Results in Engineering 21 (2024) 101889

Contents lists available at ScienceDirect

Results in Engineering

journal homepage: www.sciencedirect.com/journal/results-in-engineering

Review article

Decarbonized automotive fuel: Liquefied petroleum gas biosynthesis, benefits and drawbacks

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A R T I C L E I N F O

Keywords:
Microbial techniques
Decarbonization
Bio-LPG
Fuel cells
Bio-refining
Climate protection

A B S T R A C T

Decarbonization for climate protection through bio-LPG production and application is fast gaining attention in the automotive sector because of its numerous benefits. Despite being a promising green alternative to conventional LPG which reduces carbon footprint by 80%, notable challenges associated with the commercialization of some production processes have hindered its potential global application. While bio-refining is already established as the highest technique for commercial LPG production, the addition of microbial techniques among other routes, using either natural or engineered variants has yet to meet the volumetric demand of high-energy sectors. Environmentally, Bio-LPG is considered a means to control ice formation through CO_2 reduction active prevention of sea ice-melting, and control of glaciers and sea level rise by approximately 21.34 m. However, in automotive applications, this study highlights bio-LPG fuel synthesis processes including natural propane biosynthesis. Highlights of its benefits, for example, in fuel cells and engine oil lubricity, indicate the prospects, and the limitations, such as wall wetting, icing formation, bubble formation associated risks and lower lean misfire can be addressed by adopting controlled fuel deposition within combustion chamber or utilizing additives, introducing heating element device to de-freeze, advancing ignition timing and redesign of the combustion chamber, respectively. Up-scale or increased utilization of HD-5 vehicles is recommendable since a gallon of LPG emits 5.68 kg of carbon dioxide (CO2) compared to the 8.89 and 10.18 kg of CO_2 emitted by gasoline and diesel fuels. Bio-LPG is chemically identical and compatible with all LPG products, therefore can be used directly or as blends.

1. Introduction

The transitive independence of transport fuel from fossil products to more sustainable bio-economic products is undoubtedly vital for a positive address of climatic global concerns (Sanz-Hernández et al., 2019; [1]) and future energy supplies. The development of economically viable clean-burning fossil alternatives is derivable from the catalytic conversion of CO_2, synthesis gas, and methane to liquefied petroleum gas (LPG) products. LPG, a mixture of propane and butane, is often produced by processing natural gas or refining petroleum and is classified as an off-grid fuel. Biosynthesized LPG, or Bio-LPG, is LPG manufactured using plant and vegetable waste as feedstock [2]. Utilizing bio-LPG as an automotive fuel could further decarbonize energy needs [3], and bio-LPG is reported to have an identical chemical structure to conventional LPG [4]. In the case of fuel switch, such as bio-LPG systems transition to LPG systems, and vice versa, there is no need for infrastructural or equipment change, and it has an up to 80% lesser carbon footprint than fossil LPG (LGE, 2022). Meanwhile, decarbonized automotive fuel in this context is further supported by the European Green Deal to achieve climate neutrality of 90% by 2050 in all transport GHG emissions compared with 1990 through the role of vehicles, fuel, and transport demand (EEA Report, 2021 [5]). Bio LPG has a carbon intensity that is around 70–80% lower than oil and can be used in

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https://doi.org/10.1016/j.rineng.2024.101889
Received 2 December 2023; Received in revised form 21 January 2024; Accepted 4 February 2024
Available online 13 February 2024

Nomenclature

CC	Combustion chamber
PM	Particulate matter
CO	Carbon monoxide
CO_2	Carbon dioxide
HC	Hydrocarbon
HD-5	Propane grade specification
NO_X	Oxides of nitrogen
SO_X	Sulphur oxides
SOFC	Solid oxide fuel cell
MCFC	Molten-carbonate fuel cell
Jet A	Kerosene grade fuel
RPI	Rocket P 1
DME	Dimethyl ether
EV	Electric vehicles
CIE	Compression ignition engine
DME	Dimethyl ether
MCCI	Mixing controlled compression ignition
IDT	Ignition delay time
BTE	Brake thermal efficiency
BSFC	Brake-specific fuel consumption
EGT	Exhaust gas temperature
MAAE	Mean absolute average error
TBN	Total base number
WLPGA	World LPG Association

existing LPG appliances and storage units, allowing for a cost-effective pathway to decarbonization for industrial and commercial processing [6].

1.1. Properties of Bio-LPG

On a commercial basis, two LPG grades predominate, commercial propane and the HD-5 (GPA, 2013; [7]). They exist in both liquid and gaseous states, making them a liquid-gas automotive fuel. Fortunately, greenhouse gas (GHG) emissions reduction and de-carbonization of the electric grid can be achieved by the adoption of off-grid biofuels, including bio-LPG and the ever-increasing batteries for example, in electric vehicles to reduce the enormously increasing global energy demand for fuel, [8]. The properties of LPG and other related automotive fuels are highlighted in Table 1.

It is noteworthy that LPG varies from country to country [12], during summer and winter [12], depending on the intent and suitability (please refer to Table 4 for some countries). There is a projected report that approximately 17%–33% of new vehicle sales and 8%–14% of the world's light vehicle fleet will be made up of light-duty EVs, by 2030 [28]. However, the challenges from fossil fuel alternatives include the illustrious advancement in electrification and are unique to heavy machinery, transatlantic aircraft, and long-distance terrestrial, marine, and aerial freight transit. These applications depend on energy-dense fuels because they need high power and energy-to-weight ratios. Still on the special need for elevated power, and the ratio of energy-to-weight for energy-dense fuels, petroleum distillate-rich branching and cyclic alkanes like aviation fuel (Jet-A), Rocketry fuel (RP1), and high energy density synthetic polymers such as hydroxyl-terminated polybutadiene and HTPB-rocketry serve military and commercial aerospace purposes [29], the water-way cargoes rely majorly uses bunker fuel which consist of denser fractions distillate of petroleum with notable NOx, SOx, and particulate matter emission during combustion process [30], but the resulting pollution from them impact the environment negatively. For example, Amer et al. [22] reported that shipping alone accounts for approximately 3% of global emissions with a release of annual emissions of 1 trillion Kg of CO_2 and GHGs, whereas aviation is responsible for 2% on account of 9.15 billion Kg of CO_2 in 2019 [31]. Although there will be a continual decline in the climate impact owing to the use of electric cars for light-duty transportation, the carbonizing impact of the heavy-duty and aerospace sectors may intensify as a function of global emissions in the long term. More so, petrol-based biofuel blends may cut down on harmful emissions, however, current renewable biofuels contribute approximately 0.5% to the global fuel supply [32]. So, the question is on how to produce so much LPG (commercial) utilizing a sustainable process while considering the fuel end product-host metabolism tolerance [22], fuel separation and purification, and bio-economic techniques. For these reasons, novel and sustainable alternatives to serve high energy demand sectors are urgently needed. There are no known commercial natural biosynthetic routes to propane, including the widely adopted aldehyde deformylating oxygenase (ADO) variants that are naturally occurring or developed synthetically with approximately 3–5 h^{-1} low turnover number (Kallio et al., 2010; [33]). Meanwhile, the sole commercially viable way of producing LPG continues to be the Neste process, labor-intensive catalytic chemical conversion of biodiesel waste (glycerol) dependent on H_2-derived natural gas [34]. Hence, this research aims to highlight the synthesis techniques of bio-LPG and identify pathways for any prospective scale-up of bio-LPG, benefits, and general limitations of bio-LPG, as an automotive fuel. In addition, the novelty of this paper is evident in Bio-LPG potential for local air quality improvement by drastic elimination or reduction of emissions or transition to low-GHG energy for automotive vehicles, appropriate mitigation of global climate change, and energy security by reducing national dependence on petroleum are the central premise to foster climate protection. Whereas the main issue with alternatives to gasoline is the higher production of CO2 and NOx due to higher combustion temperature inside the cylinder, LPG has been reported to produce 18.74 and

Table 1
Properties of some common automotive fuels.

Properties	LPG	Gasoline	NG	Coal/Coal Dust
Specific Calorific Value (MJ/Kg)	46–51	44–46	42–55	≤25
Energy Density/Vol. (MJ/L)	26	46	55	24
Relative Density @15 °C (Kg/L)	0.5–0.58	0.71–0.77		
Auto-ignition/Flammability temp. (°C)	410–580	280	540	450–650 °C [9]
Molecular Weight (Kg/k mole)	44.097		19.5	2378 [10]
Detonation/Flammability limit (Vol. %)		1.1–3.3	6.3–13.5	45–450 mg/l [11]

Other sources: www.energyeducation.ca; en.wikipedia.org; www.engineeringtoolbox.com

Table 2
Propane-butane ratios in countries according to seasons [12].

Country	Summer	Winter
Turkey	30%:70%	50%:50%
Germany	100%:0%	100%:0%
Denmark	30%:70%	70%:30%
England	100%:0%	100%:0%
Austria	20%:80%	80%:20%
Holland	30%:70%	70%:30%
Sweden	50%:50%	100%:0%
Switzerland	100%:0%	100%:0%

Table 3
Some renewable LPG-related feedstock, synthesis process, and level of readiness.

Feedstock	Process Route	Remarks/ Readiness	Ref.
Bio-oil	Hydrotreatment	Commercial	[2]
Authors used vegetable oil to produce biodiesel and bio-LPG	The procedure used solid acids and sulfided nickel-molybdenum to make bio-hydrogenated diesel and LPG.	With canola oil, 5.7 wt percent of LPG was generated at 350 °C and 4 MPa hydrogen in an elevated pressure fixed-bed flow reaction system.	Liu et al., 2021
To synthesize Bio-LPG, the authors hydrotreated vegetable oils using a single step.	Sulfide Ni–Mo and solid acids were used as catalysts to produce bio-hydrogenated diesel and liquefied petroleum gas fuel.	Mixed paraffins were produced by the procedure. Propane was synthesized over Ni–Mo/ SiO_2–Al_2O_3 by the hydrogenation and deoxidization of the glycerin groups in the vegetable oils.	[13]
An up-scaling from glycerol to propane was carried out by the authors.	Starting with foundational laboratory data from microreactor testing to the kilogram scale, the author investigated the scaling up of a glycerol-to-propane process.	Four reactors were used in the study, which used a glycerol/ water combination and were run between 1000 and 3000 h. Data gathered show the technique may be sufficiently scaled up to produce between 1000 and 10,000 tonnes per year.	Hulteberg and Leveau [14].
LPG was synthesized by blending tunable bio-LPG with short-chain fatty acids (butyric, isobutyric, valeric, 2-methylbutyric, and isovaleric acid) by photodecarboxylation.	Bioengineered bacteria biomass (E. coli, Halomonas (in non-sterile seawater), and Synechocystis (photosynthetic)) were used in the process via photocatalysis. From variation G462V, which produced propane and butane, tunable bio-LPG mixes were synthesized.	Propane, butane, and isobutane were produced in the experiment using wild-type and four CvFAP variant enzymes, namely G462 V/ A/I/F. G462I with branched-chain substrates, isovaleric, and 2-methylbutyric acids, produced the best gas levels (5–8 times higher).	[15]
Fatty acid photodecarboxylase (FAP) modified versions were used to produce alkanes and alkenes.	A catalysis technique was used to convert fatty acids into n-alkanes or n-alkenes in response to blue light. Eight fully developed N-terminal His6-tagged cyanobacterial FAP homologues produced in E. coli are used in the process.	Long-chain fatty acids (C14–C18) are precisely the target of the reaction quantum yield, which is larger than 80%. The current level is proof-of-concept.	Sorigue et al. 2017, [16, 17]
Bio-oil Glycerine	Dehydrogenation	Demonstration Pilot	[2]
Authors synthesized propane from vegetable oil Glycerine	The Ni–Mo/ SiO_2–Al_2O_3 catalyst, which is sulfided, was used to convert the glycerin groups in the vegetable oils in "No. 1a" above to propane.	The resulting renewable diesel output contained BHD made from Jatropha, Palm, and Canola oils in amounts of 83.5 wt percent (LPG 4.9%), 82.1% (LPG 5.4%), and 81.4 wt percent (5.7% LPG).	Liu et al., 2021
A sequential synthesis of propane from glycerol was carried out	Glycerol was converted to acrolein, and then 1-propanol was hydrogenated and dehydrated to create propane.	For scaling from 1000 to 10,000 tonnes per year, data generated from system design calculations were sufficiently agreeable to the result.	[14]
A fungal strain was used to carry out the bacterial production of 1, 3-propane-diol from glycerol.	Various fermentation conditions (aerobic, semi-aerobic, and anaerobic) were used during the process, which used instant baker's yeast (*Saccharomyces cerevisiae*)	The ideal reaction conditions (anaerobic fermentation at 25 °C) resulted in a 42.3 wt percent yield of 1,3-propanediol and a 93.6 wt percent conversion of glycerol.	[18]
Microbial (natural) carbon capture by photosynthesis of cyanobacterium *Synechcocystis* to fix CO_2 into organic carbon for propane production	They utilized biomass that has been cultivated with halomonas strains of bioengineered bacteria. Set up in batch mode, the photobioreactor included fresh BG11 media with a starting culture diluted 3:1 in high salt glycerol medium at pH 6.8 for halomonas and Synechocystis cultivation, respectively.	Rapid growth and genetic tractability characterize microorganisms with abiotic stress tolerance and optimizable features. This process produces approx. 12.2 ± 2.6 mg propane/ g-cells/day, which happens to be at a proof-of-concept stage.	[19]; Zavrel et al., 2013; [20, 21]
Authors utilized microbial fermentation of amino acid wastes in the production of LPG	Utilized proteinaceous waste amino acids as bio-alkane precursors in the production of bio-LPG wastes (propane, butane, and isobutane) from valine (C3), isoleucine (n-C4), and leucine (i-C4).	Explored the commercial potential of bio-propane/butane blends with CvFAP-dependent bio-LPG synthesis employing recombinant E. coli, Halomonas, and Synechocystis as the microbial chassis.	[22]
Synthetic biological isolation process to synthesize LPG	Microbial Fermentation of isolated marine	The authors established that when compared	[23]

(continued on next page)

Table 3 (*continued*)

Feedstock	Process Route	Remarks/ Readiness	Ref.
	bacterium from mixed sediments of microbial cultures and bacterial monocultures. From terrestrial and marine soil sampling, incubation, colony picking, and bacteria strain culture to propane analysis took approximately 37 weeks.	to the sterile medium control, the initial mixed microbial cultures made from sea debris produced a lot of propane (25.39 ppm 2.33, p 0.0001).	
The authors conducted a catalytic reaction of fossil-based alkene and bioethanol.	Gasoline additive, Ethyl *tert*-butyl ether was reacted catalytically with fossil isobutene and bioethanol	A gasoline additive with a fossil-based energy equivalent was obtained in the reaction.	[24–26]
Authors produced bio-oil from ethylene propylene diene monomer	The process utilized employing Ziegler-Natta olefin polymerization to bio-based ethylene	Bio-oil additives made from biomaterials are utilized in the construction and automotive industries as well as in the production of oil additives.	[27].
LPG synthesis from Sugars	Fermentation	Demonstration	GTI Report, 2010
LPG from Cellulosics	The process involved hydrolysis and fermentation	Concept	GTI Report, 2010
LPG from Wet wastes	Technique utilized digestion	Concept	GTI Report, 2010
Cellulosics Organic waste	The pathway involved gaseous transformation and synthesis	Demonstration concept	GTI Report, 2010
Cellulosics Organic waste	The process utilized liquid conversion and synthesis	Concept	GTI Report, 2010
Methanol-to-Gasoline process for the co-production of LPG	N/A	Concept	GTI Report, 2010
Bio-reforming process of plant sugar via aqueous-phase reforming technology.	N/A	Concept	GTI Report, 2010
production of LPG from DME from biomass or coal-derived syngas via catalysts	N/A	Concept	GTI Report, 2010

25.92% lower CO_2, and NOx emissions respectively as compared to gasoline [35], making studies on bio-LPG worth eternal devotion to as far alternative and renewable fuels are concerned.

1.2. Bio-LPG overview

Bio-LPG (also known as futuria liquid gas) is an eco-friendly renewable energy solution that is chemically identical and compatible with all LPG products, with an 80% lower carbon footprint compared to conventional LPG, produced by bio-refining, power to gas (P2G), anaerobic digestion (AD), gasification techniques, etc. [36]. Bio-LPG can be employed to address rural and off-grid, cost-effective decarbonization, high-temperature industrial processes, household applications, etc. Based on applications, Bio-LPG can be employed as an environmentally benign substitute for ozone-depleting chlorofluorocarbons (CFCs and HCFCs) using refrigerant and aerosol propellant [37], cooking fuel [38], carbon footprint determinant in a non-homogeneous process [39]. In addition, it can proffer carbon footprint reduction through gas-powered heating combined with renewable thermal systems and hybrid systems as well as Autogas (LPG as transport fuel). Based on the hydrotreated vegetable oil (HVO) pathway, the projected capacity is forecasted to expand up to 2200 million kg/yr. by 2030 [40]. Synthesized quantities need to be scaled up to meet energy demands because this purified off-gas stream produces 50–80 kilos (5–8%) of bio-LPG for every 1000 kg of renewable diesel or kerosene. LPG (Autogas) is reported to have about a thousand applications and specifically powers about 27 million vehicles globally, mainly HD-5 (propane grade specification) vehicles containing at least 90% propane, 5% propylene, 5% butane, and 5% additional (butane and butylene) gases at most. When combusted, LPG generates 5.68 Kg of CO2 per 3.79 L as opposed to the 8.88 Kg and 10.18 Kg of carbon dioxide (CO_2) emitted by gasoline and diesel fuels (GPA, 2013).

Based on environmental impact, industrial, agricultural, and commercial sectors that fuel their processes for space heating and vehicles with oil or coal, can switch to LPG because it presents a lower-carbon alternative to oil and coal, with an emission intensity of approximately 20% and 30–40% lower (GGR, 2019), respectively. As well as lowering carbon emissions, LPG can improve local air pollution since it is a clean burning fuel that produces almost zero particulate matter (PM) when combusted [6]. On public policies with the objective is to ensuring a smooth transition to low-GHG energy for motor vehicles, the idea of displacement of most of the fossil petroleum with low-GHG energy by 50–100% by 2050 would require that the majority of new vehicles sold in 2050 are alternative fuel vehicles, which is a huge task for a large-scale energy transition [41].

2. Bio-LPG production

Earlier techniques for Bio-propane synthesis were Bio-forming, production of gasoline and diesel from biomass [42], direct selective synthesis of LPG from synthesis gas produced from natural gas, coal, and biomass [43], a conversion process of DME from glycerol, a by-product from bio-diesel production and H2 to bio-methanol which can be further converted to bio-DME using commercially available dehydration technologies to LPG [44], or utilizing hydrogen from renewable sources, e.g., via biomass gasification, or from biogas, having material incompatibility with existing LPG [45]. Other bio-synthesis processes of LPG include microbial fermentation bioprocessing (e.g., amino acids) and chemical conversion of bio-derived raw materials including waste biomass (Sorigue et al., 2017; [36]), providing a green alternative to fossil-generated LPG. Fig. 1 gives a map highlighting the multiple potential pathways to bio-LPG production from separation techniques of fuel end-products during bio-LPG manufacturing.

The well-established synthetic techniques of bio-LPG development are the hydrotreatment and dehydration methods. However, only the hydro-treatment bio-LPG is commercially viable, while the dehydration has the potential to be expanded beyond a handful quantity. In addition, utilizing glycerine in fuel applications, is noteworthy for automotive fuel applications, being a good feedstock for chemical synthesis, as it is classified as a by-product. However, among the several feedstocks that may be hydrotreated to synthesize bio-LPG, including bio-oils, propylene, butylenes, and dimethyl ether (NREL, 2018), the bio-oil is the only one that is now used commercially. Table 1 highlights this. Processes including fermentation-to-LPG, alcohol-to-jet, biogas/biomethane conversion (oligomerization), glycerin-to-propane, power-to-x, and biosynthesis, however, have not yet scaled up significantly. The bio-LPG

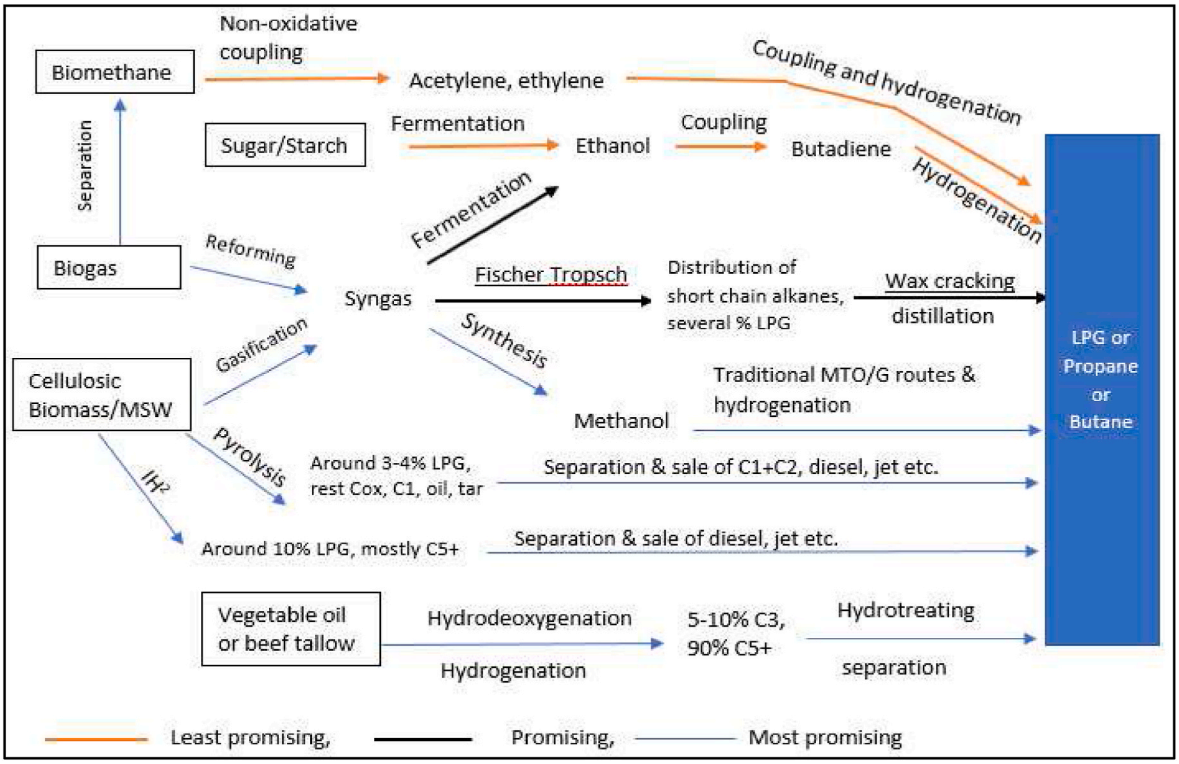

Fig. 1. Map of potential routes to bio-LPG (bio-LPG study report, 2020).

percentage varies depending on the method; a handful of them, including oligomerization, glycerin-to-propane conversion, and biosynthesis, produce 100% of propane (opisnet.com). For example, halomonas, a robust extremophile microbial chassis, was utilized in bio-LPG production under non-sterile conditions and using waste biomass as the carbon source, as presented by Amer et al [22] in a related study. Generally, bio-LPG production from biomass, biogas, or waste has a sustainable potential with a lower carbon footprint than fossil fuel LPG [46]. On the feasibility of bio-LPG in alignment with regulations and policies governing automotive fuels, there are hardly existing reports on private sector investment subsidy and regulation for refueling infrastructure, which may be a major contributor to the low volumes in availability from a commercial perspective.

2.1. *Scalability of microbial pathways*

Most proofs of concepts are limited to lab-scale production in vivo (low technology readiness level) and do not demonstrate detailed

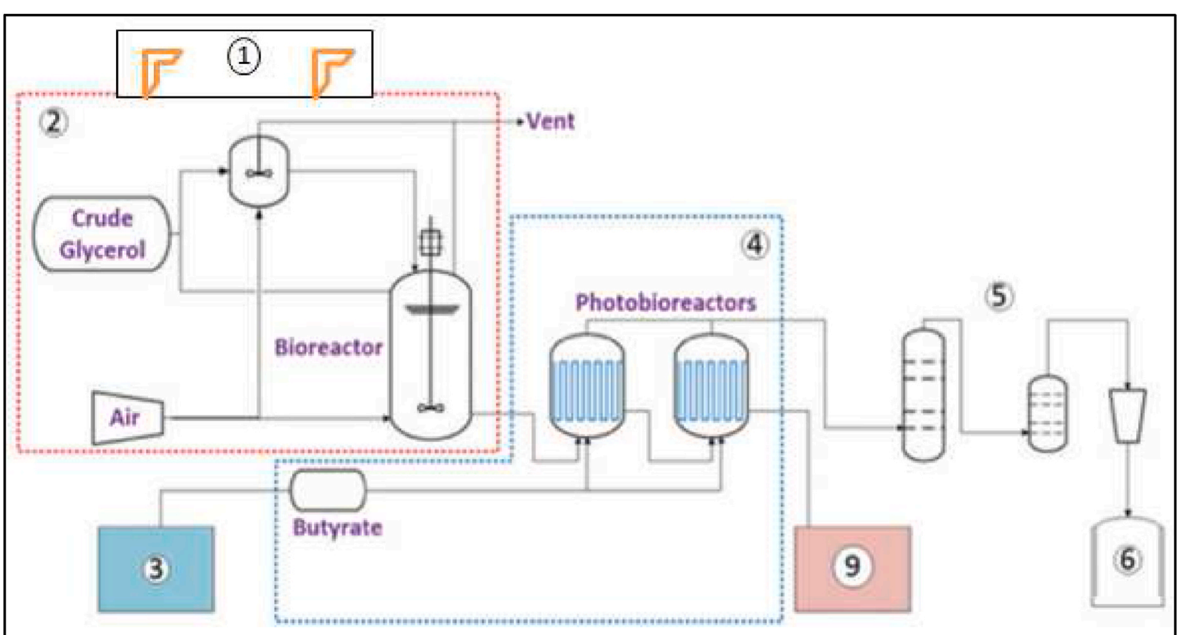

Fig. 2. Futuristic prototype bio-LPG production hub.

approaches to commercial-scaled bio-LPG production. According to Amer et al. [22], scaled production of bio-LPG is more economically feasible using Halomonas. They reported that scaled production of polyhydroxyalkanoates using Halomonas is at a 65% cost saving compared to E. coli. Halomas bio-alkane commercially viable process is reportedly achievable by Halomonas cultivation around a coastal environment with on-site seawater, an anaerobic digester (AD) for VFA production, and optionally a cyanobacteria photobioreactor for CO2 fixation and VFA supply (see Fig. 2 for typical prototype).

Where processes; (1) seawater intake and pre-treatment; (2) biomass accumulation fermentation system; (3) anaerobic digestion (AD) plant for volatile fatty acid supply; (4) photo-bioreactor for propane production; (5) propane purification; (6) propane compression and liquefaction; (7) local propane distribution by road and rail; (8) local propane usage by heavy industry such as power generation or steel mills; and (9) waste biomass treatment and fish feed production [22].

In addition, steps from typical halomonas to bio-LPG production include strain identification by gene encoding amplification and sequencing (phylogenetics), for example, Amer et al. [22] reported that their process of sampling and microbial cultures was prepared to generate inoculum slurries from both terrestrial soil and marine sediment, with seawater. Then, samples were incubated, under micro-aerobic/anaerobic conditions in tightly sealed headspace vials without shaking at 4 °C for 11 weeks, before analysis for propane in the headspace above the live cultures was conducted. On isolation, individual bacterial species were isolated by repeated colony picking and sub-culture on solid media at 4 °C for 10 weeks under anaerobic conditions. This highlights steps for which bio-LPG from the oceanic environment (Fig. 3) using microbial culture should be explored deeper with the intent that the bio-LPG production route could be deployed to address energy insecurity, clean air, and carbon management issues.

3. Benefits and limitations of LPG

Apart from the general benefits of LPG (bio-LPG) which include extended engine life due to reduction of wear on its components, for example, rings and bearings, etc. (see Table 6) by the action of lubrication, high octane rating which controls complete combustion and hence, engine knock [47]. The low stoichiometric fuel-air ratio and density reduce the specific fuel consumption and exhaust emissions. When burnt, its low carbon molecular content including particulate molecules produces low carbon dioxide (CO_2) emissions compared to conventional fuels. In addition, LPG (bio-LPG) based engines produce high thermal efficiency and improved fuel economy, high compression ratio, and subsequently high thermal efficiency without denotation compared to gasoline (Chaichan, 2019). Based on region and feedstock, LPG is mostly composed of propane and butane in varying ratios (see Table 2). According to Table 5, LPG (Bio-LPG) is seen as a replacement for gasoline and diesel to achieve better exhaust emission [48,49], replacement for marine fuel since it reduces emission and fuel costs [50], despite the high level of studies and appreciation of electric propulsion as a good fuel alternative in sole electric or hybrid propulsions, Jeong et al. [51], confirmed that the impact of battery application is far from zero-emission shipping from a life cycle perspective, concluding that electric propulsion systems are not necessarily adjudged eco-friendly. Meanwhile, LPG is adjudged to have storage and transportation benefit, better emission characteristics, low sulphur content, easy adaptation for engine or fuel change, and above all, unlike its renewable form, bio-LPG is reported to be sustainable [22].

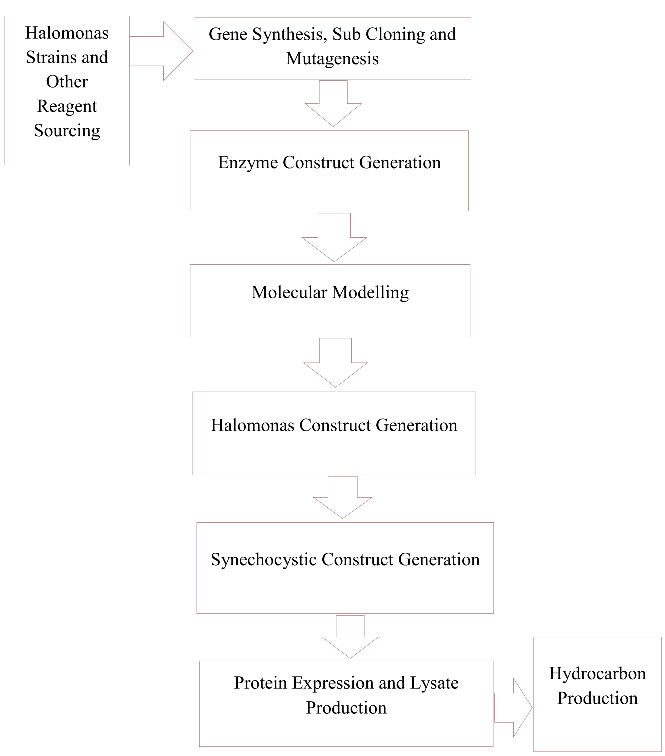

Fig. 3. Steps on the typical microbial generation of bio-LPG through Halomonas strain [22].

In its unprocessed state, LPG is not a greenhouse gas (GHG) and its fumes are not poisonous. It may be carried and kept as a liquid in straightforward steel containers due to its low vapor pressure [71]. Compared to liquid fuels, its favorable vaporization qualities encourage greater air and fuel mixing, and compared to other alternative fuels, it has a higher energy density [71]. For environmental excellence, advancement toward zero-carbon propulsion technology must not sideline the marine industry. The downside of LPG usage as aviation fuel has been linked to structural/size restrictions on tanks for LPG. However, it can be blended in a small proportion with jet A fuel [56]. The maritime sector will get closer to a greener future when retrofitted ships run on LPG, exceeding the IMO's worldwide 0.5% sulphur emissions cap and fully complying with the 0.1% sulphur cap in Emission Control Areas (ECA) and Sulphur Emission Control Areas (SECA), according to Ref. [36]. It has been reported that LPG as a marine fuel can enhance output efficiencies by 11% compared to compliant fuels, ensuring total voyage fuel economics [57]. Additionally, LPG propulsion results in cleaner, less expensive to operate, and more effective engines. Dual-fuel engines offer fuel flexibility, resulting in complete redundancy to guarantee continuous operations. Based on utilization, some of the LPG benefits can be inferred from Table 3.

3.1. Limitations of LPG

For industrial-scale biotechnology, one of the obvious challenges of having Bio-LPG emanating from synthetic biology is the yield restrictions due to substrate toxicity and cell integrity control at high doses, from genetically modified bacteria capable of generating propane [22,72,73]. In addition, on the argument that propane cannot be synthesized naturally using bio-synthetic pathways, the reasonable acceptance that geochemists may link multiple substrates to the biological formation of ethane and propane in oceanic sediments supports the microbial production of these gases [22]. This may call for the discovery of naturally occurring propane-producing bacteria in such an oceanic environment, and this may necessitate the identification and isolation of such organisms to engineer an accessible culture and processing for Bio-LPG production from it. Furthermore, apart from the explosive potential of LPG when it mixes with air within explosive limits, in the presence of an ignition source and de-oxygenation potential, it can lead to suffocation. Other limitations (for example, wall wetting, where fuel vaporization happens during idling and part-loading conditions as a result of impingement or condensing of un-vaporized fuel droplets

Table 4
Utilization of bio-LPG related fuels as a Drop-in-substitute in Transportation engines.

Process/Routes	Work Description	Remarks	Ref
The study assessed a steam reactor powered by propane fuel having a shell and tube heat exchanger.	Velocity, reformer temperature, species concentration control, and reaction rate were studied by the action of the catalyst-embedded tubes within the reformer.	Yield of hydrogen varied from 77.5 % to 92.2 % based on reactant conversion, and at 900k within the reformer outlet, propane consumption was complete.	[52]
The study utilized a blend of palm bio-diesel and decanol as a ternary blend in a compression ignition engine (CIE) using ANN and RSM models.	10, 20, and 30 vol % each of decanol was mixed with 50% of diesel at different load conditions. Output BTE, BSFC, NOx, HCs, smoke opacity and ignition delay period, CO, CO2 EGT, and MFB were examined.	ANN prediction response was R > 0.99 and the MAAE was 1.879%. They recommended an RSM-based optimization value of 30% decanol, biodiesel 20%, and diesel 50% for improved performance and decreased emission parameters.	[53]
DME/Propane mixture as renewable energy fuel option and diesel replacement in CIE using chemical kinetic mechanisms	At MCCI engine operating conditions, the ignition characteristics of the mixture were assessed at 700–1100 K and pressures of 55–84 bar	At 100; 100; 60:40 percent mixtures, IDT chemical kinetic mechanisms were compared to Aramco-3.0, NUIG, and Dames et al. mechanisms, and all mechanisms over-predicted IDT compared to experimental values	[54]
LPG systems application in layered combustion system vehicle using Volkswagen Touran 1.6 FSI.	4-stroke, 4-cylinder, direct injection, split intake manifold was utilized to determine wheel power and exhaust emission at DIN 70020 of ranging gears and speeds	10.23% power loss in LPG mode was observed which may be due to 30% energy reduction of LPG. 8.25%, 71.76% less emissions occurred for CO2, CO, and 27.15% less HC values compared to gasoline.	[55]
LPG/Jet A as fuel in a turboshaft engine.	Different dosing fractions of propane gas were combusted with Jet A fuel.	Using CFD computation, unburnt fuels reduce from 11.4 (Pure Jet A) to $6.26e^{-2}$ (0.2 fraction of Propane gas), 84 to 41 NO_x, 18, 372 to 15, 865 CO_2.	[56]
Authors compared JP-8(Jet Propellant), (LPG) and natural gas in the F110 GE100 jet engine	A low bypass ratio turbofan engine with different Mach numbers for thrust and fuel mass flow rate values for JP-8 fuel.	According to reports, LPG volume was more than JP-8 under the same flying circumstances. Natural gas has a lower adiabatic flame temperature, which uses less extra air to power aircraft engines. To employ natural gas in the airplane, it was suggested that the LPG fuel tank be cryogenic.	[57]
The authors investigated two hybrid aircraft propulsion and powering systems using alternative fuels	Energy and exergy analyses were undertaken to examine the aircraft's performance when operating in cruising mode using kerosene, methane, and hydrogen (75:25).	The report revealed that the basic turbofan's maximum thrust force was 153 kN, compared to 116 kN and 107 kN for the SOFC and MCFC turbofans. Their relative exergy and thermal efficiencies were 71% and 87.6%, 52.8% and 66.2%, and 43.4% and 52%. Using the alternative fuel mixes, carbon emissions decreased from 18 kg/s to roughly 3.7 kg/s, which is positive for the fuel blend.	Seyam, 2021
Authors showed by operating a 1-kW, 22-array stack in a 5-kW capacity SOFC system to operate a single cell on simulated pre-reformed LPG.	The authors used a micro-reactor that was scaled up to show, during a 500-h test in a prototype LPG 1-kW reformer, how to produce a combination of methane, hydrogen, and carbon oxides for SOFC stacks reform.	To produce a reformed gas on a dry basis (55% methane, 25% hydrogen, and 20% carbon dioxide) at 350–373 °C under isothermal circumstances, pre-reforming and steam reforming catalysts were tested.	Ahmed and Foger, 2002
The authors used the PYTHIA and TURBOMATCH software to simulate a three-shaft high-bypass engine similar to the RB211-524.	The model was tested on an open-works commercial aircraft that uses synthetic paraffinic kerosene. Kerosene, Kerosene, and hydrogen blend, and kerosene and diesel were tested for net thrust, fuel flow, and specific fuel consumption.	kerosene and hydrogen mixture were reported to give the best engine performance while there was a slight reduction in the engine performance of blended kerosene and diesel.	[58]
For patrol ships' electric propulsion, authors developed a waterjet-type LPG engine with a 230 kW class.	In comparison to a standard CNG engine, a 200 kW, 6-cylinder LPG fuel engine was intended to consume 96.77% propane and provide 230 kW of power and 138 kgfm of torque.	A 200 kW, 6-cylinder LPG fuel engine was created with a throttle range of 22.8%–49.8%. Depending on the load, the torque and engine output steadily increased to 202 kW and 1070 Nm, rpm at 1800 rpm, respectively. NOX production for an 1800 rpm prime mover was 1 g/kWh, within 2 g/kWh of the IMO Tier III limits.	[48]

around the intake wall, combustion chamber liners, and top of the piston) is characterized by wall-wetting parameters like fuel density, intake duct geometry, wall film thickness, wall film height, mixture preparation, and such fuel vaporization which occurs during idling and part-loading conditions of LPG fuel are briefly described in Table 5, as related to automotive applications.

3.2. Effect of LPG (bio-LPG) lubrication and wear of engine components

The lubrication effect of alternative fuels between surfaces moving

Table 5
Some notable challenges of LPG in automotive engines.

Challenge Type	Objective	Work-done	Concluding	Ref.
Wall wetting	Wall wetting as a liquid: They studied the in-cylinder wall wetting attributed to HC emissions using pre-mixed LPG.	By controlled liquid fuel deposition within a controlled combustion chamber (CC) location. This was achieved using a probe in direct-injected and port-fuel-injected CC at the desired crank angle.	Results show that the combustion chamber liquid fuel impingement has a significant exhaust cylinder liner and the piston-top wetting effect.	[59]
	Wall wetting parameters were studied hypothetically, using a model of temperature and droplet evaporation for cylinder walls.	Additives like N-butanol were mixed with gasoline fuel of different proportions in a four-stroke single-cylinder Spark Ignition engine (SIE) and analysis was conducted at varying speed and load conditions.	With ignition Limits of N-Butanol in Air (2.6–12.8 vol%) being close to 1.81–8.86% of LPG, at 2400 rev/min, mixtures of N-Butanol, Acetone, and gasoline at 90:5:5 vol% gave maximum reduction in HC (32.53%) compared to 2800 rev/min and 3200 rev/min speed.	[60]
	LPDI injector nozzle tip wetting was studied using the macroscopic spray features of four test fuels	Test fuels, including n-heptane, gasoline, LPG winter, and LPG summer, were visualized under a long-distance microscope (LDM) utilizing the Mie scattering, Schlieren, and nozzle tip wetting techniques.	Due to rapid boiling, the LPG fuels had a longer spray penetration than n-heptane and gasoline. In the following order: LPG winter $>$ LPG summer $>$ n-heptane $>$ gasoline, the moist area on the fuel nozzle tip was wider	[61]
	Investigated the cause of fuel-specific effects on wall wetting (SEWW) based on the interplay of aromatics, distillation, and particle matter index on SPI.	Real-time fuel dilution measurements were made in a running single-cylinder research engine that was operated under SPI circumstances using the laser-induced fluorescence (LIF) an SPI diagnostic. Low aromatic-low distillation, low aromatic-high distillation, and high aromatic-high distillation fuels.	Fuels were operated at two injection timings to generate the SEWW. Results showed a de-convolution on SPI propensity, offering distinctive and innovative insights into the predominant fuel impacts controlling SPI. of fuel physical and chemical features on SPI propensity Here, the highest impingement corresponded with aromatic contents.	Splitter et al., 2021
Bubble formation risk	The authors analyzed the burning of gaseous LPG in a bubbling fluidized bed and modeled the combustion process in an air-fuel bubble.	Temperature, bed mass, the position of the combustion zone, and the concentrations of NOx and CO in exhaust gases were reported as factors that contributed to an increase in NOx and CO concentrations and a decrease in nitrogen oxide emission as a result of the amount of solid that was present in them.	The maximum temperature inside the bubbles drops, and there is a decrease in nitrogen oxide production, according to the results. When self-ignition cannot occur inside the bubbles, this results in the release of CO, which is connected to the spread of combustion between bubbles.	[62]
	To evaluate the cavitation and gas backflow phenomena during the nozzle off-flow stage and the impact of residual bubbles on the initial jet in a close field, Xiaonan and Wen performed an experiment and numerical simulation.	Details of internal flow and first jet were ascertained using a well-known cavitation mathematical model and an optical nozzle made of equal-sized acrylic material with high-speed photography technology.	Cavitation develops in the orifice and sac when the needle valve begins to close, and the quantity of cavitation in the sac increases. The outside air that is slightly bigger than the entire volume of the cloud of cavitation bubbles will flow back into the nozzle as a result of the cloud of cavitation bubbles collapsing. The initial atomization form attributable to the vortex ring motion surrounding the jet is significantly influenced by the starting position of the residual bubbles.	[63]
Icing formation effect	The freezing process on the tip and body of an injector assembly (EPI) for an LPG injection system was examined.	A model was established to determine ambient factors, material characteristics, the form and size of the LPG injector assembly's EPI assembly and the thermodynamic assembly, as well as the thermodynamic process occurring inside the EPI tube by investigating the freezing process on the tip and body of an injector assembly (EPI) for an LPG injection system	The model revealed how impractical it is to eliminate freezing by producing EPI using changes in material, shape, and size. EPI size and shape input parameters were adjusted to determine optimal geometry by introducing a heating element device to erase freezing on the tip and body of the EPI.	Thanh and Phu [64]
	Studied the effect of hydrocarbon and liquid phase LPG injection bi-fuel on a motorcycle engine.	At controlled temperature, the amount of brake force used, the amount of gasoline used, and the amount of contaminants present in the exhaust gas were measured.	The author proposed the use of an electronic heating device around the nozzle at 30^{O}C to address the LPG evaporation and heat buildup that caused ice to develop around the nozzle.	Thanh and Tho [65]
Lean Misfire Limit	Experimentally assessed the lean operational limits of gasoline, LPG, NG, and hydrogen as fuels in an E6 Recardo engine.	On the engine's operational limitations, the effects of the CR, engine speed, and spark timing were investigated.	Results reveal that increase in CR (G_{CR} = 9:1, LPG_{CR} = 12:1, NG_{CR} = 15:1). Lean restrictions were increased, lean misfire limitations were interchanged from low speeds to medium rates, and lean misfiring limits were contracted from medium speeds to high speeds.	Chaichan, 2019
	The authors examined the behavior of HC emissions from a constant-speed, lean-burn LPG engine. interchange at torque transient conditions.	A steady-state value was set LPG while speed was held constant and varied. To match the requirement for the real LPG mass during the erratic operating circumstances, a control fuel valve was targeted.	Due to the overly rich mixture produced by the fuel control valve's failure to manage LPG mass during the trial operating circumstances, HC was considerably degraded.	Zhongbo, 2017

relative to each other allows for smoother operation than conventional fuels as reported by Usman and Hayat (2019). The action has a positive impact on the automotive engine's lube oil and components, thereby reducing friction and premature fatigue and consequently, wear and tear [35]. Various fuel property parameters such as total base number (TBN), kinematic viscosities, flash points, etc. are often utilized to assess the deterioration effect of oil. Some of the studies are given in Table 6.

Table 6
Wear characteristics of LPG fuel.

Objective	Work-done	Result and Conclusion	Ref.
Authors experimentally examined the performance, emission, and lube oil deterioration using gasoline and LPG for a sustainable environment	They considered the degradation of lube oil using gasoline and LPG fuels on engine metal wear and corrosion based on flashpoint, viscosities, and TBN, having run the engine for 120 h.	At 40 and 100 °C, the viscosities of lubricant oil using gasoline and LPG were 138.70 and 156.40 cSt as well as 14.73 and 16.90 cSt, respectively. It was reported that gasoline mixed more with lube oil compared to LPG (Malik et al., 2021), with gasoline causing more suspension of debris (wear) particles.	[35]
An analysis of the impact of fuel and oil charge and engine wear using a laser particle analyzer.	Three fuels LPG (in a Skoda Felicia 1.3 MPi), n-butanol (Briggs & Stratton small electric power generator), and diesel (Diesel engine, Cit-roen C3 Picasso, 1.6 HDi) were studied in different engine types.	Non-metallic particle contents increase observed while using n-butanol, LPG and diesel were 37%–78%, 57%–62%, and 12%–46%, respectively. Comparison of the wear effect is limited because of the difference in engine for each fuel.	[66]
Authors conducted a long-term continuous use of auto-LPG causes thermal pitting in automotive S.I. engine parts	Bottled LPG and gasoline in a spark ignition outboard engines and emission test, Temperature at different operating conditions for potential damage to the engine structure were conducted.	While he noted that component life is extended using LPG over gasoline, on SI Engine, it was observed that hot spots however due to temperature rise lead to surface pitting on the Engine components, such as cylinder block, head, valves, and valve stem, increasing valve guides which may lead to cracks & distortion in cylinder heads	Mandloi and Ajay, 2015
The study investigated the corrosive characteristic of LPG rubber hose for safety using primary data and secondary data for an effective Kerosene to LPG implementation.	The effect of raw materials, additives, and usage conditions (time, temperature, pressure, and environment) was used to analyze the shelf and service life of hose rubber	A report from ¾th of respondents from LPG hose manufacturers indicated that the service life period of the hose is one year before expiry.	[67]
PN-EN ISO 6251 standard level of LPG corrosiveness was conducted over copper material which serves varying automotive components.	Using the visual evaluation of four different LPG samples' impact on the copper, the color change was deemed the qualifying term for the degree of corrosion, e.g., Slight tarnish, Moderate tarnish, Dark tarnish, and Corrosion.	They reported that on a scale of four, only one sample case that the presence of hydrogen sulphide was detected for an LPG sample whose corrosiveness to copper was on a level resulting in the copper corrosion class 4.	Bukrejewski et al. [68]
The study simulated a broad range of hardware malfunctions (15) on a Toyota Crown Comfort LPG taxi engine	The impact of hardware deterioration and failures was determined using emissions, fuel consumption, and drivability from a chassis dynamometer	They reported significant THC and CO increases of up to 317% (0.604 g/km) and 782% (5.351 g/km) respectively for a simulated oxygen sensor high voltage fault and a sticky mixture control valve	[69]
The authors conducted an LPG analysis, in particular, the determination of total sulphur content and corrosion against copper	Non-damaging and damaging tests of two samplers of two different samples, non-demountable (chromium-nickel 316L steel) and demountable (chromium-nickel 316Ti steel) were exposed to LPG.	Microscopic scans of the internal surface of the sampler showed the surface structure in both types of solutions LPG impact analysis. Corrosion control of the demountable had low microporosity and was due to surface electro-polishing.	[70]

4. Conclusion

Different synthesis pathways may find significance at a level where quantity is essentially the target for approaching an independent decarbonized "bio-LPG" future, as may be inferred from this study. Quality bio-LPG output may then be the next cause for concern. On synthesis, a feedstock balance and sustainability are essential if the proposition by the existing methods, which are known to use waste and residual materials (60%) and renewable vegetable oils (40%) are any indication, the current 7% restriction on crop-based biofuels in the European Union will be gradually cut to 3.8% by 2030, meanwhile, alkanes may be produced from both terrestrial and marine soil, according to predictions. A significant amount of propane was produced by mixed microbial cultures taken from marine sediment in the demonstration, showing potential for culture optimization and scale-up toward a fermentation method for bio-propane synthesis. The benefits of bio-LPG, it can mitigate climate change, improve air quality, mitigate deforestation, eliminate fugitive emissions, and impact when adopted as fuel, but there still exists a possible explosion if the mixture of LPG and air is within the explosive limits and there is an ignition source. Also, there can be suffocation due to LPG displacing air, causing a decrease in oxygen concentration. Feedstock sourcing and preparation for biomass-related routes may pose a few challenges but the microbial route which is most advocated for herein, utilizes materials that can be sourced easily including artificial seawater. LPG sourced from oil and NG produces CO_2 that contributes to climate change, hence low-carbon and naturally occurring biological pathways are proposed as a deplorable route for the biosynthesis of Liquefied petroleum gas. Policies on conventional fuel disincentives should be promoted among other regulations to encourage the future development of bio-LPG, particularly through microbial synthesis.

CRediT authorship contribution statement

L.O. Ajuka: Writing – review & editing, Investigation, Conceptualization. **R.A. Kazeem:** Writing – review & editing, Supervision, Investigation, Conceptualization. **O.A. Kuti:** Writing – review & editing. **T.C. Jen:** Writing – review & editing, Supervision, Conceptualization. **A.S. Afolalu:** Writing – review & editing, Investigation. **E.T. Akinlabi:** Writing – review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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