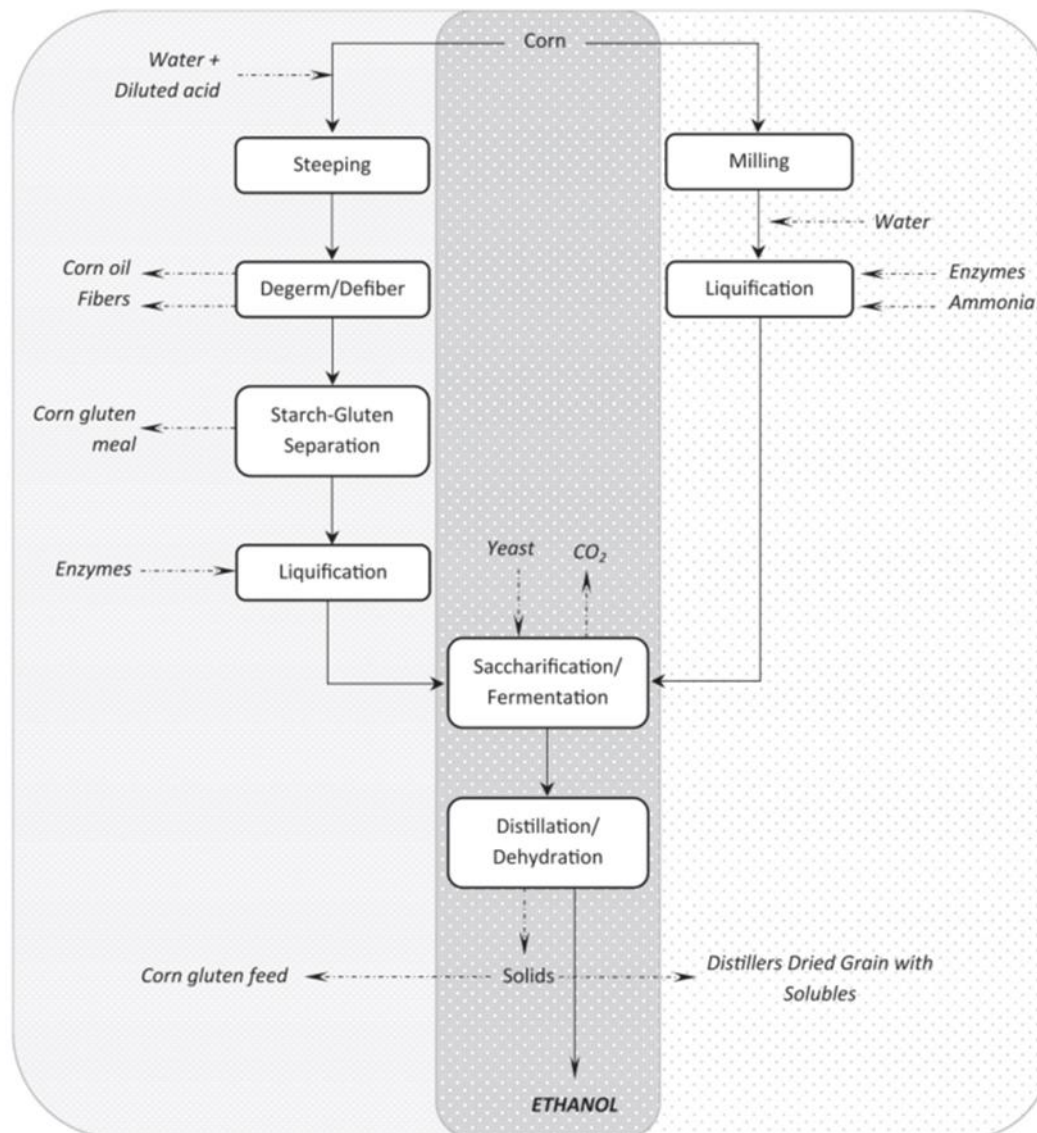


Figure 4: Simplified scheme of corn to ethanol production. The wet milling process is depicted on the left side, dry milling on the right side and common steps at the centre. Extracted from (Manochio et al., 2017)

2.2.5. Second-generation ethanol

The use of Lignocellulosic residues (LC) such as conventional food crop remains, is an attractive way to increase feedstock availability without the investment in additional land area. Ideally, any residue containing cellulose/hemicellulose is a suitable feedstock, e.g., forestry remains, food waste, crops and their remains, leaves, straw, paper and garden residues. Moreover, it is compatible with the circular economy principles, as this provides an answer to concerns around water and food security. Although LC is rich in carbohydrates, 40 – 90 wt% (Brandt et al., 2013), these sugars are not readily converted due to their molecular structure. Consequently, it must be treated, so that LC's molecular nature is changed into a more convenient arrangement favouring subsequent conversions. Such a process is called pretreatment (PT) and is considered the most important step to obtain an efficient conversion of LC's constituents (Ferrari et al., 2021).

LC materials are composed of three main constituents, namely cellulose, hemicellulose and lignin, as depicted in Figure 5, and the use of each component may vary based on process needs. Cellulose is the most abundant organic compound in nature. It is a linear polymer with high molecular weight, composed of glucose molecules. The glucopyranosyl monomers are linked by β 1-4 glycosidic bonds, which gives a stretched chain conformation for the molecule. Hydrogen bonds link those chains in a flat position, which differs from starch. The latter has α bounds in anomeric carbon, conferring it a helicoidal shape. The linear configuration enables cellulose chains to be packed in crystalline fibrils which hinders cellulose depolymerization into glucose (Ferrari, 2021). Hemicellulose has xylose and arabinose as major components, and mannose, galactose and glucose in lower proportion. Lignin is an amorphous polymer responsible for the vegetal inert property, providing hardness, hydrophobicity and resistance to enzymatic and chemical attacks (Ferrari, 2021).

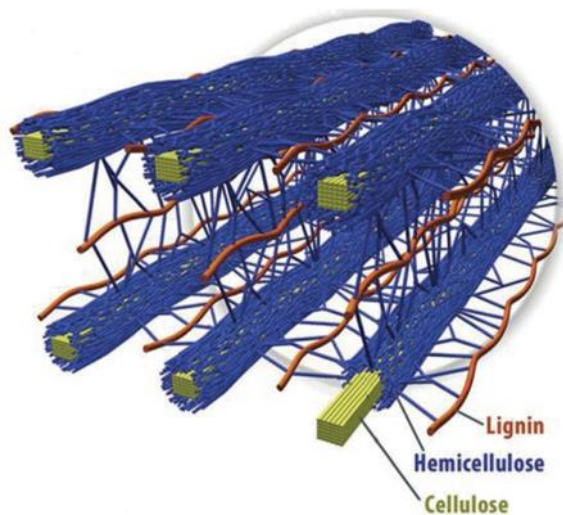


Figure 5: Lignocellulose polymer structure. Source: U.S Department of Energy Genome Program image gallery

The overall objective of pretreatment is to destabilize the LC matrix, making it more susceptible to further conversion. Efficient pretreatment processes should target:

- i) full carbohydrates recovery;
- ii) high yields on subsequent conversion steps, for instance during saccharification through enzymatic hydrolysis;

- iii) do not produce undesirable compounds from sugar and lignin decomposition decreasing overall yield of feedstock into products;
- iv) efficiently separate carbohydrate fractions and lignin;
- v) low energy demand; vi) low capital and operating costs (Ferrari, 2021). More information on pretreatment can be found elsewhere (Beig et al., 2020).

After pretreatment, the resulting slurry is separated into carbohydrates and lignin, depending on the selected method. The carbohydrate-rich stream is headed to the saccharification process, while lignin is mostly burned for heat recovery. The saccharification process consists of hydrolysis using a cocktail of different enzymes, specially endo-xylanases, cellulases and β -glucosidase. The resulting sugars prevent from cellulose are often addressed as C-6 sugars, whereas C-5 corresponds to those from hemicellulose, referring to the number of carbons present in the resulting sugar, glucose and xylose, respectively. In a scenario where the electricity production is covered by a large share of renewables, lignin can be diverted to chemical production, improving processes' overall economics and life cycle emissions (Ferrari et al., 2021; Cao et al., 2019; Maga et al., 2019).

Currently, 2G ethanol production is often annexed to 1G ethanol production to minimize CAPEX and OPEX. Even though improvements have been achieved over the past years, some hurdles need to be further addressed in order to bring 2G as cost-effective as 1G production, namely:

- i) high power and energy consumption;
- ii) recovery and recycling of auxiliary materials such as catalysts and solvents, when applicable;
- iii) scale-up towards lower CAPEX and OPEX per unit of product. OPEX hotspots are enzyme, capital and feedstock costs.

The overall process of 2G ethanol is depicted in **Figure** .

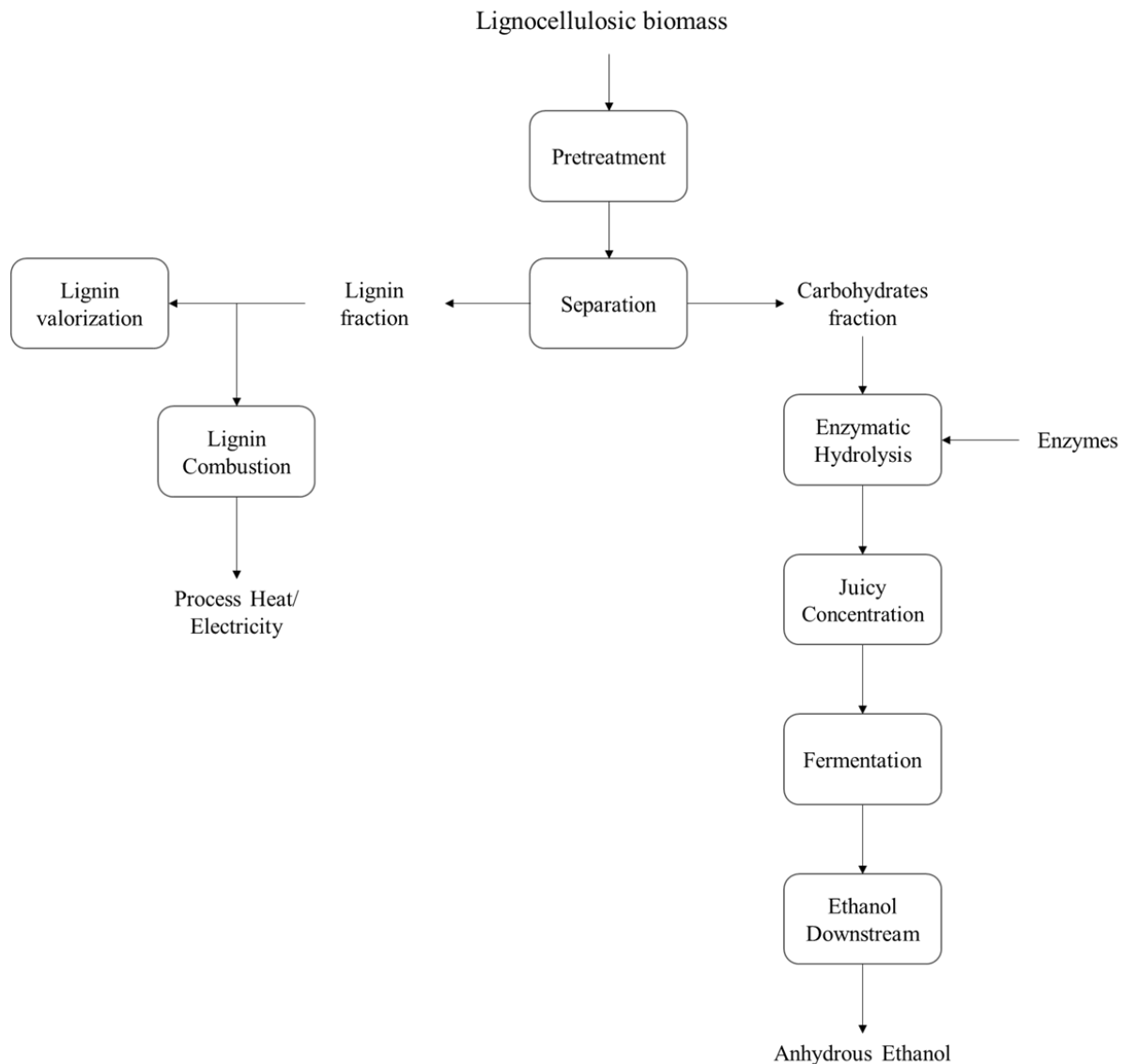


Figure 6: Overall production process of 2G ethanol

2.3. Ethanol from syngas fermentation

Ethanol production from gas, or syngas, fermentation has been considered an alternative to carbohydrate and lignocellulose-based processes due to the alleged feedstock flexibility and the potential to convert all parts of the biomass (including lignin). Moreover, such a route can benefit from off-gases that are currently being produced, for instance in the cement and steel industry.

The process consists of the use of syngas, instead of carbohydrates, as feedstock to microorganism fermentation to produce ethanol, usually using *Clostridium* genus bacteria. The conversion takes place anaerobically at 37 °C and does not need a specific H₂/CO ratio or the absence of CO₂ as requested by the chemical catalytic process and, therefore, the water-gas shift step may be needless (de Medeiros et al., 2017). The main by-product of the process is acetic acid, which is removed during the purification step. Ethanol recovery follows the same principle as these previously described carbohydrate-based processes.

A simplified process flowchart is given in Figure 7, where the carbon source follows biomass gasification to syngas. Processes considering syngas fermentation annexed to other industries, for instance, steel production, would benefit from flue gases and, consequently, the process would be assumed to start at the fermentation step (A300). A pre-cleaning of the gas stream is usually required to avoid inhibition by syngas contaminants. Detailed information on the syngas process can be found elsewhere (de Medeiros et al., 2017, 2021). The ethanol yields are comparable to other 2G processes found to be within 205 – 330 L per ton of dry biomass (de Medeiros et al., 2021). Currently, LanzaTech is the main player in this technology.

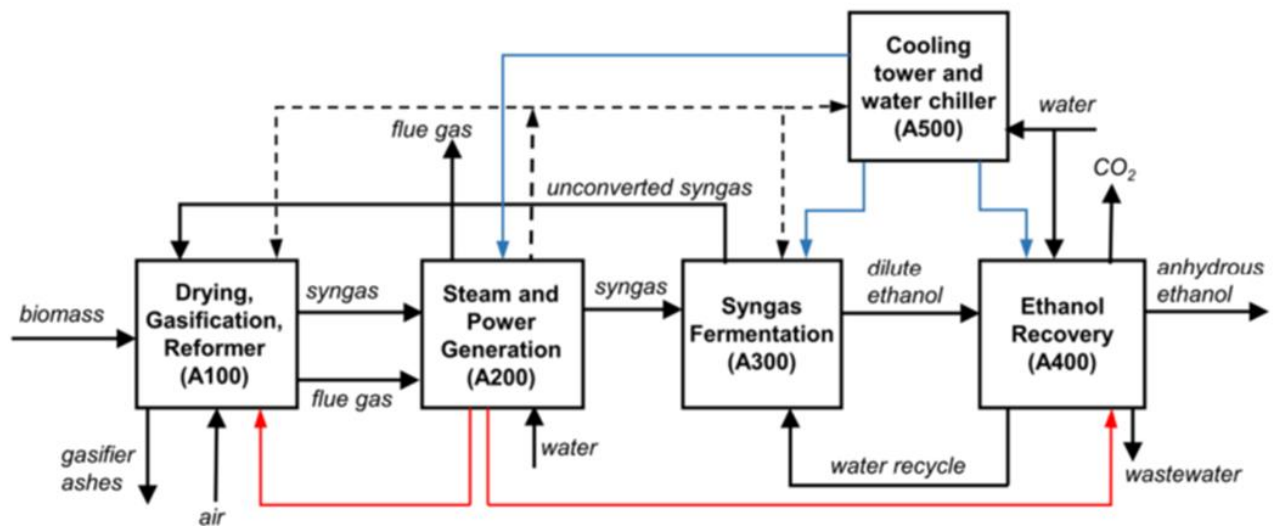


Figure 7: Syngas fermentation process example. Extracted from (de Medeiros et al., 2021).

2.4. Ethanol market

Ethanol global production is around 100 billion litres, led by USA and Brazil as depicted in Figure 8, and accounted for USD 93 billion in 2020, expected to grow at a CAGR of 5.2 % (Precedence Research, 2022).

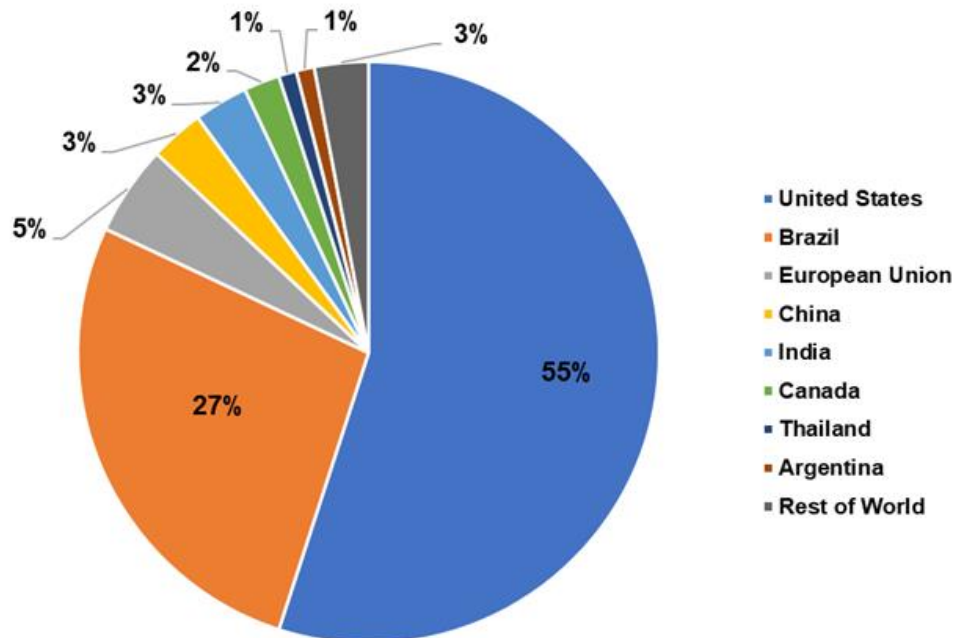


Figure 8: Global ethanol production breakdown (Renewable Fuels Association, 2022)

Sugarcane-based ethanol is the most cost-effective production; its production cost in Brazil is 0.24–0.42 USD/L, while corn-based US ethanol is 0.50–0.87 USD/L, and sugar beet-based EU ethanol costs 0.46–0.77 USD/L (Mizik, 2021).

For advanced ethanol, it is found a production cost of 0.60 – 1.21 USD/L for 2G ethanol and 0.71 – 1.20 USD/L for the syngas fermentation process (de Medeiros et al., 2017).

Although ethanol (2G) production dates back to 1938, Borregard (Sapsborg – Norway), nearly all of the current production follows 1G processes.

Table 3 summarizes the current major cellulosic ethanol projects at a commercial scale.

Table 3: Major projects on cellulosic ethanol production at commercial scale. (Padella et al., 2019)

Company	Project	Country	Output Capacity (ktons)	Status	Start-Up Year
Abengoa Bioenergy Biomass of Kansas, LLC	Commercial (acquired by Synata Bio Inc. [21])	US	75	idle	2014
Aemetis	Aemetis Commercial	US	35	planned	2019
Beta Renewables (acquired by Versalis [22])	Alpha	US	60	on hold	2018
Beta Renewables (acquired by Versalis)	Energochemica	EU (Slovakia)	55	on hold	2017
Beta Renewables (acquired by Versalis)	Fujiang Bioproject	China	90	on hold	2018
Beta Renewables ¹ (acquired by Versalis)	IBP-Italian Bio Fuel	EU (Italy)	40	idle	2013
Borregaard Industries AS	ChemCell Ethanol	Norway	16	operational	1938
Clariant	Clariant Romania	EU (Romania)	50	under construction	2020
COFCO Zhaodong Co.	COFCO Commercial	China	50	planned	2018
DuPont	Commercial facility Iowa (acquired by VERBIO [23])	US	83	idle	2016
Enviral	Clariant Slovakia	EU (Slovakia)	50	planned	2021
Fibrigh LLC	Commercial Plant	US	18	under construction	2019
GranBio	Bioflex 1	Brazil	65	operational	2014
Henan Tianguan Group	Henan 2	China	30	Idle	2011
Ineos Bio	Indian River County Facility (acquired by Alliance Bio-Products in 2016 [24])	US	24	idle	NA
Longlive Bio-technology Co. Ltd.	Longlive	China	60	Idle	2012
Maabjerg Energy Concept Consortium	Flagship integrated biorefinery	EU (Denmark)	50	on hold	2018
POET-DSM Advanced Biofuels	Project Liberty	US	75	operational	2014
Raízen Energia	Brazil	Brazil	36	operational	2015
St1 Biofuels Oy in cooperation with North European Bio Tech Oy	Cellunolix®	EU (Finland)	40	planned	2020

In 2020, the fuel market accounted for about 80% of renewable ethanol use in Europe. Total domestic production was around 5.6 billion litres, which corresponds to 86 % of the total installed capacity. Figure 9 illustrates the European renewable ethanol market by application. Figure 10 depicts the historical and projected prices of ethanol by region.

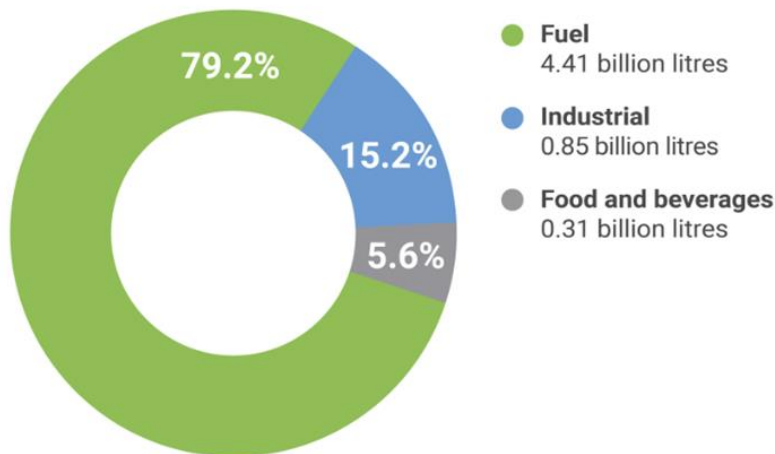


Figure 9: European renewable ethanol production by end-use. (ePure, 2022)

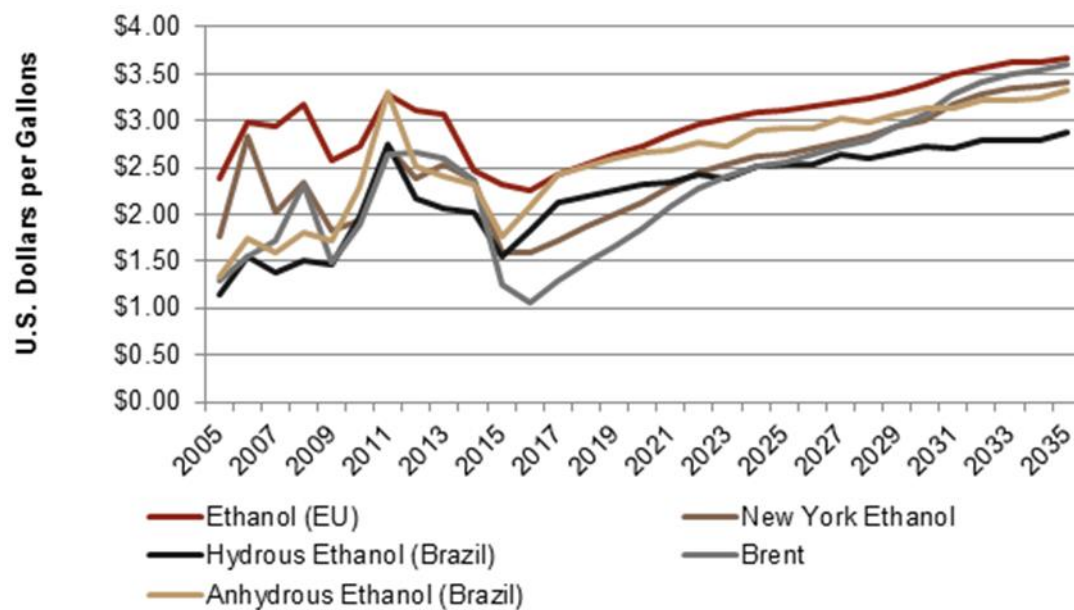


Figure 10: Historic and projected ethanol prices (Stratas Advisors, 2017)

2.5. Sustainability of Ethanol

Environmental assessment provides critical criteria for renewable energy technology development. The life cycle assessment (LCA) tool is widely applied to identify potential environmental impacts of a given product, by considering not only the production process itself but also the background activities and disposal of every relevant input and output. Historically, LCA studies regarding first-generation ethanol manufacturing point to the agricultural phase as the main emission hotspot in the product cycle (Ferrari et al., 2021).

In the second generation, where different chemicals and inputs are introduced, there are more process-bound emission contributions to be expected, which generally give rise to the industrial phase as the main emitting phase. Figure 1111 depicts GHG emission breakdown for 1G and 2G ethanol production in Brazil, where energy use during the industrial phase is mitigated by burning the excess of bagasse and straw in boilers for heat recovery. For the corn and sugar beet process, a major share of emissions in 2G comes from external energy requirements, added to these shown in **Table 4** (Murali & Shastri, 2022).

Nevertheless, the efficiency of the second-generation process in mitigating GHG emissions is usually also dependent on the agricultural phase, where the choice of feedstock is of great importance (Ferrari et al., 2021). Therefore, one must evaluate the current scenario for feedstock availability, thus considering existing economic, social and environmental figures while assessing ethanol production technologies.

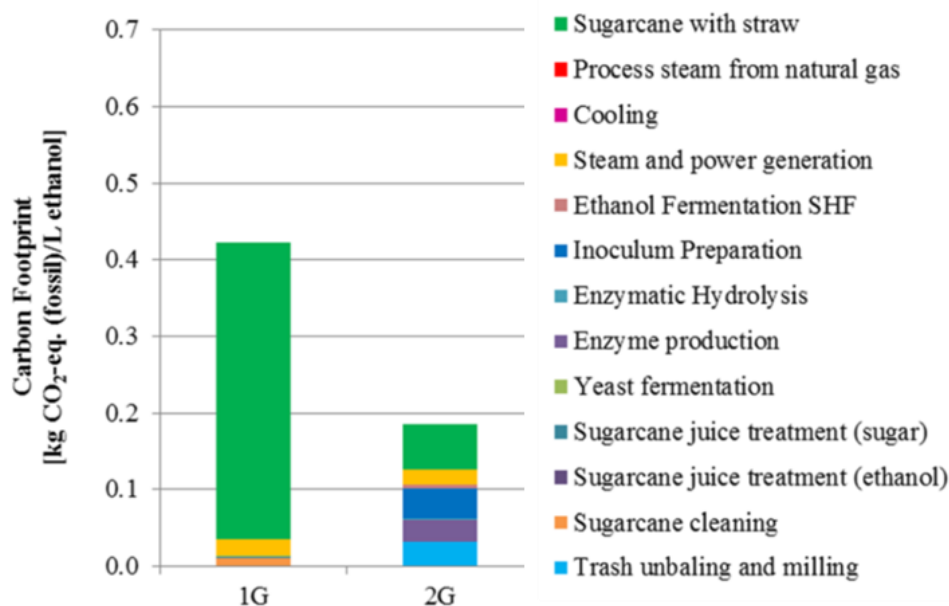


Figure 11: GHG emission breakdown of 1G and 2G ethanol, Brazilian scenario. Extracted from (Maga et al., 2019)

The production of ethanol from any kind of feedstock requires considerable amounts of energy, especially in the form of heat and electricity. A significant share of energy can be provided by the residues of feedstock harvesting and processing, in the sugarcane scenario, the energy balance within the industrial boundary can be positive, thus the excess of heat converted to electricity is sold as a by-product as bio-electricity. For the sugar beet and corn, on the other hand, the industrial process hardly benefited from residues, whether by destitute of residues in the case of sugar beet, or, due to soil fertility requirements in the case of straw and corn stover for the second. Moreover,

starch-based ethanol processes present a higher energy consumption than sugar-based feedstock due to the saccharification step, which requires on average 4 MJ per litre of ethanol produced. Taking together, feedstock cultivation and energy input during the industrial phase are highlighted as the hotspots affecting the sustainability and energy efficiency of ethanol processes, as summarized in Table 4 for ethanol 1G. Emissions from sugar beet and corn processes may be reduced when using renewable heat, for instance, wood pellets rather than natural gas.

Table 4: Greenhouse gas emissions of first-generation (1G) ethanol production based on corn, sugarcane and sugar beet within the production phases.

Sector	Average emissions (g CO ₂ MJ ⁻¹)		
	Sugarcane	Corn	Sugar beet
Agricultural phase	18.35	28.3	12
– Crop cultivation	2.79	10.3	8.4
– Straw burning	3.72	n.a.	n.a.
– Farm machinery	0.26	n.s.	1.2
– Soil emissions	6.36	14.1	n.s.
– Transport and agricultural operations	5.22	3.90	2.4
Industrial phase	1.14	28.8	26.8
– Chemicals and lubricants	0.84	19.7	n.s.
– Plant and equipment	0.30	9.10	n.s.
Final product distribution	2.28	1.40	1.20
Products and co-products credits	–9.41	–16.5	–2.20
Life cycle net emissions	12.4	42.0	37.8
Total emissions (kg CO_{2eq} L⁻¹ ethanol)	0.25	1.70	0.41
Avoided emissions (%)	69–89	–30–38	35–56

Extracted from (Manochio et al., 2017)

Advanced or 2G ethanol LCA emissions will be most impacted by the industrial phase, especially by energy consumption and solvent/catalyst recycling deployed during pretreatment (Ferrari et al., 2021). Usually, biomass is used both as an energy heat source and feedstock for ethanol production. The more energy intense the process is, the more biomass will be demanded heating purposes, decreasing overall productivity. Lower productivity leads to higher emissions per unit of ethanol and, following the same principle, higher production costs per unit of product. Therefore, heat integration is a vital part of process design in 2G ethanol projects.

Figure 112 depicts the range of GHG emissions on the LCA well-to-wake approach for ethanol in comparison to other fuels for marine use. In terms of GHG reduction, both ethanol of the first generation (1G) and ethanol of the second generation (2G) are comparable with bio-methanol.

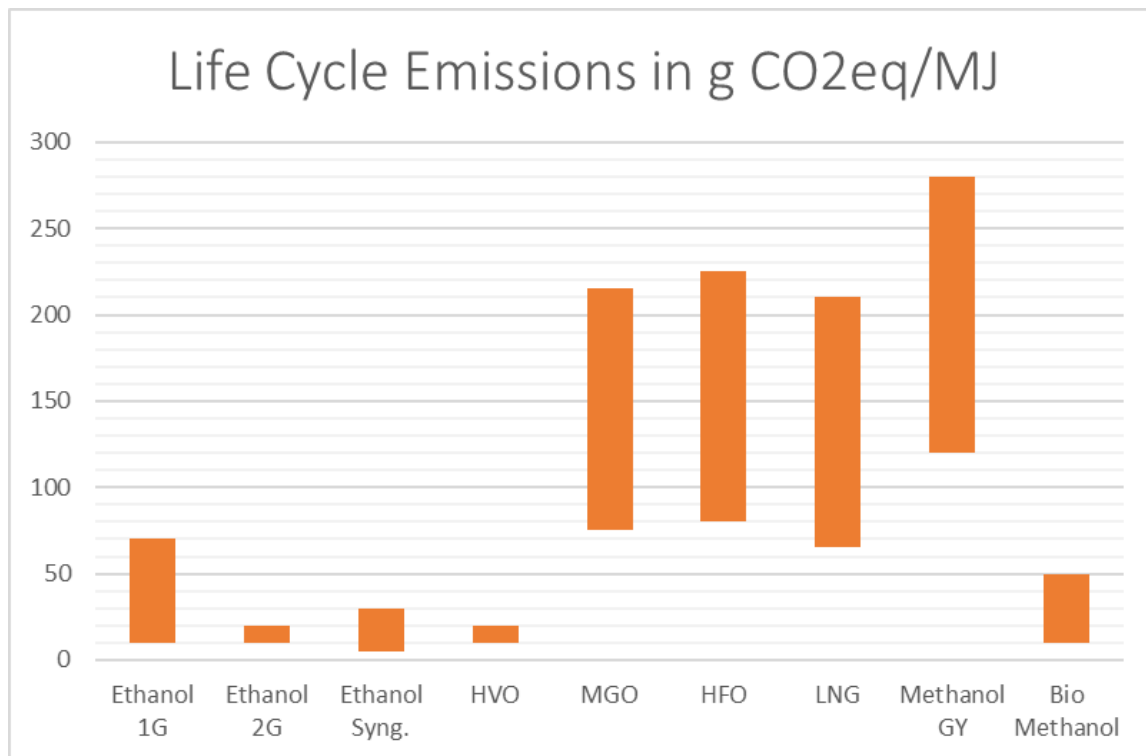


Figure 12: Greenhouse gases emission in g CO₂eq/MJ for different fuels on well to wake LCA.

(Data extracted from Irena (Brynolf et al., 2014; Handler et al., 2016; Hsieh & Felby, 2017; Pereira et al., 2019; Balcombe et al., 2019; de Souza et al., 2021; Ferrari et al., 2021; Studio GearUp 2021)

Based on these values the following average emissions are used for further calculations as depicted in Figure 13.

	Average Emissions in g CO ₂ eq/MJ
MGO	150
HVO	15
Grey Methanol	200
Bio-Methanol 2G	30
Ethanol 1-1,5G	40
Ethanol 2G	20

Figure 13: Average emissions in g CO₂ eq/MJ used for calculations

It should be noted that the Average Life Cycle Net Emissions of Bio-ethanol produced from sugarcane are considerably lower than from Bio-ethanol produced from Corn or Sugar beet. This is not reflected in the average value used (40) for further calculations.

It should also be considered that HVO is mainly produced from Used Cooking Oil, which primarily has palm oil as its feedstock. The debate that bio-ethanol is not considered a sustainable fuel, because it is part of the food-for-fuel discussion can also be indirectly applied to the discussion on HVO with its feedstock of palm oil.

3. Ethanol as a marine fuel

3.1. Ethanol as a marine fuel with regard to safety

Although ethanol as a fuel for road transport is well developed, ethanol as a fuel for maritime applications has hardly developed. The rules and regulations of many class societies are developed for both methanol and ethanol fuels, e.g. American Bureau of Shipping, Lloyds Register, Bureau Veritas, ClassNK etc. In general, there is little distinction in the class rules for methanol and ethanol as fuel. However, ethanol is less toxic than most other alternative marine fuels when looking at the different hazard classes. (see also Figure 14 and 15)

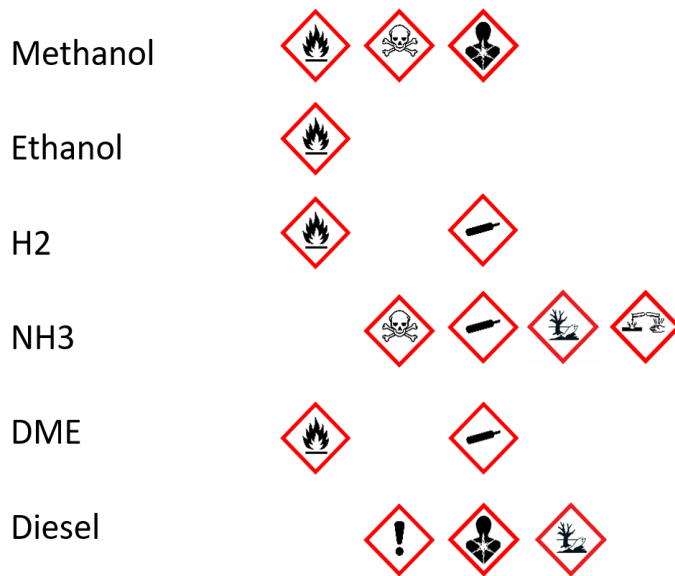


Figure 2: Hazard classes for several alternative marine fuels

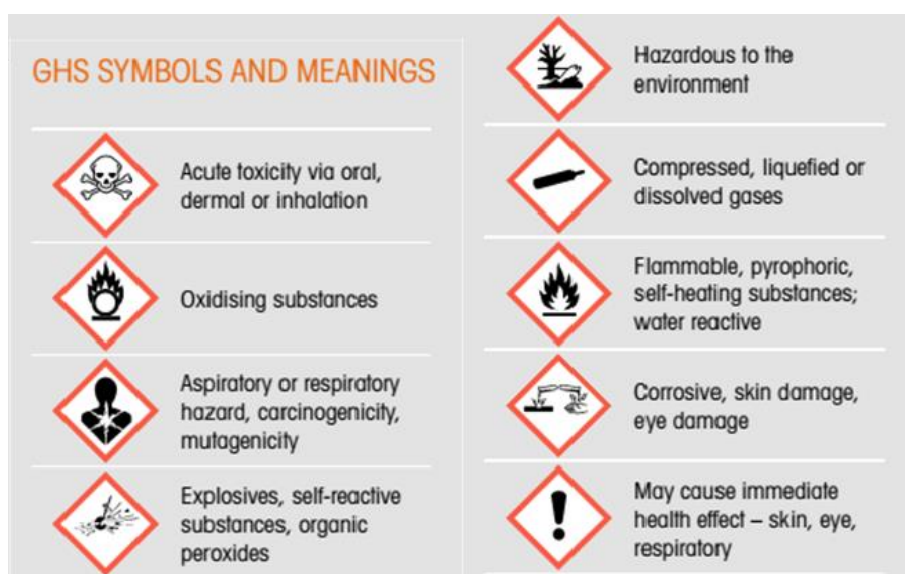


Figure 35: Hazard class symbols and meanings

The EMSA report describes the Derived No Effect Levels (DNEL) and Predicted No-effect Concentrations (PNEC) of methanol and ethanol in marine water as are depicted in table 5 and 6.

Table 5: Toxicity levels of methanol and ethanol from the EU Chemicals Agency Database

Toxicity Measure	HFO	MGO (Fuel oil No. 2)	LNG	Methanol	Ethanol
DNEL (Acute tox., inhalation) [mg/m ³]	not calculated	0.12	not calculated	260	950
DNEL (Acute tox., dermal) [mg/kg bodyweight per day]	not calculated	0	not calculated	40	343
PNEC Secondary poisoning oral [mg/kg food]		not calculated	not calculated	not calculated	720
PNEC Marine water [mg/L]	not calculated	not calculated	not calculated	2.08	0.79

Extracted from (EMSA, 2015)

It can be concluded that the DNEL for Methanol inhalation is 130 mg/m³ while the DNEL for Ethanol is 950 mg/m³.

Also, the DNEL for methanol via dermal contact is 40mg/kg body weight per day, while for ethanol this is 343 mg/kg body weight per day.

Although the values for both methanol and ethanol are safe when handled properly, it also shows that ethanol is less toxic than methanol.

The EMSA report also describes the compatibility of selected materials with methanol and ethanol.

Table 6: Compatibility of selected materials with methanol and ethanol.

Material	Methanol	Ethanol
Lead	mildly corrosive	sensitivity to degradation [33]
Aluminium alloys	Pure anhydrous methanol is mildly corrosive - periodic inspection and non-destructive testing recommended. Methanol-water solutions can be corrosive depending on application and environmental circumstances.	sensitivity to degradation [33]
Mild steel	Typically used as a construction material in cases where moisture can be excluded from the system. In presence of moisture and inorganic salts potential for corrosion within weld-heat-affected zones. Weld integrity can become an issue.	acceptable resistance to corrosion [33]
316 L stainless steel or a titanium or molybdenum stabilized grade	Recommended instead of mild steel in cases where moisture and inorganic salts may exist	acceptable resistance to corrosion [33]
low carbon 300 series stainless steel	Best practice	acceptable resistance to corrosion [33]
nitrile (Buna-N)	Suitable. Service in flowing methanol not recommended, not recommended for gaskets.	Recommended for hoses and gaskets but not for seals [34]
rubber	Natural rubber considered good, butyl rubber is poor. Many others ok.	Natural rubber degrades when in contact [33], urethane rubber is not recommended [34]
nylons	suitable	nylon 66 not recommended [34]
neoprene	Suitable	Recommended for hoses and gaskets but not for seals [34]
ethylene propylene (EPDM)	Suitable	Polypropylene and polyethylene recommended, polyurethane not recommended [34]
methyl-methacrylate plastics	No statement	degrade when in contact [33]
Teflon	good dimensional stability and is resistant to attack and degradation	Recommended [34]

Extracted from (EMSA, 2015)

Limited test results are available with regard to corrosion of methanol and ethanol in non-coated integrated steel and aluminium tanks on board ships and their maritime environment.

3.2. Ethanol as a marine fuel with regard to engine technology

The combustion-relevant physicochemical parameters for ethanol have been summarized and compared with popular engine fuels in table 7. The description of these properties provides the necessary background for discussing possible engine conversion paths.

3.2.1. General properties

The chemical formula for ethanol is C_2H_5OH , which stands for ethyl alcohol. Since ethanol has a hydrogen to carbon (H/C) ratio of 3 to 1, it can be categorized as a fuel with a comparatively low carbon content. When molar mass and lower heating value are taken into account, ethanol combustion emits around 10% less CO_2 than a diesel with the same efficiency.

When used in larger quantities, ethanol can be fatal to humans. However, other living organisms can decompose it relatively fast. Consequently, compared to other fuels, it provides essentially no ecological threat when spilled into the sea. Large-scale spills would, however, result in more sea vegetation. Additionally, unlike LNG, vapour slip has no effect on GHG emissions.

Ethanol is mixable in water, gasoline and alcohol, yet creates a stratified mixture with diesel and other oils. As shown in table 7, the boiling point of ethanol is $78.2^{\circ}C$ and its freezing point is $-114^{\circ}C$, which results in a liquid phase of ethanol at room temperature. This gives the possibility to use storage tanks with the same provision as gasoline. The flash point refers to the temperature at which the fuel forms an ignitable mixture with air. The value of this parameter for ethanol ($12^{\circ}C$) is lower compared to diesel ($78^{\circ}C$), yet much higher compared to LNG ($-45^{\circ}C$ and $-136^{\circ}C$ respectively). Despite this, ethanol is still considered a low flash point fuel, which carries risks during storage and requires handling procedures similar to those for LNG.

Additionally, ethanol is infamous for being corrosive. Some components of contemporary combustion engines may need to be redesigned to accommodate ethanol, or corrosion inhibitors may need to be added to the fuel to increase fuel durability.

3.2.2. Combustion-related properties

Cetane and octane numbers are used to categorize fuels for combustion engines. The ability to self-ignite is measured by the cetane number, and the capacity to withstand impacts is measured by the octane number. Ethanol is excellent for SI engines with a greater compression ratio because it has a higher octane number than gasoline and won't cause knocking. As a result, compared to a gasoline engine, a SI engine can achieve better efficiency. Low cetane number indicates poor self-ignition characteristics, which are supported by high auto-ignition temperature. Therefore, without significant hardware modifications or fuel reforming, ethanol is typically not preferred for direct deployment in CI engines.

Because ethanol doesn't include sulphur (S), there are no SO_x emissions produced during combustion. The amount of oxygen required to accomplish full combustion is indicated by the stoichiometric air-to-fuel ratio (AFR). In comparison to diesel and LNG, ethanol requires less air for combustion because to its oxygen content.

The lower heating value (LHV) of methanol is roughly two-thirds that of diesel, necessitating the use of more fuel to provide an equivalent amount of power. As a result, larger fuel storage facilities have ranges similar to diesel. To meet the increased fuel flow demand, it is also necessary to install new injectors. Since ethanol's stoichiometric air/fuel ratio is around two-thirds that of diesel, its higher injection mass needs about the same amount of air to achieve complete combustion. Therefore, no

power loss is anticipated when the engine is changed to ethanol because the engine volume and volumetric efficiency remain the same.

Because ethanol has a lower kinematic viscosity than diesel, it may be harder for injection pumps and injectors to remain lubricated. However, this problem can be solved by using sealing oil for pump lubrication in addition to the regular fuel line. For direct injection applications, lower kinematic viscosity will also affect spray patterns. Other solutions include employing viscosity improvers in addition to gasoline or altering the injection pumps to directly facilitate ethanol.

Ethanol vaporizes at a heat of vaporization (kJ/kg) that is nearly 4 times higher than diesel fuel. During the compression stroke, when liquid fuel is delivered into the cylinder, it absorbs heat energy through evaporation. In order for liquid fuel to evaporate, it must absorb a greater amount of energy, which causes the temperature inside the cylinder to drop. For Direct Injection Compression Ignition (DICI) concepts operating on ethanol, this results in longer ignition delays and, generally, lower NO_x emission, which is a highly temperature-dependent process.

Compared to gasoline, alcohol fuels often have a larger range of flammability restrictions. It permits the use of thinner mixes, which could, in theory, result in higher thermal efficiency. Because ethanol has a laminar flame propagation velocity that is similar to that of conventional fuels, its combustion times are also similar.

Table 7: List of most relevant combustion engine-related physicochemical parameters of several alternative marine fuels

Properties	Diesel	Ethanol	Methanol
Chemical structure	C ₁₂ H ₂₆ –C ₁₄ H ₃₀	C ₂ H ₅ OH	CH ₃ OH
Molecular weight	190–220	46.07	32.042
Density (kg/m ³)	830	789	790
Viscosity at 298.15 K (mPa s)	3.35	1.2	0.59
Boiling point (C)	180-360	78.2	65
Freezing point (C)	-1 to -4	-114	-98
Auto-ignition temperature (C)	220-260	365	450
Lower heating value (MJ/kg)	42.60	26.7	19.9
Vaporization heat (kJ/kg)	260	924	1110
Octane number	15-25	113	111
Cetane number	45–50	12	3
Stoichiometric air/fuel ratio	14.5	9.1	6.5
Flame speed (cm/s)	35-40	35.4	45–52.3
Flammability limits (vol)	1.85-8.2	3.3-29	6.7-36
Adiabatic flame temperature (C)	2054	2082	1870
Flash point (C)	78	12	11

4. Fuel cost and business case for various alternative fuels

4.1. Availability of various alternative marine fuels

The two most important factors for the success of any alternative marine fuel are fuel cost and availability.

From the International Energy Agency, an interesting graph was derived providing insight into the production of three alternative fuels, i.e. ethanol, biodiesel and HVO for the year 2019 and a forecast until 2025. Extracted from (IEA, 2019, updated 2022)

Bio-methanol was added to the graph since it is also considered a promising alternative fuel. However, the worldwide production capacity of bio-methanol in 2019 was estimated at a maximum of one million tons. To this date, it has not increased much and although Maersk is putting considerable efforts into securing green methanol for its new vessels it is not expected that the global production capacity of bio-methanol will exceed 3 million tons in 2025 with an average of 2 million tons in 2023- 2025. This is a serious issue for the ongoing development of green methanol as an alternative marine fuel.

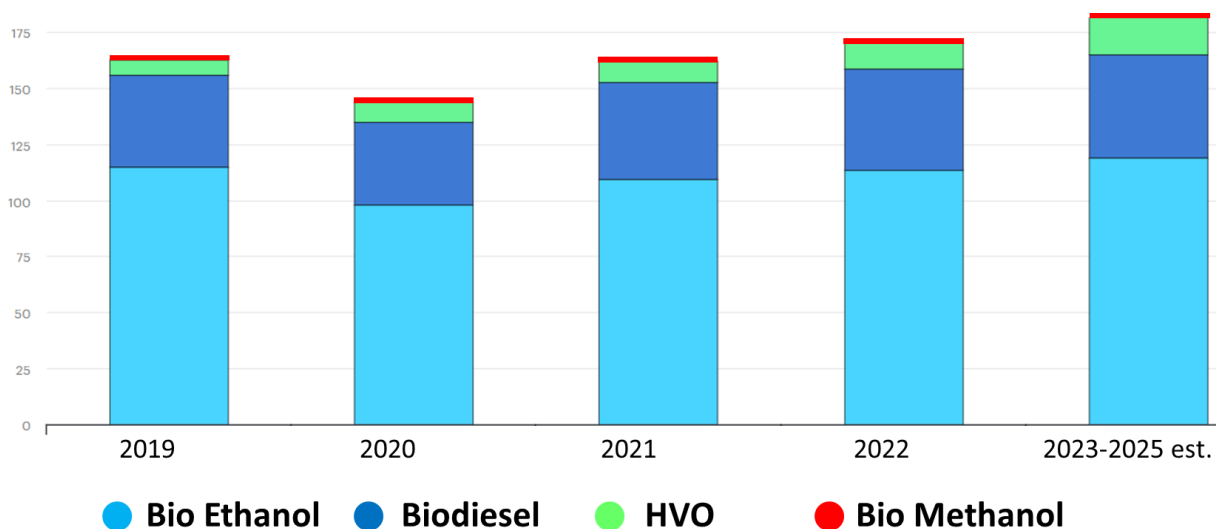


Figure 16: Availability of various alternative marine fuels in million tons per year.

At present, the average HFO and MGO consumption in the marine sector is estimated at approximately 350 million tons.

As of performance on feedstock conversion, ethanol and methanol have similar figures regarding carbon efficiency and energy efficiency, as depicted in Figure 17. Carbon efficiency relates to the amount of carbon in the starting raw material that ends up in final product. Energy efficiency will consider both the heating value of raw material and energy inputted into the production process in relation to the heating value of product, in this case, without considering the by-products.

It is important to mention, however, when considering by-products, efficiencies might change to higher values, specially in the case of ethanol production where several by-products are present, for instance electricity, sugar and protein. Methanol process is usually designed to avoid by-products formation by improved catalyst selectivity.

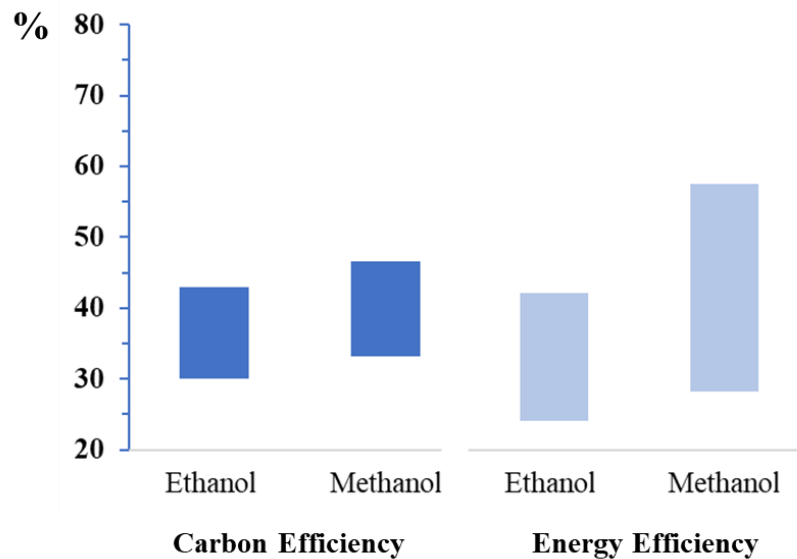


Figure 17: Carbon and energy efficiencies for bio ethanol and bio methanol production without considering by-products. (Haris *et al.*, 2021, Medeiros *et al.*, 2020 Manochio *et al.*, 2017)

4.2. Production costs of various alternative marine fuels

In this chapter, Bio-Ethanol is compared to different other alternative fuels and the base case of Marine Gas Oil (MGO). Hydrotreated vegetable oil (HVO) is an interesting alternative fuel in a regular diesel engine since it can be used as a so-called drop-in fuel, without having to make any adjustments to the existing diesel engine. Since HVO is usually produced from Used Cooking Oil (UCO) and other waste products and non-fossil. Therefore its emissions are regarded as not contributing to climate issues. In general, a 90% GHG emission reduction is used in calculations when using a 100% HVO blend. However, HVO has limited availability and fuel production costs tend to rise quickly.

Methanol is a promising alternative to diesel. It is not a drop-in fuel and therefore the engines need some modifications. At the moment, the most favoured option is a dual fuel engine on both diesel and methanol, where both fuels can be used in the engine. In the methanol mode, a small amount of diesel (max 5%) is used to ignite the methanol-diesel mixture in the combustion chamber. At present several ultra-large container vessels from e.g. Maersk and OOCI are built with two-stroke engines using methanol as a fuel. Also, four-stroke engines are developed for the use of methanol by Wartsila, ABC, MTU, Scania and others. In the Netherlands Van Oord and Acta Marine have ordered several ships with dual fuel engines using methanol as a marine fuel.

As can be seen in figure 12 the GHG emissions from fossil methanol are worse than MGO, but the GHG emissions of bio methanol are far better than any other fossil fuels (HFO, MGO and LNG). At the moment, methanol is mainly produced from fossil sources (coal and natural gas) resulting in relatively low production costs, comparable to MGO. Bio-methanol from wastes or biomass is more costly to produce and has limited availability. E-methanol produced from wind- and/or solar energy is starting to pick up as big players like Maersk are securing green methanol for their future vessels. Production costs for E-methanol are referred to in this study as compared to the costs mentioned in the IRENA report. An overview of production costs for the various fuels in Euro/GJ is depicted in figure 17.

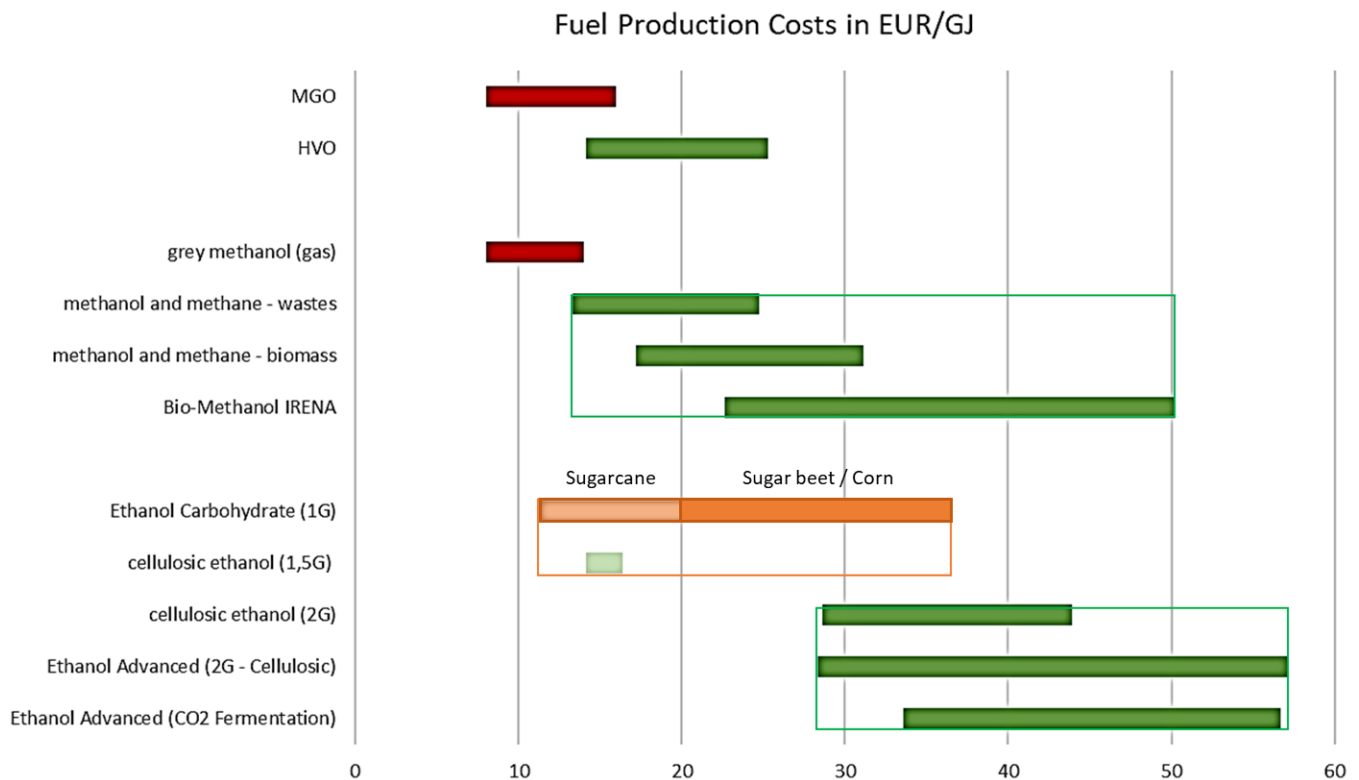


Figure 18: Production costs for the various fuels in Euro/GJ

Also, Bio-ethanol is an interesting alternative to diesel. As an alcoholic fuel, it has comparable characteristics to methanol and performs even better regarding energy density and safety issues. First-generation bio-ethanol is made from sugar cane, corn and sugar beet. In the European Union, the use of 1G bio-ethanol is not encouraged since it contributes to the discussion of fuel for food. In other countries, the use of 1G bio-ethanol as a fuel is not regarded as such a big issue. 1G Bio-ethanol is already produced in considerable amounts and is used in road transport in a mix with gasoline (E5 and E10 gasoline, indicating 5% and 10% ethanol in gasoline).

Production costs for 1G bio-ethanol vary considerably based on the feedstock, with sugar cane on the lower end, competing with grey and bio-methanol. 2G bio-ethanol is considerably more expensive and is therefore not considered suitable as a marine fuel.

4.3. Production costs of fuel blends and associated emissions.

The fuel production costs of figure 18 (low, average and high) and the average emissions of figure 13 can be combined into a new graph with different blends, blend fuel costs and blend average emissions.

In table 8 the three costs scenarios (low, average and high fuel costs) and average emissions for various fuel blends are presented.

Only six blends, of two different fuels, that were deemed the most practical were selected, in order to keep the report readable. (1. MGO/HVO, 2. Grey Methanol/ Methanol2G, 3. Methanol2G/HVO, 4. EOH1-1,5G/Methanol2G, 5. EOH1-1,5G/HVO and 6. EOH1-1,5G, EOH2G).

The first two graphs still use the fossil fuel, MGO and Grey Methanol respectively and therefore these fuel blends contain red shades in the first column.

HVO, Methanol2G and Ethanol 2G are green fuels and therefore have green shades in their columns. Ethanol 1-1,5G is indicated with yellow shades in their columns. (following the colours of figure 16)

The first two columns of each graph provide the percentage of the blended fuels (e.g. 0% MGO and 100% HVO). The third, fourth and fifth columns indicate the fuel costs for the low, average and high costs scenarios (e.g. 14, 20, 25). The last column (in light blue) indicates the average emissions for the various blends in gr. CO₂eq /MJ (e.g. 15).

Now it is easy to compare different blends for a given required average emission.

In table 8 an example is given with an average emission of 30gr. CO₂eq/MJ, which is indicated in red fonts. For a low cost scenario and a required average emission of 30gr. CO₂eq/MJ it can be observed that a blend of 60% Bio Ethanol 1-1,5G and 40% HVO results in the lowest total fuel costs.

It should again be noted that the bioethanol costs are based on the averages of sugarcane, sugar beet and corn and that cellulosic ethanol 1,5G is also included in this cost range (see also figure 18). If cellulosic ethanol 1,5G and/or bio-ethanol 1G from sugarcane are considered individually the ethanol cost and their associated emissions would drop even further.

Table 8: Pricing of fuel blends and associated emissions

BLENDS in USD/GJ					AV EMISSION	BLENDS in USD/GJ					AV EMISSION
MGO %	HVO %	LOW PR	AV PR	HIGH PR	in g CO2eq/MJ	GY. MEOH %	MEOH 2G %	LOW PR	AV PR	HIGH PR	in g CO2eq/MJ
0%	100%	14	20	25	15	0%	100%	13	31	50	30
10%	90%	14	20	25	29	10%	90%	12	29	46	47
20%	80%	13	19	24	42	20%	80%	12	27	43	64
30%	70%	13	19	24	56	30%	70%	11	25	39	81
40%	60%	12	18	23	69	40%	60%	11	23	36	98
50%	50%	12	18	23	83	50%	50%	10	21	32	115
60%	40%	11	17	22	96	60%	40%	10	19	28	132
70%	30%	11	17	22	110	70%	30%	9	17	25	149
80%	20%	10	16	21	123	80%	20%	9	15	21	166
90%	10%	10	16	21	137	90%	10%	8	13	18	183
100%	0%	9	15	20	150	100%	0%	8	11	14	200
BLENDS in USD/GJ					AV EMISSION	BLENDS in USD/GJ					AV EMISSION
MEOH 2G	HVO %	LOW PR	AV PR	HIGH PR	in g CO2eq/MJ	EOH 1-1,5G %	MEOH 2G %	LOW PR	AV PR	HIGH PR	in g CO2eq/MJ
0%	100%	14	20	25	15	0%	100%	13	31	50	30
10%	90%	14	21	28	17	10%	90%	13	30	49	31
20%	80%	14	22	30	18	20%	80%	13	30	47	32
30%	70%	14	23	33	20	30%	70%	12	29	46	33
40%	60%	14	24	35	21	40%	60%	12	28	44	34
50%	50%	13	26	38	23	50%	50%	12	28	43	35
60%	40%	13	27	40	24	60%	40%	12	27	42	36
70%	30%	13	28	43	26	70%	30%	12	26	40	37
80%	20%	13	29	45	27	80%	20%	11	25	39	38
90%	10%	13	30	48	29	90%	10%	11	25	37	39
100%	0%	13	31	50	30	100%	0%	11	24	36	40
BLENDS in USD/GJ					AV EMISSION	BLENDS in USD/GJ					AV EMISSION
EOH 1-1,5	HVO %	LOW PR	AV PR	HIGH PR	in g CO2eq/MJ	EOH 1-1,5G %	EOH 2G %	LOW PR	AV PR	HIGH PR	in g CO2eq/MJ
0%	100%	14	20	25	15	0%	100%	28	43	57	20
10%	90%	14	20	26	18	10%	90%	26	41	55	22
20%	80%	13	21	27	20	20%	80%	25	39	53	24
30%	70%	13	21	28	23	30%	70%	23	37	51	26
40%	60%	13	22	29	25	40%	60%	21	35	49	28
50%	50%	13	22	31	28	50%	50%	20	34	47	30
60%	40%	12	22	32	30	60%	40%	18	32	44	32
70%	30%	12	23	33	33	70%	30%	16	30	42	34
80%	20%	12	23	34	35	80%	20%	14	28	40	36
90%	10%	11	24	35	38	90%	10%	13	26	38	38
100%	0%	11	24	36	40	100%	0%	11	24	36	40

4.4. Annual fuel cost based on Thetis MRV- data

For further comparison, vessel types were selected that are representative of the Netherlands maritime sector. The selection was made using the earlier study on marine fuels (Verbeek et al 2020) For these vessels, the EU Thetis MRV database was consulted, providing actual data on annual time at sea and fuel spent for the selected vessel type. The vessels selected are depicted in table 9.

Table 9: Selected vessels for the use of EU Thetis MRV data

	Power installed	Bunker Capacity	GJ	Time at sea	Fuel spent	
	kW	Ton Fuel		days	Ton Fuel/Day	GJ/Day
Multipurpose vessel of 3,500 DWT	1500	350	15000	213	6	256,2
Multipurpose vessel of 8,250 DWT	3000	550	23500	188	6	256,2
Multipurpose vessel of 12,500 DWT	5500	1150	49500	167	7	298,9
Multipurpose vessel of 17,250 DWT	7250	1500	64500	146	9	384,3
Chem Parcel Tanker of 17,250 DWT	5750	800	34500	158	8	341,6

The cost for conversion of these vessels towards the selected propulsion configuration and its alternative fuel are derived from table 10 and are based on the values of the previous EMSA report and work done by Brynolf, as no updated values seem to have been published in the meantime.

Based on the data in this table and the fuel cost values of figure 16 (low, average and high fuel costs) the annual fuel cost are calculated per vessel type in table 10.

Table 10: Annual fuel costs for selected vessel types based on Thetis MRV data.

		Diesel-MGO	Diesel-HVO	MEOH-Grey	MEOH-2G	EOH 1-1,5G	EOH 2G
Annual Fuel costs (average)	GJ/year	mIn USD/yr	mIn USD/yr	mIn USD/yr	mIn USD/yr	mIn USD/yr	mIn USD/yr
MP vessel of 3,500 DWT	93.513	1,40	1,87	1,03	2,90	2,24	4,02
MP vessel of 8,250 DWT	93.513	1,40	1,87	1,03	2,90	2,24	4,02
MP vessel of 12,500 DWT	109.099	1,64	2,18	1,20	3,38	2,62	4,69
MP vessel of 17,250 DWT	140.270	2,10	2,81	1,54	4,35	3,37	6,03
CP Tanker of 17,250 DWT	124.684	1,87	2,49	1,37	3,86	2,99	5,36
Annual Fuel costs (Low)	GJ/year	mIn USD/yr	mIn USD/yr	mIn USD/yr	mIn USD/yr	mIn USD/yr	mIn USD/yr
MP vessel of 3,500 DWT		0,85	1,31	0,75	1,21	1,03	2,62
MP vessel of 8,250 DWT		0,85	1,31	0,75	1,21	1,03	2,62
MP vessel of 12,500 DWT		1,00	1,53	0,87	1,41	1,20	3,05
MP vessel of 17,250 DWT		1,28	1,97	1,12	1,82	1,54	3,93
CP Tanker of 17,250 DWT		1,14	1,75	1,00	1,61	1,37	3,49
Annual Fuel costs (High)	GJ/year	mIn USD/yr	mIn USD/yr	mIn USD/yr	mIn USD/yr	mIn USD/yr	mIn USD/yr
MP vessel of 3,500 DWT		1,90	2,34	1,31	4,68	3,37	5,33
MP vessel of 8,250 DWT		1,90	2,34	1,31	4,68	3,37	5,33
MP vessel of 12,500 DWT		2,22	2,73	1,53	5,45	3,93	6,22
MP vessel of 17,250 DWT		2,86	3,51	1,97	7,01	5,05	8,00
CP Tanker of 17,250 DWT		2,54	3,12	1,75	6,23	4,49	7,11

From this table, it can be concluded that for the average fuel and the high cost scenarios, HVO as a sustainable fuel is a clear winner. However, for the low fuel cost scenario, bio-ethanol 1-1,5G is performing better than HVO. Bio-Ethanol 2G is in all cases the most expensive option for shipping.

Although Bio-Ethanol 1-1,5G has an excellent position to be used as an alternative marine fuel with regard to cost, availability, energy density and safety, there are to this date no vessels built with bio-ethanol 1G and 1,5G as the first fuel of choice.

5. Conclusions and recommendations

5.1. Conclusions

Bio-ethanol is a very interesting alternative marine fuel when compared to bio-methanol and HVO.

Bio-ethanol 1G produced from sugarcane and cellulosic ethanol 1,5G is performing better concerning production costs and life cycle emissions than bio-methanol and can even compete with HVO.

Bio-ethanol 2G is more expensive than bio-methanol 2G and HVO in all three researched scenarios (low fuel production cost, average fuel production cost and high fuel production cost).

The production volumes of bio-ethanol 1G and 1,5 are much higher than the current production volumes of bio-methanol and HVO and are therefore an interesting (temporary) option in the transition pathway towards zero-emission marine transport.

Bio-ethanol is less toxic than methanol with regard to the safety of crew and passengers. Bioethanol is also less harmful to the environment when compared to HVO.

Despite all these positive aspects of bio-ethanol as an alternative marine fuel, there are no vessels built with bio-ethanol as the first fuel of choice.

5.2. Recommendations

It is recommended to research the possibilities of the use of ethanol as marine fuel in more detail for special ship types, e.g. passenger vessels, work vessels and naval ships, especially where many people can be on deck. The toxicity levels of ethanol are considerably lower than methanol (see also table 5) and could prevent casualties in case of emergencies.

It is recommended to include the requirements for bio-ethanol as a marine fuel in vessels that are currently built with methanol as the first fuel of choice. This provides that ship owners with more flexibility in the choice of fuels for the long term.

In general, this implies that (dynamic) stability of the vessel and other safety issues with regard to corrosion and wear and tear (see also table 6) should be chosen with both methanol and ethanol in mind.

In general, the following research questions do remain:

- a. Ethanol combustion can reduce NO_x emissions, but the reduction is not expected to be sufficient for compliance with Tier 3 and Euro 5 regulations. Which additional measures have to be taken to comply with NO_x regulations?
- b. A higher efficiency of the engine may not be the case, and the lower heating value is lower compared to diesel fuel or gasoline. So the higher specific fuel consumption will result in higher total fuel consumption (in terms of total mass flow and required fuel storage). With a

reference to the operation profile of the ship, what will be the effect on the fuel storage facilities of the ship and the logistic refuelling opportunities?

- c. Although existing engines may be modified to spark-ignited ethanol engines, which engine and systems parts will have to be re-engineered with better corrosion-preventive materials?
- d. The transient behaviour and acceleration/deceleration performance of a single-fuel ethanol engine are expected to have lesser quality than the control stability of a diesel engine. Which control dynamics, control system and/or energy storage or electrical configuration should be applied to ensure the operational stability of an ethanol-driven ship propulsion system?
- e. Given the operational profile of the ship, what will be the investment cost and the exploitation cost of the resulting configuration and operational exploitation of the ship?
- f. Given the targets as defined in the Paris Agreement with regard to CO₂ emissions, what measures should be taken by international, European and national governing bodies to facilitate the transition of the maritime industries towards zero-emission in shipping?

6. New projects for bio-ethanol in marine applications

Projects for vessels that can sail on bio-ethanol could be developed in two different directions

6.1. Testbed projects

The first direction is the direction of developing more knowledge on the combustion processes in ethanol engines. This can be executed in testbed situations to obtain more detailed information on engine efficiency, robustness and exhaust gas emissions under different (simulated) operation conditions.

The most preferred and the most efficient way to do test bed research is to start with smaller high-speed engines for both single-fuel and dual-fuel concepts. TNO Automotive Centre in Helmond operates these testbed facilities and can run these tests for methanol engines with mono-fuel and dual-fuel concepts.

NLDA also develops a test bed location in Den Helder for testing engines for NLDA research and defence purposes. These facilities can also be used for executing test bed research on ethanol engines.

Finally, test bed locations of engine suppliers located in the Netherlands can be used for executing test bed research on ethanol engines. This research can be verified by experts from TNO and TU Delft to obtain independently verified results.

Depending on the support of the industry and especially the engine suppliers a project can be developed in 2023 on ethanol engine performance in a test bed situation.

6.2. Demonstrator projects

Next to the initial test bed project demonstrator projects, pilot projects are pursued on board real live ships. Talks have already started with interested organisations in the maritime industries that have a drive for green and emission-free shipping. This includes engine manufactures, marine equipment suppliers, marine services suppliers, classification societies, government bodies, shipyards, ship owners and ethanol suppliers.

It is envisioned that a vessel will be outfitted or retrofitted with an ethanol engine that can be tested for an initial period of 2-4 years on engine performance, combustion principles, exhaust gas emissions, robustness, etc.

These results will be used to provide ship-owners, classification societies and governmental bodies and ethanol suppliers with the required data regarding safety, durability, maintenance intervals etc. etc. Finally it will provide ship-owners with the required financial information about the integral cost for zero-emission in shipping.

References

- Balcombe, P., Brierley, J., Lewis, C., Skatvedt, L., Speirs, J., Hawkes, A., & Staffell, I. (2019). How to decarbonise international shipping: Options for fuels, technologies and policies. In *Energy Conversion and Management* (Vol. 182, pp. 72–88). Elsevier Ltd.
<https://doi.org/10.1016/j.enconman.2018.12.080>
- Beig, B., Riaz, M., Raza Naqvi, S., Hassan, M., Zheng, Z., Karimi, K., Pugazhendhi, A., Atabani, A. E., & Thuy Lan Chi, N. (2020). Current challenges and innovative developments in pretreatment of lignocellulosic residues for biofuel production: A review. *Fuel*.
<https://doi.org/10.1016/j.fuel.2020.119670>
- Brandt, A., Gräsvik, J., Hallett, J. P., & Welton, T. (2013). Deconstruction of lignocellulosic biomass with ionic liquids. *Green Chemistry*, 15(3), 550–583. <https://doi.org/10.1039/c2gc36364j>
- Brynolf, S., Fridell, E., & Andersson, K. (2014). Environmental assessment of marine fuels: Liquefied natural gas, liquefied biogas, methanol and bio-methanol. *Journal of Cleaner Production*, 74, 86–95. <https://doi.org/10.1016/j.jclepro.2014.03.052>
- Bušić, A., Mardetko, N., Kundas, S., Morzak, G., Belskaya, H., Šantek, M. I., Komes, D., Novak, S., & Šantek, B. (2018). Bioethanol production from renewable raw materials and its separation and purification: A review. In *Food Technology and Biotechnology* (Vol. 56, Issue 3, pp. 289–311). University of Zagreb. <https://doi.org/10.17113/ftb.56.03.18.5546>
- Cao, Y., Chen, S. S., Zhang, S., Ok, Y. S., Matsagar, B. M., Wu, K. C. W., & Tsang, D. C. W. (2019). Advances in lignin valorization towards bio-based chemicals and fuels: Lignin biorefinery. *Bioresource Technology*, 291(May). <https://doi.org/10.1016/j.biortech.2019.121878>
- Cruz, V. M. v., & Dierig, D. A. (Eds.). (2015). *Industrial Crops* (Vol. 9). Springer New York.
<https://doi.org/10.1007/978-1-4939-1447-0>
- de Almeida, M. A., & Colombo, R. (2021). Production Chain of First-Generation Sugarcane Bioethanol: Characterization and Value-Added Application of Wastes. *Bioenergy Research*.
<https://doi.org/10.1007/s12155-021-10301-4>
- de Medeiros, E. M., Noorman, H., Filho, R. M., & Posada, J. A. (2021). Multi-objective sustainability optimization of biomass residues to ethanol via gasification and syngas fermentation trade-offs between profitability, energy efficiency, and carbon emissions. *Fermentation*, 7(4).
<https://doi.org/10.3390/fermentation7040201>
- de Medeiros, E. M., Noorman, H., Maciel Filho, R., Posada, J. A. (2020). Production of ethanol fuel via syngas fermentation: Optimization of economic performance and energy efficiency. *Chemical Engineering Science*, Volume 5. <https://doi.org/10.1016/j.cesx.2020.100056>.
- de Medeiros, E. M., Posada, J. A., Noorman, H., Osseweijer, P., & Filho, R. M. (2017). Hydrous bioethanol production from sugarcane bagasse via energy self-sufficient gasification-fermentation hybrid route: Simulation and financial analysis. *Journal of Cleaner Production*, 168, 1625–1635.
<https://doi.org/10.1016/j.jclepro.2017.01.165>
- de Souza, N. R. D., Klein, B. C., Chagas, M. F., Cavalett, O., & Bonomi, A. (2021). Towards comparable carbon credits: Harmonization of lca models of cellulosic biofuels. *Sustainability (Switzerland)*, 13(18).
<https://doi.org/10.3390/su131810371>

Ellis, J., Tanneberger, K. (2015) Study on the use of ethyl and methyl alcohols alternative fuels in shipping. <https://www.emsa.europa.eu/damage-stability-study/items.html?cid=77&id=2726>

ePure. (2022, August 1). *European Renewable Ethanol*. <https://www.epure.org/>

FAOSTAT. FAOSTAT database on agriculture. FAO—food agric organ. United Nations; 2015

Ferrari, F. A. (2021). *Processing Lignocellulosic Feedstock Using Ionic Liquids for Biorefinery Application* [PhD, TUDelft]. <https://doi.org/10.4233/uuid:6acd402e-4436-440d-a5bf-fbd68c2bfdde>

Ferrari, F. A., Nogueira, G. P., Franco, T. T., Dias, M. O. S., Cavaliero, C. K. N., Witkamp, G. J., van der Wielen, L. A. M., & Forte, M. B. S. (2021). The role of ionic liquid pretreatment and recycling design in the sustainability of a biorefinery: A sugarcane to ethanol example. *Green Chemistry*, 23(22), 9126–9139. <https://doi.org/10.1039/d1gc02245h>

Handler, R. M., Shonnard, D. R., Griffing, E. M., Lai, A., & Palou-Rivera, I. (2016). Life Cycle Assessments of Ethanol Production via Gas Fermentation: Anticipated Greenhouse Gas Emissions for Cellulosic and Waste Gas Feedstocks. *Industrial and Engineering Chemistry Research*, 55(12), 3253–3261. <https://doi.org/10.1021/acs.iecr.5b03215>

Gartland, N. , Pruyn, J.F.J. (2021). Marine Biofuels Costs and Emissions Study for the European Supply Chain Till 2030. <https://repository.tudelft.nl/islandora/object/uuid%3A3be84817-975b-42bf-b0a1-3e9fa07709a1>

Hamelinck et all (2021), Conversion efficiencies of fuel pathways for Used Cooking Oil. https://www.studiogearup.com/wp-content/uploads/2021/03/2021_sGU_EWABA-and-MVaK_Options-for-the-deployment-of-UCO.pdf

Harris, K., Grim, R. G., & Tao, L. (2021). A Comparative Techno-Economic Analysis of Renewable Methanol Synthesis Pathways from Biomass and CO₂. Preprint www.nrel.gov/publications.

Hsieh, C.-W. C., & Felby, C. (2017). *Biofuels for the marine shipping sector Biofuels for the marine shipping sector An overview and analysis of sector infrastructure, fuel technologies and regulations*.

IEA (2022) Global biofuel production in 2019 and forecast to 2025. <https://www.iea.org/data-and-statistics/charts/global-biofuel-production-in-2019-and-forecast-to-2025>

Jambo, S. A., Abdulla, R., Mohd Azhar, S. H., Marbawi, H., Gansau, J. A., & Ravindra, P. (2016). A review on third generation bioethanol feedstock. *Renewable and Sustainable Energy Reviews*, 65, 756–769. <https://doi.org/10.1016/j.rser.2016.07.064>

Lam, E., Carrer, H., da Silva, J. A., & Kole, C. (Eds.). (2016). *Compendium of Bioenergy Plants*. CRC Press. <https://doi.org/10.1201/b19601>

Maga, D., Thonemann, N., Hiebel, M., Sebastião, D., Lopes, T. F., Fonseca, C., & Gírio, F. (2019). Comparative life cycle assessment of first- and second-generation ethanol from sugarcane in Brazil. *International Journal of Life Cycle Assessment*, 24(2), 266–280. <https://doi.org/10.1007/s11367-018-1505-1>

Manochio, C., Andrade, B. R., Rodriguez, R. P., & Moraes, B. S. (2017). Ethanol from biomass: A comparative overview. In *Renewable and Sustainable Energy Reviews* (Vol. 80, pp. 743–755). Elsevier Ltd. <https://doi.org/10.1016/j.rser.2017.05.063>

Mizik, T. (2021). Economic aspects and sustainability of ethanol production—a systematic literature review. In *Energies* (Vol. 14, Issue 19). MDPI. <https://doi.org/10.3390/en14196137>

