

Citation for the published version:

Kesieme, U., Pazouki, K., Murphy, A., & Chrysanthou, A. (2019). Biofuel as alternative shipping fuel: technological, environmental and economic assessment. Sustainable Energy & Fuels. DOI: 10.1039/C8SE00466H

Document Version: Accepted Version

Link to the final published version available at the publisher:

<https://doi.org/10.1039/C8SE00466H>

© Royal Society of Chemistry 2019

General rights

Copyright© and Moral Rights for the publications made accessible on this site are retained by the individual authors and/or other copyright owners.

Please check the manuscript for details of any other licences that may have been applied and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights. You may not engage in further distribution of the material for any profitmaking activities or any commercial gain. You may freely distribute both the url (<http://uhra.herts.ac.uk/>) and the content of this paper for research or private study, educational, or not-for-profit purposes without prior permission or charge.

Take down policy

If you believe that this document breaches copyright please contact us providing details, any such items will be temporarily removed from the repository pending investigation.

Enquiries

Please contact University of Hertfordshire Research & Scholarly Communications for any enquiries at rsc@herts.ac.uk

Biofuel as alternative shipping fuel: technological, environmental and economic assessment

Uchenna Kesieme^{1,2*}, Kayvan Pazouki², Alan Murphy² and Andreas Chrysanthou¹

¹School of Engineering and Technology, University of Hertfordshire, Hatfield, AL10 9AB,

²School of Marine Science and Technology, Newcastle University, Queen Victoria Road, Newcastle upon Tyne, NE1 7RU, UK

*Corresponding author: u.kesieme@herts.ac.uk

Abstract

Fossil derived fuels available for application within the maritime sector have been dominated by heavy fuel oil (HFO), being conventionally used in slow speed (main) engines, and more refined fuels such as marine diesel oil (MDO), being consumed in fast or medium speed engines. However, increasing fuel costs and regulatory pressure such as the restrictions placed on sulphur content have increased interest in the use of alternative fuels. A number of alternative fuels are identified and maybe viable for use within the maritime sector including straight vegetable oil (SVO) as alternative to HFO in low speed engines, biodiesel to replace MDO/ MGO in low to medium speed engines and bio-liquefied natural gas (Bio –LNG) in gas engines using LNG. The potential sources of biomass feed stocks, conversion pathways and technologies were identified. The key parameters limiting the potential application are examined in particular, availability, technological development, technical integration, and operational consequence. A proposed solution to overcome these limitations were recommended. The effective implementation of these strategies will enable the more widespread use of biofuels in marine applications, significantly reducing emissions from ships and improving global air quality and also protecting the ecological environment

Keywords: Bio-derived fuels, Emissions and Shipping

1. Introduction

1.1. Background

Fossil derived fuels available for application within the maritime sector have been dominated by heavy fuel oil (HFO), being conventionally used in slow speed (main) engines, and more refined fuels such as marine diesel oil (MDO), being consumed in fast or medium speed engines. Marine diesel, or bunker fuel oil, is of a very low quality with high sulphur content and a low cetane number.¹ Carbon dioxides (CO₂), carbon monoxide (CO), particulate matter (PM), nitrogen oxides (NO_x), and sulphur oxides (SO_x) are the most significant pollutants emitted from diesel engine-powered vessels.¹ Approximately 14–31%, 4–9%, and 3–6% of the global emissions of NO_x, SO_x, and CO₂, respectively, are from marine vessels.¹⁻⁵ Marine transportation is facing harder requirements and to act upon the Paris Agreement and reduce greenhouse gas on fuel quality and exhaust emissions as stricter regulations are enforced in different regions of the world.²⁻⁴ The introduction of Sulphur Emission Control Areas (SECAs) by the International Maritime Organization (IMO) with a maximum of 0.1 % sulphur allowed in marine fuel since 2015 will increase the demand for low sulphur fuels.^{6, 7} Nitrogen oxides (NO_x) emission regulation is also introduced in a stepwise manner since 2016 increasing the pressure on low NO_x energy conversion.⁶⁻⁸ In addition, climate change concerns on shipping for reducing its greenhouse gas (GHG) emissions.¹⁻³ Both the demand for low sulphur fuels, as well as the need to reduce NO_x and GHG emissions have created a pressure for ships to operate more efficiently and in an environmentally friendly manner. Reducing the emissions of sulphur dioxide, nitrogen oxides and greenhouse gases to comply with the current regulations and reduce impact on climate change will require a significant change in the shipping propulsion.¹ One alternative is to change fuels.

Biofuels is seen as most viable option for reducing shipping emissions.¹⁻⁷ Compared to the currently used marine fuel oil and marine diesel, bio-derived fuels is environmentally friendly, renewable and clean. Furthermore, the fuel properties and combustion characteristics are similar to the fossil fuels (HFO, MDO and LNG).²⁻⁴ The promising renewable alternatives to HFO, distillate fuels and LNG in short to medium term perspective are SVO, biodiesel and bio-LNG respectively. Pyrolysis oil, FT-diesel and bio-methanol are also promising alternative but in longer term perspective.²⁻⁴ All these fuels are virtually sulphur free, and maybe used for compliance with sulphur content and other emission regulations.

However, to change fuels may involve engine technology changes, e.g. to gas or dual-fuel engines, but can also be performed with new fuels that can be used in old engines with small modifications and adjustments. Furthermore, they can be used either in combination with conventional, oil-based marine fuels, thus covering only part of a vessel's energy demand, or to completely replace conventional fuels. The type of alternative fuel selected and the proportion of conventional fuel substituted will have a direct impact on the vessel's emissions, including GHG, NO_x, and SO_x. The concept to use biofuel for shipping is new and not well reported in the literature. Although not many practical experiences of using bio-based fuels in ships have taken place, technical compatibility with marine engines seems high and integration manageable.¹⁻¹⁷

A number of studies have assessed the performance of the currently used fossil marine fuels.¹⁰ Winebrake et al. also included biofuels, but only soybean based biodiesel.¹¹ Numerous studies have also explored alternative (bio-based) fuels for land based

transportation.¹⁴⁻²⁹ However, there are some aspects in road based transport that differs to that of shipping. Firstly, the basis for comparison differs, as the fuels used at present in shipping (mainly heavy fuel oils) are different from those used for road vehicles (gasoline and diesel). The infrastructure need and the storage requirements also differ as do the engines. It is therefore possible that fuels not well adjusted for road transport maybe advantageous as marine fuels and vice versa. In contrast to the successful development of biofuel such as biodiesel use in land-based transportation, there are still many obstacles to the promotion of biofuels as alternative fuel of marine vessels, such as technological development, technical integration, relatively higher price of over marine diesel or bunker fuel oil, feedstock availability and operational issues. A widespread change from fossil to biofuel in marine applications would improve the quality of marine fuel and also improve air quality, protect the ecological environment and improve people's health.

1.2. Rationale for the selected fuels, major feedstock and exporting regions

1.2.1. SVO and biodiesel

The most promising bio-derived fuels for use in ships are SVO and biodiesel; however pyrolysis oil and other types of biodiesel such as Fischer-Tropsch (FT) biodiesel may prove to be potential alternatives.¹⁻¹⁶ SVO is most suitable for replacing residual fuels while biodiesel is most suitable for replacing marine distillate.¹⁻⁴ The properties of SVO and biodiesel are similar to conventional HFO and diesel, but also this depends on the raw feedstock selected.¹⁻⁴ However, the sustainability of first-generation biofuels is debated. Issues raised include competition for land with food production, limited production potential and questionable environmental performance.²⁻⁴ The risk of indirect land use change has led some to question the carbon savings that are achieved through some crop-based biofuels, and to turn attention to feedstock such as wastes and residues. Using these feedstock in advanced production processes could, in the longer-term, allow for the production of liquid bio-derived fuels such as pyrolysis oil and FT diesel. It is argued that second-generation biofuels can avoid many of the concerns facing first-generation biofuels, but they still face economic and technical challenges.^{14, 15} More advanced bio-derived fuels are still immature with little prospective of significant market penetration before 2020.¹⁻⁹

1.2.2. Pyrolysis oil, FT-biodiesel and bio-methanol

This study assumes that second generation biofuels will be available for the shipping industry in the year 2030, this is not a prognosis year but rather a reference to a point in time in the future when second generation biofuels could be implemented. The rationale not to proceed with pyrolysis oil, FT biodiesel and bio-methanol are as follows: Pyrolysis oil consists of an emulsion with 20–30% water.¹⁶⁻²⁰ The high oxygen content leads to low pH values, which makes the fuel acidic and corrosive, with low heating values and high viscosities. Large-scale production of pyrolysis oil is still in early stages of development and no commercial scale facilities are known worldwide.¹ Several institutes are researching the possibilities for upgrading pyrolysis oil in a regular oil refinery.^{18, 19} The final product would then have characteristics, which are very comparable to fossil derived fuels. More specifically, ReShip – a project involving the Paper and Fibre Research Institute and Aston University are exploring the concept of fast pyrolysis to produce a low sulphur bio-derived fuel.²⁰ However, upgrading pyrolysis oil may be complex and expensive. In addition, the commercialisation of bio-derived FT diesel remains in its infancy, as it is strongly linked to the immature technology of biomass gasification. Furthermore, creating a clean and stable enough bio-syngas through gasification at commercial scales remains a bottleneck.^{1, 16} Also, the required investment for commercial scale biomass gasification-FT plants is very high in relation to other biofuel technologies. For the bio-methanol, the global commercial

production is still limited to one installation in the Netherlands, which uses crude glycerine (from biodiesel production) as a feedstock. Again, the technological development and commercial availability of biomass gasification is the limiting factor.^{1, 16}

1.2.3. Bio-methane/Bio-LNG production route

The interest in LNG as alternative shipping fuel opens up a possibility to use bio-methane in the shipping sector. While LNG is a finite fossil fuel and does not contribute much to lower greenhouse gas emissions, bio-methane would be a better alternative. Bio-methane is defined as methane produced from biomass with properties close to natural gas; it could connect to existing and upcoming LNG terminals.¹ Bio-methane can be generated from various sources of biomass including the following two processes: Anaerobic digestion (AD) and Thermochemical gasification.²² The choice of technology depends on the feedstock characteristics and scales for conversion etc. AD is an established technology in particular the waste water industry; however, current operational production is de-centralised and at small scale.^{1, 16} Production of bio-methane from lignocellulose biomass via gasification could be performed at a much larger scale, but this has not been commercialised yet.¹⁻⁴ When produced by thermal conversion (e.g. gasification and methanation), the methane-rich product gas is normally referred to as bio-based synthetic natural gas (bio-SNG). Similarly, when it is produced by biological processes, the initial product is raw biogas, which must be cleaned and upgraded to reach the high methane content (>95%) that is referred to as bio-methane.²¹⁻²⁴ Anaerobic digestion and biogas upgrading are successfully demonstrated.^{1, 21} On a global level, about 277 biogas upgrading plants, connected to anaerobic digesters, were in operation in the end of 2012.²² Following the production of bio-methane, liquefaction reduces the gaseous products to a liquid via a cooling process. Liquefied bio-methane is then stored in large insulated tanks, prior to transportation to the dispensing point. North America and the EU are the potential producers of bio-LNG. Due to the existing forestry industry, it is assumed that US supplied bio-LNG is derived through a dry, thermal conversion route utilising gasification. Despite this, as with FT diesel, gasification and methanation of biomass to produce bio-SNG is still in the research and demonstration stage.¹

1.2.4. Major feedstock and production regions

Argentina, Brazil, Malaysia, Indonesia and the United States (US) are currently the main exporters of biodiesel and SVO.^{1, 16} It is anticipated that this trend will continue in the short-to medium-term. The EU imports a substantial amount and also produces SVO and biodiesel indigenously for intra-EU use. Argentina, Brazil and United State are the main producer of soybean oil while the EU is a key producer of rapeseed oil. Argentinian exports are anticipated to continue to grow out to 2020.²¹ Canada and the US are anticipated to become globally significant for the production of wood pellets and other lignocellulosic feedstock.²¹ These may provide a feedstock for the production of FT diesel, pyrolysis-oil and bio-methanol.

2. Fuel production pathways and fuel characteristics

2.1. SVO and biodiesel

SVO are usually produced by mechanical extraction of oil from an oil-bearing biomass as feedstock such as soybean and rapeseed grains. With respect to biodiesel, SVO is much easier to produce because it includes fewer processes and less energy consumption.^{1, 16} The production steps often includes five stages: feedstock production (including cultivation and harvesting), feedstock transportation, fuel production, fuel distribution and fuel end use.¹⁴ SVO have a chemical composition that corresponds in most cases to a mixture of 95%

triglycerides and 5% free fatty acids, sterols, waxes and various impurities.^{14, 15} While biodiesel is a mixture of fatty acid alkyl esters produced by transesterification of SVO with a short chain alcohol.¹⁻⁹ The purpose of the transesterification process is to lower the viscosity of the oil.¹ SVO and biodiesels are characterized by their cetane number, heating value, viscosity, density, cold flow properties such as cloud and pour points, flashpoint, ash content, sulphur content, carbon residue, and acid value.²⁵ These physical and chemical properties depends on the characteristics of feedstock such as carbon chain length, saturation, location and types of double bond (cis or trans) etc. It is unlikely that vegetable oil could be blended with HFO. Rather, vegetable oil would be applied as a pure replacement (100% blend) of HFO.^{1, 16} Biodiesel can be used as a replacement of MDO or blended with convectional fuel. A biodiesel blend is pure biodiesel blended with Petro diesel. Blends containing up to 5% volume are considered the same as conventional diesel and are fully compatible with all engines and infrastructure.²⁶

2.2. Fuel characteristic and suitability in marine diesel engines

The viability of SVO and biodiesel as a potential marine fuel stems from its high energy content, molecular structure and high cetane number, a very positive property for low to medium speed diesel engine operations.^{27, 28} These are characteristics also shared by the marine fuels (HFO and MDO) now used in these engines. The chemical and physical properties differs from the currently used marine fuels and hence a slight engine modifications maybe required. SVO and biodiesel can utilise the same infrastructure as HFO and marine gas oil (MGO) as it is a liquid fuel.²⁷ In Tables 1 and 2, the major characteristics of SVO and biodiesel are compared with respect to that of HFO and MDO/MGO as quoted in the ISO 8217 technical standard for marine fuel. Based on the general specifications, it can be concluded that SVO and biodiesel are options closest to HFO and MDO/MGO respectively. The major characteristics of SVO and biodiesel is described in the subsections below.

2.2.1 Cetane number (CN)

High CN increases the thermodynamic efficiency of the engine and minimize emissions, notably those of HC (non-burnt hydrocarbons) and NO_x.²⁵ The lower the CN, the longer the ignition delay, which should not be shorter than 20 ms for low-speed, two-stroke diesel engines.²⁷ When ignition delay is excessive, the combustion can take the form of a detonation that harms the piston, piston rings and bearings.²⁵ For heavy fuels, an alternative formulation to CN, is the calculated ignition index (CII), developed by British Petroleum that gives values of the order of those associated with CN.²⁵ The higher the CII the better the ignition characteristic of the fuel. Equation 1 provides a basis for comparison between SVO and HFO.^{25, 27}

$$\text{CII} = (270.795 + 0.1038T) - 0.245 D + 23.708 \log [\log (V + 0.7)] \quad (1)$$

Where D is the density at 15°C (kg/m³); V is kinematic viscosity (mm² /s) and T is temperature to which viscosity is measured (C).

The manufactures of low-speed marine diesel engines recommend a value above 30 for CII, a recommendation that all SVOs satisfy, and are higher than for HFO (Table 3), endowing vegetable oils with better combustion characteristics with regard to ignition delay. A fuel of low ignition quality reduces CII and hinders the start-up of an engine as well as resulting in low load operations. When ignition delay increases, the phase of premixed combustion increases elevating the maximum pressure and combustion temperature, affecting the

mechanical integrity of the engine, increasing the formation of NO_x, and increasing the noise level.²⁵ The shorter the ignition delay, and the higher the CII, the lower are HC emissions. Excessive ignition delay produces deposits in the piston, the exhaust valves, the exhaust collector, and the turbocharger. A high CII will prolong the efficiency of the low-speed diesel engine.²⁵

2.2.2. Calorific Value

The low calorific value of SVO and biodiesel are lower than that of HFO and MDO respectively. The existence of oxygen atoms in the SVO and biodiesel molecule are responsible for the decrease of heat value in contrast to that of HFO and MDO (Table 1 and 2). This means that for the same volume injected by cycle and the density of SVO and biodiesel being slightly inferior to that of HFO and MDO, the energy introduced in each engine cycle is decreased, and, therefore, an adjustment of the injection system is required so as not to diminish the propulsion capacity.²⁵

2.2.3. Pour point (PP)

This parameter indicates the minimum temperature at which fuel can be pumped easily under test conditions; the temperature should stay between 5°C and 10°C above the PP. Table 1 shows that the PP for most SVOs is below that of HFO. Thus for most SVO, the current solutions for storage and pumping of HFO used in large ships are valid.

2.2.4. Flash point (FP)

It represents the minimum temperature at which gases from the fuel ignite when, under test conditions, a flame is applied. This is important for a ship's security and affects the storage and distribution systems of the fuel. Some insurance companies demand the use of fuels with a flash point higher than 60 C.²⁵ SVO and biodiesel presents flash temperatures are of the order above 400 C, which is much higher than the HFO and MDO, and, therefore, there are fewer security requirements.²⁵

2.2.5. Cloud point (CP)

This indicates the temperature from which the solidification of the fuel begins, usually visible by means of the formation of crystals.

2.2.6. Acid value

Acid value is the measurement of free fatty acid content in biofuel. It is usually referred as the weight in milligrams of potassium hydroxide (KOH) required to neutralize 1 g of fatty acid in a biofuel sample. Biofuels are generally has more acidic value than the conventional marine fuels. Highly acidic fuels have the potential to cause corrosion in fuel supply systems, especially in fuel injectors. ASTM D664 and EN 14104 standards are used to determine the acid value of biofuels. Both standards define the maximum levels of acid number for biodiesel as 0.50 mg KOH/g.⁵

Table 1: Fuel characteristics: SVO, Pyrolysis oil and marine heavy fuel oil.^{1, 16-29}

	Soybean oil	Palm oil	Rapeseed oil	Pyrolysis oil	Heavy fuel oil (ISO 8217(RMG))
Calorific Value (MJ/kg)	39.62	36.51	36 -37	22.7	40
Density (288 K)	914 - 920	915 - 918	900 - 930	1100 -1250	< 991
Flashpoint (K)	527- 603	540	493 - 519	313-373	>333
Pour point (K)	260.8-273	241.3	241-262	240 - 261	< 303
Kinematic viscosity (mm ² /s)	39.60	39.60	39.20	14.5	< 380
Cetane number (CN)	36 - 38	38-42	37.60	10	>20

Table 2: comparison of different biodiesel oil and marine diesel oil ^{1, 16-29}

	Soybean biodiesel	Palm oil biodiesel	Rapeseed biodiesel	MDO (ISO 8217 DMB)	MGO (ISO 8217 DMA)
Calorific Value (MJ/kg)	39-40.5	37.4-38.2	37	42	-
Density (kg/m ³) (15oC)	885	864-871	900 - 930	<900	< 890
Flashpoint (K)	414-440	408	420-443	>333	>333
Pour point (K)	266-272	287-289	261	273- 279	273-279
Kinematic viscosity (mm ² /s)	3.9-4.65	4.05-5.1	3.5-5.0	2-11	2-6
Cetane number (CN)	46-45	58-65.5	50-56.6	>40	>35

Table 3 Ignition index (CII) for different SVO ²⁵

Fuel	Density kg/m ³ (15oC)	Viscosity cSt (mm ² /s)	Temperature (C)	Ignition index (CII)
HFO	960-990	180-380	50	32.7

Rapeseed oil	900 - 930	37	38	47.8
Soybean oil	914 - 920	32.6	38	47.4
Palm oil	920	39.6	38	45.4

2.3. Biomethane production route

Production of biogas via AD involves a series of biochemical processes, primarily comprised of four steps: hydrolysis, acidogenesis, acetogenesis, and methanogenesis.³⁰ The primary products from hydrolysis and acidogenesis are acetic acid, CO₂ and hydrogen.³⁰ The final process, methanogenesis, produces the biogas.^{22, 30} Raw biogas usually contain between 55-70% methane, with the remainder being largely CO₂ and small amounts of water vapour, fine grit, hydrogen sulphide (H₂S) and ammonia.²² To use the fuel in a marine engine, biogas needs to be upgraded by removing the CO₂ and other contaminants so that it is at least 95% methane.²² The ability to utilise a wide range of feedstock such as biodegradable commercial, industrial and municipal wastes represents another potential advantage of gaseous fuels produced by AD. However, the requirement to upgrade the biogas to biomethane of adequate quality for transport fuel use, liquefaction of the gas for storage and transport and the lack of refuelling infrastructure are considered to be significant barriers to the deployment of biogas based marine fuels.

2.3.1. Biogas upgrading

In order to transform biogas into bio-methane, two major steps are performed: a cleaning process to remove the trace components (such as H₂O, H₂S and other contaminants) and; an upgrading process, in which CO₂ is removed to adjust the calorific value and relative density in order to meet the specifications of the Wobbe Index.²² After transformation, the final product is referred to as 'bio-methane', typically containing 95-97% CH₄ and 1-3% CO₂. Although a number of different technologies are available to fulfil the task of producing a bio-methane stream of sufficient quality, a small percentage of methane is lost during the upgrade stage.²² This can vary considerably between the upgrading technologies chosen, although all equipment suppliers can provide off-gas treatment to deal with methane losses.²² Methane slip from upgrading biogas to bio-methane can make a significant contribution towards the overall lifecycle greenhouse gas emissions. The different technologies for biogas upgrading are described in the following subsections and some performance information are summarised in Table 4

2.3.1.1. Water and the organic physical scrubber

The biogas is pressurized (5-10 bar) and the carbon dioxide is dissolved in the water or a selective organic solvent. The biogas is upgraded and the dissolved carbon dioxide is released from the solvent in a desorption vessel at atmospheric pressure during air stripping.¹⁶

2.3.1.2. Chemical scrubber

The in water dissolved carbon dioxide (carbon acid) reacts with an added amine and thus can be separated from the gas stream. This process can be carried out at atmospheric pressure since it is a chemical reaction that drives the process.²⁴ Heat is needed to reverse the reaction and release the carbon dioxide in a stripper vessel and restore the amine.

2.3.1.3. Pressure swing adsorption (PSA) system

The raw biogas is pressurized (3-10 bar) and fed into an adsorption column filled with an adsorbent, such as carbon molecular sieves. Carbon dioxide is adsorbed by the bed material and the biomethane passes through. The carbon dioxide is desorbed from the adsorbent by reducing the pressure and using a purge gas (commonly biomethane).

2.3.1.4. Membrane separation

The biogas is pressurized (5 – 20 bar) and fed into the membrane unit. The carbon dioxide, as well as other gas components, permeates through the membrane, whereas the methane is retained. The performance varies widely depending on the settings (e.g. pressure stages, loops) and the unique design adopted by each manufacturer.

2.3.1.5. Cryogenic separation

Cryogenic separation is a developing technology with so far only one plant in operation.²² Methane and carbon dioxide are separated by gradually cooling down the raw biogas.²² All compounds with higher condensation temperature than methane, such as water, hydrogen sulphide, siloxanes and nitrogen, can be separated in this process.²² Since this is still a developing technology it is not included Table 4. In Table 4, in a water scrubber, hydrogen sulphide is commonly separated together with carbon dioxide. For the other technologies, an external H₂S removal device is needed.²² Commonly, this is an activated carbon filter, but other technologies also exist on the market.²² Regarding siloxanes (derived from waste consumer products and especially prevalent in landfill gas), preliminary results suggest that they are effectively separated by most upgrading technologies.²³ However, more detailed research is needed for verification. More detailed information about the different technologies used for biogas upgrading can be found in the literature.²⁶

Table 4: Overview of the properties and the performance of the mature biogas upgrading technologies

Parameter	Water scrubber	PSA	Membrane (2-4 stages)	Chemical scrubber (amine)	Organic physical scrubber
CH ₄ in product gas	96 – 98 %	96 – 98 %	96 – 98 %	96 - 99 %	96 – 98 %
Availability	95 - 98%	95 – 98 %	95 - 98%	95 - 98%	95 – 98 %
H ₂ S removal	Yes	External	External	External/yes	External
H ₂ O removal	External	yes	yes	External	External
Pure CO ₂	No	yes	yes	yes	No

2.3.2. Liquefaction of bio-methane to produce Bio-LNG

Liquefaction of the gaseous form of methane produced from AD is reduced to a liquid via a cooling process. To apply biogas for propulsion purposes, it will need to be stored in liquefied form. In liquid form the biomethane occupies only 1/600th of its gaseous volume, while for it to be in liquid form a temperature of around -162°C is required.

2.3.3. Biomethane fuel characteristics and suitability in marine engine

Bio-LNG has high energy density, but needs to be stored in cryogenic tanks.³¹ A new fuel infrastructure maybe needed in the form of terminals, bunker possibilities, new storage facilities and engines on board.³² LNG has previously been used as a fuel for LNG carriers, by utilisation off the boil-off gas in steam turbines, but gas or dual-fuel engines can also be used for LNG propulsion.³² Dual-fuel engines can run in either gas mode or diesel fuel mode. The engine works according to the Otto principle in gas mode, and the lean gas and air mixture is ignited by injection of a small amount of diesel fuel into the combustion chamber. The injected diesel fuel normally corresponds to about 1% of the total amount of energy supplied to the engine at full load.³² The gas engine operates according to the Otto cycle and combustion is triggered by sparkplug ignition.³³ Bio-LNG contain more than 97% methane and can therefore be used to replace LNG in both dual fuel and gas engines. Several types of prime movers are possible for methane e.g. two-stroke and four-stroke diesel engines, Otto engines, fuel cells, making the fuels rather flexible from a technological perspective.³² The LNG propelled ships in operation in Norway are either equipped with spark-ignited lean burn gas engines or dual fuel (DF) engines. DF engines can run on LNG, HFO or marine gas oil (MGO).^{32, 33} When using LNG, a small amount of diesel pilot fuel is injected for ignition. One of the downsides with LNG is the rather complicated and costly retrofits for existing engines. The four-stroke LNG engines comply with Tier III NOX limits (1.96–3.3 g/kWh dependent on engine speed).³² To switch from LNG to bio-LNG investments and technological development is needed to produce the needed amount of biogas. Biogas is currently produced mainly through digestion of agricultural residues (food and manure) in small scale widely spread installations, but in long term could switch towards biomass gasification of woody residues. At this point in time the scattered availability of biogas in Europe would be limiting the introduction of bio-LNG, as long as no intra-European biogas certification scheme allows local biogas production facilities to introduce their biogas at central LNG terminals within Europe. The fuel properties characteristics of biogas to natural gas are shown in Table 5.

Table 5: Characteristic raw biogas compared to natural gas

Substance	Biogas from anaerobic fermentation	Natural gas (H-gas quality)
methane	50 – 85 %	83 – 98 %
carbon dioxide	15 – 50 %	0 – 1.4 %
nitrogen	0 – 1 %	0.6 – 2.7 %
oxygen	0.01 – 1 %	-
hydrogen	traces	-
hydrogen sulphide	up to 4,000 ppmv	-
ammonia	traces	
ethane	-	up to 11 %

propane	-	up to 3 %
siloxane	0 – 5 mg/m ³	-
Wobbe Index	4.6 – 9.1	11.3 – 15.4

3. Recent progress in biofuel application in marine engine

Wärtsilä, one of the world leading marine engine manufacturers located in Helsinki, Finland, started test on alternative fuels. In 2001, several biodiesel fuels were tested using feedstock such as palm oil, olive oil and other vegetable oils on their engines.⁵ The experimental test were carried out on a stationary Wärtsilä 6L32 engine in the Vaasa Engine Laboratory, Finland. In 2003, the first Wärtsilä power plant using biodiesel was built in Karlburg, Germany.⁵ Since then, research into biodiesel have been further enhanced, where in 2015 Wärtsilä collaborated with several marine fuel companies to identify the suitable marine biofuel for their engine.⁵

In addition, MAN Diesel Company, another world leading designer and engine maker, had experience with biofuels. They reported using several biofuel feedstocks to find the most suitable fuel associated with their engine.⁵ In 2006, the first test of biodiesel on their two-stroke low speed engines was carried out in Copenhagen, Denmark. A new milestone was achieved in 2007 when MAN Diesel employed palm biodiesel in their four-stroke medium speed engine in Belgium.¹⁻⁶ As for current, MAN Diesel offers a wide range of marine engines that are ideal for biofuel fuel applications without any modifications. World medium-speed engine manufacturer, Rolls-Royce stated that they had no experience dealing with biofuels on their engines but on a general basis, biofuel should be compatible with marine engines. Another marine engine manufacturer, Caterpillar Incorporated located in the United States also had extensive experience running with biofuels. The test work conducted on Caterpillar's ferry engines show that biodiesel can be used without any short-term problems.⁵ Since then, further studies have been carried out to define the potential long-term effects on the use of biodiesel in marine engines. Nowadays, most of Caterpillar's new and existing marine diesel engines are capable of using up to 30% of biodiesel without modifications.¹

4. Major issues in promoting bio derived fuel in marine application

A new marine fuel for shipping must be technically feasible, economically competitive, environmentally acceptable and easily available. To determine the potential of a new marine fuels for ships, a clearer picture is needed on technical and organizational limitations in ships, both on board of the ship and in the fuel supply chain to the ship. Biofuels may display superior fuel characteristics compared to those of marine fuel oil and distillate fuels. Some of the advantages includes renewability, higher combustion efficiency, lower sulphur and aromatic content, higher cetane number and higher biodegradability. Although these fuel benefits exist, there are certain obstacles to the development of biofuel use in marine applications. The major hindrance encountered in promoting alternative fuel use such SVO, biodiesel and Bio-LNG in marine are described in the following subsections.

4.1. Technical issues affecting biofuels as marine fuel and potential solutions

The key parameters limiting the potential application biofuels includes availability, technological development, technical integration, and operational consequence. The technical issues includes the systems on board the ships which deal with the fuel, e.g. engines, storage tanks, pumps, pipes, exhaust funnel, etc., the bunkering ships and the fuel storage terminal.

All these systems need to be technically feasible and it is a prerequisite that it must be possible to apply biofuels as an alternative marine fuels. The key technical issues and potential solutions were identified are described in the following subsections

4.1.1. Lack of marine grade fuel specifications for biofuels

Most marine fuel products are manufactured according to ISO 8217 standards.⁵ However, there are currently no international marine market fuel specification for alternative marine fuels such as SVO, biodiesel and Bio-LNG. This is relevant, as design of engines should base its work on a known fuel composition and its potential variability. In order to guarantee optimum and durable engine operation, manufacturers recommend using standardized fuels. To that end, the physico-chemical properties of the fuel must correspond to the specifications set down by the standards. The purpose of the standards is to certify a set of characteristics and a composition for each fuel that (i) guarantee good performance when used in engines (efficiency, mechanical performance, endurance, atmospheric emissions, etc.) and (ii) make it possible to estimate and foresee the potential impacts of using, transporting and/or storing these fuels on health and the environment. These standards are issued by national or international organizations present in the different geographical zones of the world including, the American Society for Testing and Materials (ASTM) in the United States. The aim of these organizations is to guarantee a minimum quality for fuels according to their uses, and to protect users and the environment. For example, the current international biodiesel specifications, including EN14214 and ASTM D6751 for biodiesel manufactured and used in the European Union and the US respectively, are primarily applied to automotive diesel vehicles or land-based combustion equipment. Diesel fuel blended with biodiesel has been practically introduced to the specifications of diesel fuel in a number of countries. For example, in the EN590 specification of automotive diesel fuel, a maximum addition of 5% of biodiesel (denoted as B5) is allowed, which meets the emission legislation of diesel vehicles. If neat biodiesel (i.e. B100) satisfies the ASTM D6751 specification, the blend of B20 or a lower biodiesel ratio in diesel fuel can meet the ASTM D975 specification for automotive diesel fuel without any, or with slight, engine modification.³⁴ However, the operating environments of marine vessels is not the same as land-based equipment. For instance, the fuel-feeding system of some marine vessels contains metal components such as copper, which is not adaptable to biodiesel compound.³⁵ However, no marine-grade biodiesel specification has been proposed or proved by any international standard authorities such as the IMO, ASTM, or the European Committee for Standardization. It is considered that comprehensive field tests using bio-derived fuels and including blends of marine fuel with in various proportions of biofuels in representative types of marine vessels are requisite before establishing a globally acceptable marine-grade bio-derived fuel specification.

4.1.2. Cold flow properties of biofuels

The low temperature fluidity of SVO and biodiesel as compared to that of petroleum-derived fuel oil) restricts their wide spread use in low-temperature regions or cold seasons. The cloud point (CP), the cold filter plugging point (CFPP), and the pour point (PP) are the three key indicators of low-temperature fluidity for liquid fuel. The temperature at which crystals are first found in liquid fuel is known as CP. Crystals continue to form and come together, and consequently plug the fuel filter of a fuel feeding system at a lower temperature defined as the biofuel CFPP. The CFPP is the most widely adopted indicator of the low-temperature fluidity of biodiesel under biodiesel specifications such as the European Union's EN14214.³⁶ The PP is the temperature at which continuously agglomerated crystals prevent liquid fuel from being pumped through the fuel feeding pipe to the engine chamber. SVO and Biodiesel has relatively high CFPP and may cause engine breakdown, and may even threaten driving

safety, particularly when vessels sail in cold climate regions. A saturated fatty acid and long carbon-chain fatty acid content higher than C20 in biofuel results in a higher CFPP. For example, palm oil biodiesel has a higher CFPP (ranging from about 9 °C to 14 °C) than rapeseed oil biodiesel (ranging from about -19 °C to -8 °C).³⁷ Blended biodiesel will exhibit better cold weather properties than B100. Suitable approaches or technologies should be adopted if biofuel with a higher CFPP is to be used as an alternative fuel for marine vessels sailing in low-temperature environments to avoid possible damage to their marine engine systems.³⁶⁻⁴⁰

4.1.3. Effect of Impurities and engine

Biofuels may contain impurities that will lead to engine faults or damage when used as marine fuel. The most harmful impurities for diesel engines are phospholipids, sediments, high free fatty acid contents and water.²⁵ Phospholipids come directly from the breakdown of cell membranes within the plant biomass.²⁵ Their concentration depends on the extraction techniques used, and especially the temperatures reached during cooking treatment and pressing; high temperature conditions cause phospholipids to dissolve in oils. When the oils are used in an engine, the phospholipids polymerise under the effect of heat and are responsible for the formation of deposits that clog injectors and valves, and build up on the combustion chamber walls and cylinder surfaces.²⁵ Sediments can be of two kinds, either organic or mineral. In the first case it may involve fragments that come directly from the breakdown of plant tissues, or from particles that are formed via reactions polymerising free fatty acids, or other minority compounds formed during storage. Unsuitable storage conditions (presence of air, light, metal tanks, etc.) are conducive to the formation of organic sediments. Sediments of mineral origin come from impurities (sand, soil) that have not been totally separated from the biomass prior to extraction. As some sediments dissolve when hot, it is preferable to filter oils cold (50°C), after a possible sedimentation stage enabling separation of the densest sediments by gravity.²⁵ Although sediments do not cause any real combustion difficulties, they can cause peripheral engine parts, such as filters or pumps, to malfunction. Indeed, sediments may clog the fuel filter and cause additional losses in the circuit, leading to a very significant increase in the injection pressure. Mineral sediments, which are the most harmful because they are highly abrasive, damage fuel feed circuits and the inner wall of the combustion chamber.²⁵ The acidity of biofuel is another important issue caused mainly due to the existence of free fatty acids from the hydrolysis of triglycerides in the presence of water. Such hydrolysis reactions may take place in the biomass if it is stored under poor conditions (moisture), during pressing if the temperatures are too high, and during oil storage in the presence of water and light.²⁵ Oil acidity is responsible for damage to engine feed circuits (hose, gasket, etc.), engine corrosion and instability during storage. Water present in biofuels comes directly from biomass that has been poorly dried, or from condensation under poor oil storage conditions.²⁵ Water hydrolyses triglycerides to form free fatty acids. The presence of water in vegetable oil deteriorates fuel filter cartridges. In addition, during combustion, the existence of water causes cavitation events, particularly at the piston head, which may cause serious damage. In general, the presence of water in a fuel is detrimental, as it lowers the heating value, disrupts ignition and slows down flame propagation.

In the case of biomethane, bio-methane is upgraded from biogas, which consists mainly of methane and CO₂ and some minor/trace components which greatly depend on the feedstock. Final quality/composition of biomethane depends on the operational parameters of the final

use and on the upgrading technology used. Depending on the source, several trace components have to be closely controlled when using biomethane as a marine fuel, components such as Siloxanes can cause abrasion and increased probability for knocking.³⁸ The presence of water and H₂S can cause corrosion, which could affect the engine devices and combustion products could create problems by sticking the engine valves.³⁸

4.1.4. Compatibility of fuel feeding and storage materials

Regular contact between biofuel and elastomers, rubbers, or plastic materials in fuel feeding systems such as hoses, valves, filters, and seals may cause material leaking, softening, or degrading. For example, polypropylene, nitrile rubber compounds and polyvinyl are the materials most susceptible to biodiesel and SVO.³⁹ The quantity of degradation rates of materials exposed to biofuel depend on the chemical composition of fatty acids methyl esters.⁴⁰ For example, fuel feeding system's materials deteriorate at a slower rate when biodiesel has a higher stearic acid (C18:0) content than they do when exposed to linolenic acid (C18:3), due to the greater oxidative stability of the former compound.

Furthermore, bio derived fuels that deteriorates as a result of its prolonged exposure to atmospheric air or a high-temperature environment contains organic acids, water, and ionized compounds that further accelerate the degradation of rubbers and plastics. A higher proportion of biodiesel blended with petroleum-derived fuel oil is likely to cause more serious material compatibility issues in fuel feeding system's elastomers. Storage tanks made of tin, brass, copper, bronze, and zinc are vulnerable to biofuel due to the oxidation reaction of these storage materials with biofuel chemical compounds.⁴¹ Sediments with higher molecular weights, metallic compounds, salts, and gels may thus be produced from such chemical reactions, which would result in clogged fuel filters, changes in fuel colour, and storage tank corrosion. Hence, fuel pipes, fittings, regulators, and linings should not be made of the above materials to avoid possible leakages, seeping or breakages.

4.1.5. Availability of biomass feedstock

Biofuels in general have a lower energy density than marine fuels, and also a different overall density differing per type. This means on average a higher quantity of bio-based fuel is needed to meet the same final energy content as with conventional marine fuels. For example, biomass feedstock is the most important factor in the production of SVO and biodiesel. The cost of the feedstock accounts for up to 75% of the total cost of biodiesel production.⁴¹⁻⁵⁰ Therefore, obtaining an inexpensive, reliable and stable supply of biomass is the critical issue for a successful business operation. If the cost of the feedstock is too high, the price of the final product is not competitive. On the other hand, if the bio derived fuels product is cheaper than fossil and meets the quality specifications, then the product has a competitive edge in the marine fuel market. The widespread use of bioderived fuels such as SVO and biodiesel in global marine vessels will demand tremendous biomass feedstocks and thus create competition for these biomass products. Food cost spike and shortage of the biomass would therefore appear. In addition, much more farm land is required to grow energy crops for bio-derived fuel production for marine applications.

4.1.6. Fuel storage/ Infrastructure/engine

4.1.6.1. Bio-methane

Gaseous fuels such bio-mthane will require a different type of fuel handling system, fuel tanks and gas burning engines that are not currently in use on most ships. The gaseous fuels that are available for marine use are biomethane and LNG. Cryogenic storage requires an insulation layer and low pressure containers (often cylindrical in shape), adding few weight

and some volume.³² Experiences from Norwegian LNG ferries suggests that about 3 to 4 times more space fuel for an equivalent quantity of energy is needed for fuel storage on board.³² This will imply that LNG as a fuel will not be suitable for all ship types. There are two types of LNG engines available at present. Spark-ignited gas engines using the Otto-cycle operating only on LNG or dual-fuel diesel engines where both LNG and other fuels can be used. The engine efficiency is of the same order of magnitude as for medium speed diesel engines. Today bunkering of LNG is not fully developed and regulated and there is a lack of infrastructure for distribution and storage.

4.1.6.2. SVO and biodiesel

The main problem with the use of biofuel is its oxidation and polymerization occurring during combustion or storage. Due to these reactions, the biofuel can become acidic, and forms gum-like sediments which can plug the fuel filters. Furthermore, the presence of unsaturation in the parent fatty chain, the double bond reacts with oxygen as soon as it is exposed to air. The oxidation process is influenced by various factors like light, temperature, extraneous metals, peroxides, and the surface area between air and biodiesel. SVO can be used in large ships propelled by slow speed two-stroke engines as the fuel properties are similar and current methods for storage and distribution are compatible. Biodiesels, according to the standard EN14214:2008 can replace low sulphur fuel oils in marine diesel engines and be blended with distillate fuels.^{42, 43} However, slight engine adaptations are required and specific operating precautions need to be observed. For instance, SVO temperature has to be closely monitored to keep the correct viscosity levels. The viscosity of the SVO must be reduced by preheating it.³⁹ This is often done through a dual fuel system, in which the engine is started on regular diesel and after a short while switches to the use of biofuel. It is unknown if the vegetable oil has been tested for marine application, but there is some experience with land-based power stations that replaced HFO with vegetable oil, e.g. with engines from Man B&W and Wärtsilä.⁴³ MAN B&W Diesel gives a rough estimate that an existing ship engine can be converted to run on biofuels for less than 5% of the engine cost.^{42, 43} However, when using biofuels in ships, all ship installations such as; fuel storage, fuel treatment system, piping, centrifuges, etc. need to be evaluated for possible modifications.

4.2. Economics and cost

4.2.1. SVO and biodiesel

The global scenario of biofuel is promising. One of the reasons hindering the widespread application of biofuel is cost. The cost of the SVO and biodiesel production are high due to limited arable land for growing energy crops and the relatively higher cost of agricultural operations. The cost of biodiesel is higher than diesel fuel. In the US the biodiesel sells for about US\$0.396 to US\$0.528 per litre before taxes.³⁴ At the same time the pre-tax diesel priced is US\$0.18/l in the US and US\$0.20–0.24/l in some European countries.³⁰ There is no single cost for biodiesel production, but rather a wide range of costs prevailing in different countries depending upon a number of factors. The cost of biofuel could be broken into raw material cost, capital cost and operating cost. Raw materials contribute to a major portion of the cost of biodiesel production more so than the size of the industrial plant. In fact, the average cost of raw material for biodiesel production is nearly 60 to 75% of the total production cost. The overall cost of the biodiesel is also affected by the season of the year, low quality, inconsistent in the product quality and poor product yield etc.²⁵ Further, the price of biofuel depends on factors such as fuel preparation, transportation, consumption and requirement in the country.¹⁶ However, reductions in cost of biodiesel can achieve through scale economies and learning effects. In addition more investment is required in technologies and systems for second generation biofuels.²² The global biomass resources are still rather limited, resulting in significantly higher biofuel production costs compared to marine residual fuel oil.

4.2.2. Bio-LNG

The investment cost for LNG propulsion systems are outlined in a report by the Danish Maritime Authority. This highlights that especially the retrofit cost for LNG engines are considerable.³⁸ Gullberg and Gahnström stated that LNG is expected to have a competitive price development in comparison to conventional fuels, but is connected with a high initial investment cost.³¹ The price of LNG is strongly influenced by transportation costs as this accounts for a large share of the overall costs.⁴⁴ While large-scale liquefaction of natural gas is an established technology, small-scale liquefaction of bio-methane is a recent concept and as such, cost reduction and efficiency improvements will occur over time.⁴⁴⁻⁵⁰

In the overall, the government need to play an important role in reducing alternative fuel production costs by introducing several incentive schemes, such as tax relief, financial subsidies and low fuel tariffs associated with biofuel. Biofuel production industries indirectly play a significant role in the country's economy by giving employment opportunities for the rural population, increasing income tax revenues, investing in plants and equipment. Price competitiveness of marine-grade biofuel can be improved by reducing overall production costs and increasing government support toward biofuel policies itself.

4.3. Environmental aspect

Air emissions from shipping have received much attention in recent years and the focus has been on SO_x, NO_x, particulate matter (PM) and GHG emissions. It is a requirement that the fuel alternatives fulfil the present environmental regulations (emissions of NO_x and SO_x). It is also expected that the environmental regulations will become even stricter in the future and the fuel alternatives need therefore to be able to meet tougher upcoming environmental requirements. The emissions of NO_x, SO_x and PM are significantly expected to reduce using biofuels as compared to conventional fuels. However, for a fuel to be environmentally sustainable, it must not only be associated with low emissions during the combustion of the

fuel, but also in the whole fuel life cycle starting from raw material extraction, followed by fuel production, distribution and finally combustion in marine engines for ship propulsion.

4.3.1. SVO and biodiesel

SVO and Biodiesel is generally cleaner burning than HFO and MDO and reduces most regulated emissions. Compared to conventional diesel, biodiesel reduces particulate matter (PM) by 47%, carbon monoxide (CO) by 48%, and unburned hydrocarbons (HC) by 67%. According to the National Biodiesel Board, NO_x emissions with pure biodiesel can increase by 10%, but research articles have shown that increases in NO_x may be load dependent and a minor number of articles have actually reported a decrease in NO_x emissions.³ In addition to the regulated emissions, biodiesel also decreases non-regulated emissions such as sulphates, polycyclic aromatic hydrocarbons (PAH), nitrated PAHs, and ozone generating hydrocarbons. However, in life cycle perspective, different methods of lowering environmental impact should be taken into account including land use change, improving agricultural practices such as fertilizer application and oilseed yield and also optimizing transportation routes. In the event of a spill (e.g., during fuel transfer), SVO and biodiesel degrades about two to four times faster than petroleum diesel.^{4, 6} A very important environmental benefit from using biodiesel comes from the CO₂ life cycle improvement. Through the photosynthesis process of growing the fuel feedstock, CO₂ is recycled which helps to control greenhouse gases and fight global warming.

4.3.2. Bio-LNG

The key parameter when considering the environmental performance of Bio-LNG is the level of methane losses associated with the production process and engine. High methane losses represent a significant contributor to climate change considering that CH₄ is 25 times higher global warming potential (GWP) than for CO₂ over a 100-year time perspective.³⁸ Whilst the minimisation of methane losses during upgrading are important, these should be considered alongside the potentially much more significant methane losses which may occur in the engine and also due to operational factors associated with biogas production such as incomplete stabilisation or unnecessary release of biogas during digestate storage. A study of full scale biogas plants operating under varying conditions indicated that between 5% and 15% of methane was collected during digestate storage.⁴⁶ Furthermore, unburned methane, is important to consider for the engines. Different engine concepts have different methane slip, with the highest methane slip reported for the lean burn dual fuel concept. The emissions of methane can be very high at low engine loads, up to 15%.⁴⁵ More than 90% reduction of the methane slip may be possible with an oxidation catalyst, but this have so far not been tested.⁴⁵⁻⁵⁰ This illustrates that optimising and managing the whole bio-methane production process including effective digestate storage and use is required in order to generate maximum economic value and minimum environmental impact.

In addition to methane slip, ship accidents such as collisions, groundings, and foundering will continue to result in spills of fuel and cargo, as they have in the past for heavy fuel oil. Environmental consequences of spills depend on factors such as spill volume, nature of the fuel spilled, and sensitivity of the receiving environment and biota that are exposed. Compared to heavy fuel oil and residual oil, the environmental consequences of spills of Biofuels are expected to be lower. LNG spills on to water will spread and boil at a very high rate and thus not remain on the water surface for long. Localized short-term effects on the water surface may result from cooling due to the cryogenic liquid.⁴⁷

5. Conclusions

The existing and upcoming environmental restrictions can be met by alternative fuels such as SVO, biodiesel and Bio-LNG. It is technically possible to replace marine fossil fuels with biofuels for use in ship engines. However, all alternative fuel options are accompanied by benefits and challenges. The most relevant parameters limiting the potential of biofuels includes availability, technological development, technical integration, and operational consequences. Furthermore, the key issues to promoting alternative fuels in marine transportation need to be addressed including establishing a marine-grade specification, increasing the price competitiveness of marine-grade fuels by reducing its manufacturing costs, providing tax cuts, exemptions, and government subsidies, adopting compatible elastomers and metallic materials in fuel feeding systems and storage tanks, and also applying approaches or technologies suitable for improving the low-temperature fluidity of biofuel blends.

The assessment of technology readiness of biofuel as marine fuel shows that the biofuels fuel system, consists mostly of well-known components, and that the individual components are of a mature technology and have been used in the maritime industry. The new application is the connection of all these components along the biofuel flow and their interaction. The assessment also shows that additional safety barriers are needed in every part of the biofuel fuel system. From a technical aspect this is very much achievable for ship-owners, both for new build and a retrofit systems.

Acknowledgement

The financial support of Engineering and Physical Sciences Research Council (EPSRC) Shipping in Changing Climates project (EP/K039253/1) is gratefully acknowledged.

References:

- 1 S. Bengtsson, K. Andersson, E. Fridell, Proc. Inst. Mech. Eng. Part M J. Eng. Marit. Environ, 2011, 225, 97-110
- 2 C.Y. Lin, T.H. Huang, Marine Pol, 2012, 36, 103–107
- 3 P. Gilbert, C. Walsh, Traut, U. Kesime, K. Pazouki and A. Murphy, J. Clean. Prod, 2018, 172, 855-866
- 4 U. Kesime, K. Pazouki, A. Murphy, A. Chrysanthou, J. Environ. Manag, 2019, 235, 96-104
- 5 C.W. Mohd Noor, M. Noor, and R. Mamat, Renew. Sustain. Energy Rev, 2018, 95, 127-142
- 6 S. Bengtsson, E. Fridell, K. Andersson, Energy Policy, 2012, 44, 451-463
- 7 A.A Banawan, M. M El Gohary, I.S. Sadek, Proc. Inst. Mech. Eng. Part M J. Eng. Marit. Environ, 2010, 224, 103–113
- 8 M. Mondou, G. Skogstad, J. Bognar, Biomass and Bioenergy, 2018, 116, 171-179
- 9 S. Lim, K.T. Lee, Renew. Sustain. Energy Rev, 2012, 16, 1790-1800
- 10 J.J. Corbett, In: Cutler, J.C. (Ed.), Encyclopedia of Energy. Elsevier, New York, 2004, 745–758.
- 11 J.J. Corbett, J.J. Winebrake, J.J., J. Air Waste Manag. Assoc, 2008, 58, 538–542
- 12 E. Esteban, G. Baquero, R. Puig, J. Riba and A. Rius, Biomass and Energy, 2011, 35, 1317-1328
- 13 J. Blin, C. Brunschwig, A. Chapuis, O. Changotade, S. Sidibe, E. Noumi, P. Girard, Renew. Sustain. Energy Rev, 2013, 22, 580-597
- 14 J. Malca, A. Coelho and F. Freire, Appl. Energy, 2014, 114, 837-844.

- 15 M. F. Milazzo, M, F. Spina, S. Cavallaro and J.C.J Bart, *Renew. Sustain. Energy Rev*, 2013, 27, 806-852.
- 16 Biofuels in ships, <https://zero.no/wp-content/uploads/2016/05/biofuels-in-ships.compressed.pdf> (Accessed, February, 2019)
- 17 A. Demirbas, *Energy Policy*, 2007, 35, 4661-4670
- 18 A.V. Bridgwater, *Environmental Progress & Sustainable Energy*, 2012, 31, 261-268.
- 19 J. Lehto, A. Oasmaa, Y. Solantausta, M. Kyto, M and D. Chlaramonti, *Appl. Energy*, 2014, 116, 178-190.
- 20 Paper and Fibre Research Institute, <http://www.pfi.no/Biorefinery/Biorefinery-Projects/ReShip/> (Accessed, February, 2019)
- 21 IEA Report, https://publik.tuwien.ac.at/files/PubDat_183836.pdf (Accessed, February, 2019)
- 22 IEA Bioenergy. <http://task40.ieabioenergy.com/wp-content/uploads/2013/09/t40-t37-biomethane-2014.pdf> (Accessed, February, 2019)
- 23 M. Poschl, S. Ward and P. OWENDE, *Appl. Energy*, 2010, 87, 3305-3321.
- 24 T. Patterson, S. Esteves, R. Dingsdale, R. Dinsdale, and A. GUWY, *Bioresource Technology*, 2011, 102, 7313-7323.
- 25 F. Espadafor, M. García, J. Villanueva, J, M. Gutiérrez, *Transportation Research Part D*, 2009, 14, 461–469
- 26 NREL Report, <https://biodiesel.org/docs/using-hotline/nrel-handling-and-use.pdf?sfvrsn=4> (Accessed, February, 2019)
- 27 A. Takeda, H. Nakatani, E. Shimizu, T. Ura, T. Kato, 25th CIMAC conference, 2007 https://www.jstage.jst.go.jp/article/jime2001/43/1/43_1_21/_article/-char/en (Accessed, February, 2019)
- 28 S. Bhattacharyya, C.S. Reddy, *Journal of Agricultural Engineering Resources* 1994, 57, 157– 166
- 29 F.I. Rizwanul Fattah, H. Masjuki, A. Liaquat, R. Ramli, M. Kalam and V. Riazuddin., *Renew. Sustain. Energy Rev*, 2013, 18, 552-567
- 30 E. Ryckebosch, M. Drouillon, M. Vervaeren, *Biomass and bioenergy*, 2011, 35, 1633-1645
- 31 M. Gullberg, J. Gahnström, *Baseline report, North European LNG Infrastructure Project – a Feasibility study for an LNG Filling Station Infrastructure and test of Recommendations* (2011)
- 32 S. Brynolf, E. Fridell and K. Andersson, *J. Clean. Prod*, 2014, 74, 86-95.
- 33 W. Doug, Ninth edition Butterworth-Heinemann, Oxford, 2010, 41–60
- 34 B.R. Moser, A. Williams, M.J. Haas, R.L. McCormick. *Fuel Processing Technology*, 2009, 90, 1122–1128
- 35 P. Nayyar, *The use of biodiesel fuels in the U.S. marine. Report for the U.S. Maritime Administration (MARAD)*; 2010.
- 36 A.E. Atabani, A.S. Silitonga, I.A. Badruddin, T.M.I. Mahlia, H.H. Masjuki, S. Mekhilef, *Renew Sustain Energy Rev*, 2012, 16, 2070–2093
- 37 C.Y. Lin, H. H. Cheng, H.H, *Energy Conversion Management*, 2012, 53, 128–134
- 38 *European LNG Strategy*, London, 24 March, 2015
- 39 A. Andriyana, A.B. Chai, M.R. Johan, M.R. *Mech Res Commun*, 2012, 43, 80–86
- 40 A.S.M.A Haseeb, M.A, M.I. Jahirul, H.H. Masjuki, *Fuel*, 2011, 90, 922–931
- 41 M.A. Fazal, H Asma, H.H. Masjuki (2010) Comparative corrosive characteristics of petroleum diesel and palm biodiesel for automotive materials. *Fuel Processing Technology*, 2010, 91, 1308–1315

- 42 L.Haraldsson, Online,
http://www.iffship.com/PublicPresentations/Symposium_2010-11-16/Haraldson%202010-11-16%20rev.1.pdf (Accessed, February, 2019)
- 43 IMO Report, Online
<http://www.imo.org/en/OurWork/Environment/PollutionPrevention/AirPollution/Documents/LNG%20Pilot%20Study%20-%20Trinidad%20and%20Tobago%20-%20final%20report.pdf> (Accessed, February, 2019)
- 44 A. Miola, M. Marra, B.Ciuffo, B., Energy Policy, 2011, 39, 5490–5498.
- 45 T.E. Patterson, R. Dinsdale, A. Guwy, Energy policy, 2011, 39, 1806–1816
- 46 I. Angelidaki, A. Heinfelt, L. Ellegaard, Water Science Technology, 2006, 54, 237–244
- 47 A. Luketa-Hanlin, J. Hazard. Mater, 2006, 132, 119e140.
- 48 F. Burel, R. Taccani, N. Zuliani, Energy, 2013, 57, 412–420, DOI: 10.1016/j.energy.2013.05.002
- 49 G. Karavalakis, E. Tzirakis, L. Mattheou, S. Stournas, F. Zannikos, D. Karonis, Journal of Environmental Science and Health—Part A Toxic/Hazardous Substances and Environmental Engineering, 2008, 43, 1663–1672.
- 50 N. Bruckner-Menchelli, N. US Navy Targets 2016 for Green Fuel Use, Sustainable Shipping. Petromedia Ltd, 2011