MERCK

2023 Merck Research Grant

Green Hydrogen

Sponsored by Group Coprorate Sustainability and Science & Technology Office

Science and technology are at the heart of everything we do, driving innovations that enable us to contribute to a sustainable future. **In this endeavor, we are seeking for research proposals in the field of Green Hydrogen.**

Progress is currently made in green hydrogen production, e.g.:

- innovative electrolysis technologies
- system and industrial integration of hydrogen technologies, e.g., storage, distribution and application areas
- fuel cell development

Submitted proposals should include a proof of concept (Technology Readiness Level 3) and describe the innovativeness of the proposal as well as the impact on the future implementation of green hydrogen supply to the chemical and pharmaceutical industry.

The best proposal will be awarded with one grant up to 200K € for one year with potential further collaboration

Apply now to become part of our green hydrogen journey!

Researchgrants.merckgroup.com

Merck is a leading science and technology company, operates across life science, healthcare and electronics. More than 60,000 employees work to make a positive difference to millions of people's lives every day by creating more joyful and sustainable ways to live.

Received: 21 October 2022 | Revised: 26 March 2023 | Accepted: 3 May 2023

DOI: 10.1002/ep.14175

REVIEW

Sustainable Energy

ENVIRONMENTAL PROGRESS & SUSTAINABLE ENERGY

Sustainable fuels: Lower alcohols perspective

Ifeanyi Michael Smarte Anekwe[1] | Nhlanhla Nyembe[1] | Loyiso Clemence Nqakala[2] | Mbaliyezwe Madikizela[1] | Yusuf Makarfi Isa[1]

[1]School of Chemical and Metallurgical Engineering, University of the Witwatersrand, Johannesburg, South Africa

[2]Department of Chemistry, University of Western Cape, Cape Town, South Africa

Correspondence
Ifeanyi Michael Smarte Anekwe, School of Chemical and Metallurgical Engineering, University of the Witwatersrand, Johannesburg 2050, South Africa.
Email: anekwesmarte@gmail.com

Funding information
International Collaborative Project, Grant/Award Number: BRICS2019-040; BRICS STI Framework Programme with government funding organizations of South Africa NRF, Grant/Award Number: BRIC190321424123; Brazil CNPq, Grant/Award Number: 402849/2019-1; Russia RFBR, Grant/Award Number: 19-58-80016; India DST, Grant/Award Numbers: CRG/2018/004610, DST/TDT/TDP-011/2017; China MOST, Grant/Award Number: 2018YFE0183600

Abstract

In the coming years, energy sources will play a vital role in global development. Biofuels made from sustainable sources are essential for the global economy's long-term viability and the reduction of greenhouse gas emissions. Clean, renewable, and sustainable must be the watchwords for future energy strategy. Alcohol fuels are again becoming a popular term in the context of green fuel usage in relation to climate change mitigation and clean fuel technology. In this review, low alcohol synthesis, applications and limitations as fuel and its catalytic conversion to fuel and petrochemicals were discussed, in addition to the techno-economic evaluation, environmental implications and prospects for practical application of low alcohols as fuels and petrochemicals. The study shows that lower alcohols have emerged as a fundamental feedstock for the synthesis of fuels and value-added chemicals due to the increased accessibility of conversion technologies in recent years, but the cost of producing lower alcohols affects their commercialization and availability.

KEYWORDS
biofuel, catalyst, ethanol, low alcohol, zeolite

1 | INTRODUCTION

The establishment of sustainable techniques that make use of renewably synthesized feedstock to the greatest extent possible is a major contemporary topic of interest in the fields of chemistry, engineering, agriculture, and environmental policy.[1–3] This discovery in the transportation fuels industry is particularly pertinent, which relies heavily on petroleum, a fossil fuel-based energy source. However, as the world's availability of petroleum shrinks, it is getting highly costly and, as a result, less competitive as a carbon-generating fuel. The utilization of fossil fuels or their derivatives for generating heat and electricity is also linked to an overall rise in greenhouse gas concentrations worldwide.[4–6] Compared with the current scenario, where all the demand is fulfilled by a particular source (i.e., petroleum), a more functional approach that draws on various energy resources should be an attractive long alternative. Energy-efficient vehicles, solar-powered transportation systems, hydrogen fuel cells, and biofuels are all being investigated intensively to lessen our reliance on petroleum as an energy source. Despite this, it will take time for these emerging innovations to become commercially and technically feasible. As a consequence of the shortage of facilities to assist cutting-edge techniques, the transformation will come gradually to a market presently controlled by interests and behaviors centered on the overall accessibility of liquid hydrocarbon fuels. In this regard, liquid biofuels created from sustainable plant biomass are distinct in that they are chemically identical to the fuels that are now utilized. Due to their application, they do not necessitate significant modifications to the transportation systems or the internal combustion engine, especially when blended with gasoline. As a result, the employment of biomass as a renewable carbon source for the generation of transportation fuels is a potential substitute that may be realized in a relatively short period.[7]

To combat rising oil prices, increasing build-up of greenhouse gas emissions, and tight emission legal rules, it is vital to develop alternative fuels that are both renewable and eco-friendly rather than relying on traditional fossil fuels to address these concerns. As a result of their unlimited supplies, low emissions enhanced mixing and combustion properties, the low alcohols, notably methanol, butanol and ethanol, have the opportunity to provide some answers to these challenges. Low alcohols can be applied as a blending additive in petroleum-derived gasoline and diesel fuels, now available on the market or used as a renewable feedstock in the catalytic conversion process for fuel and petrochemical synthesis. In the petrochemical sector, crude oil is fractionated and processed to obtain several grades of liquid transportation fuel, and hydrocarbon feedstocks are functionalized to generate intermediates and speciality petrochemicals. Bioalcohols, particularly low alcohols, would be comparable in scale to the petroleum refining approach. The primary distinction is that biomass—rather than petroleum—would be exploited as a sustainable supply of carbon that can be converted into fuels and valuable chemicals within a single plant. The application of biomass derivatives in the generation of heat and electricity helps reduce greenhouse gas (GHG) emissions by utilizing phases of regeneration and burning, which reduce GHG emissions of GHGs.[8]

Ennaert et al.[9] conducted a thorough review of zeolite chemistry, potentials, and challenges of catalytic conversion of biomass into low alcohols. The effect of using low alcohol content as a fuel additive has been studied; Yusaf et al.[10] focused on the impact of blending methanol with diesel, while Yilmaz and Sanchez[11] studied the effect of using ethanol and methanol as additives for diesel fuel. The recent study by Kianfar et al.[12] provided a thorough overview of the many zeolite-based catalysts and the impact of modifying the surface or framework of the zeolite on the selectivity, stability, and conversion of methanol to gasoline. In addition, the effects of the operational reaction parameters were also investigated. The limitation of these studies is that they focus only on zeolite catalysts. Bin Samsudin et al.[13] focused on recent advances in the catalytic transformation of ethanol to butadiene, while Phung et al.[14] addressed the production of biopropylene from bioethanol and the factors affecting the conversion processes. On the other hand, Xiang et al.[15] provide a comprehensive overview of the catalytic conversion of bioethanol into a wide range of chemicals and fuels, focusing on the relationships between the catalyst, the reaction process, and the catalytic activity and stability of the catalyst. These studies did not include the economic and environmental implications of low alcohol conversion. Therefore, this review study provides a comprehensive overview of the application and limitations of low alcohols as fuels and the various catalysts for their transformation into fuel and petrochemicals, while presenting an up-to-date techno-economic and environmental assessment of the feedstock for the catalytic conversion process. The challenges and prospects for effective conversion of low alcohols were also discussed to assist researchers in developing a viable process for producing improved biofuels.

2 | APPLICATION AND LIMITATIONS OF LOW ALCOHOL AS FUEL AND ADDITIVE

2.1 | Application of low alcohol as fuel additive

The use of additives for fuel improvement has recently attracted much attention due to the positive effects of these chemicals on the overall fuel quality and the associated economic consequences.[16] Like gasoline, diesel fuel is also widely used in various machines, especially in the engines of vehicles, which are recognized as a significant source of pollution.[17] This pollution negatively impacts the health of all living beings and the environment.[18] Therefore, it is imperative to develop a cost-effective strategy to improve diesel and gasoline fuel to reduce emissions. The introduction of these additives should aim to reduce emissions while ensuring optimal fuel performance, which should contribute to adequate engine efficiency. Gad and Ismail[19] studied a combination of waste cooking oil biodiesel with gasoline and kerosene in a diesel engine to evaluate combustion and emissions and compare the results with those of fossil diesel. They found that peak cylinder pressure, CO, hydrocarbon, and smoke emissions decreased significantly.[19] However, the experimental studies on blending biodiesel with kerosene did not receive sufficient attention due to several undesirable factors, such as decreased kinematic viscosity, as Baral and Raine[20] reported. Moreover, Yadav et al.[21] revealed that this mixture (diesel and kerosene) decreased the opacity value. On the other hand, Bergstrand[22] provided information on the cetane number of kerosene, which is lower than that of diesel, and the increase in ignition delay, both of which are considered detrimental, although the study also found some positive characteristics, including a reduction in soot emissions at low load. Other researchers examined the effects of kerosene on spark-ignition engines (SI) used to generate electricity. They reported that kerosene is less expensive than gasoline and produces far less noise than diesel.[23]

Several studies have investigated the feasibility of using low alcohol as a fuel additive in SI engines, with and without engine modifications.[24] The study by Turner et al.[25] on gasoline-ethanol blends showed significant CO_2 and NOx emissions reductions at all loading conditions. Kang et al.[26] studied the dual-fuel ethanol-gasoline engine. They found that increasing the ethanol content led to an improvement in the combustion phase, which promoted combustion and resulted in a more significant improvement in the engine's thermal efficiency. Yusaf et al. studied the effects of combining methanol and diesel in different proportions (10%, 20%, and 30%) and evaluated the engine efficiency at speeds between 1000 and 2000 RPM. The study evaluated the effects of blending methanol with diesel on a number of characteristics such as input and output power, brake specific fuel consumption (BSFC), torque, brake thermal efficiency (BTE) and exhaust gas temperature. According to the results, the optimal blend ratio that improves engine performance is 10% methanol.[10] Cenk Sayin also evaluated combining methanol with diesel in volume ratios of 5% and 10% on engine performance and exhaust emissions. In addition, the study used a single-cylinder, four-stroke diesel engine to compare the results of blending methanol with diesel and diesel with ethanol at the same ratios. The results showed that smoke opacity, emissions of CO, and total HC content decreased with increasing BSFC for each fuel blend.[27] Nevertheless, there is still too little information on using a methanol-diesel combination in a four-stroke diesel engine with different blend ratios. Due to the lower heat evaporation and heating value of methanol than diesel fuel, blending methanol with diesel fuel could lower the temperature in the engine cylinder.[28]

A study on the effects of blending biodiesel with methanol and biodiesel with ethanol was conducted by Yilmaz and Sanchez.[11] In this case, a 2% castor was added to counteract the disadvantages of low alcohols, which include poor lubrication, problematic evaporation, and increased temperature for auto-ignition. According to the results, the brake-specific fuel consumption (BSFC) of biodiesel-methanol was higher than that of biodiesel-ethanol. However, the BSFC of both fuels is higher than that of pure diesel. Biodiesel-alcohol produces more CO and HC than pure diesel at full load but emits less NOx, smoke, and soot. In another study, Yilmaz[29] compared biodiesel-ethanol-diesel and biodiesel-methanol-diesel blends and found that the ratio of biodiesel-methanol-diesel resulted in higher levels of BSFC and NO than the ratio of biodiesel-ethanol-diesel. On the other hand, biodiesel-methanol-diesel shows a decrease in CO, NOx and exhaust gas temperature. It can be inferred that the addition of low alcohol promotes engine efficiency while reducing emissions. For effective performance, however, an optimum blending ratio is necessary.

2.1.1 | Engine modifications and tolerance for biofuel blends

A blend ratio of approximately 14.6 air:1 fuel is required for complete combustion when using 100% gasoline. This means that 14.6 kg of air is necessary to completely combust 1 kg of oxygen-free gasoline. The oxygen concentration in an ethanol-E10 fuel blend is typically 3.5%. The amount of oxygen contained in bioethanol can affect the air-fuel ratio at which the engine operates.[30] Therefore, for some vehicle engines, it is often necessary to adjust the air-fuel ratio to compensate for the oxygen concentration of the bioethanol blend. When ethanol (oxygenated) fuels are added to the engine, the engine control components in most current motor vehicles electronically detect the air/fuel mixing ratio and modify it to maintain the stoichiometric ratio. Since biodiesel is also an oxygenated fuel, the effect described above can be applied to it. The highest oxygen level that can be adjusted on certain vehicles is 3.5% of the total oxygen content (E10 ethanol fuel blends).[31] In most cases, older vehicles do not have an engine management system but use a more conventional carburetor system. Therefore, the carburetor air-fuel mixture must be modified to account for the high oxygen concentration in ethanol fuel blends. The engine modifications required to run conventional internal combustion engines on biofuels are discussed below.[32] The fuels under consideration are bioethanol, used in spark-ignition engines, and biodiesel, used in compression-ignition engines. In the 1970s, when cars in Brazil ran on bioethanol blends between 14% and 24% ethanol, Brazilian automakers made the following engine modifications:

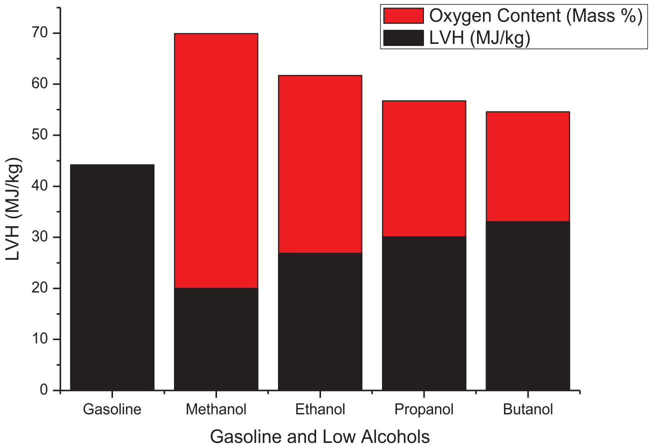

FIGURE 1 The correlation between oxygen content and heating value of gasoline and low alcohols (Adapted from Awad et al.[33]).

i. Modifications to the cylinder walls, cylinder heads, valves, and valve seats
ii. Adjustments to the intake manifolds, carburetors, pistons, and piston rings
iii. Coating of the steel fuel lines and gasoline tanks with nickel to prevent corrosion from ethanol E20
iv. Injectors with a higher fuel flow rate to account for the oxygenated properties of ethanol
v. Since bioethanol blends can loosen solid deposits within gasoline tanks and fuel lines, it is recommended that vehicles' fuel filters be changed more often.

Vehicle owners who use bioethanol blends should follow the manufacturer's guidelines. As for the maximum amount of ethanol that may be blended into gasoline, most automobile manufacturers in the United Kingdom recommend a maximum of 5% by volume. In the United States of America, virtually all car manufacturers stipulate that the maximum amount of ethanol that can be blended into gasoline must not exceed 10%.[34] Thus, if the owner of a vehicle chooses to blend ethanol at a higher level than recommended by the manufacturer, in most cases, the vehicle's warranty will be voided. Most car manufacturers warn that using a higher-than-recommended ethanol concentration in the fuel can damage the vehicle and impair its roadworthiness.

2.2 | Limitations of low alcohols as transportation fuel

Due to their high-octane number, low alcohol can be used in their pure form or blended with gasoline in an automobile engine, but its application is faced with some challenges. Ethanol has a calorific value of 27 MJ/kg, which is about 65% of that of gasoline (44 MJ/kg). The fundamental distinction between gasoline and low alcohol is that the latter are strong solvents and highly corrosive to the metal components of automobile engines. Low alcohol in fuel results in detrimental corrosion owing to the significant water content and the organic acids produced in commercial oxygenates. As a result of the low viscosity of alcohols, conventional fuel injection systems often have lubrication issues which translate to engine corrosion. In addition to that, alcohol fuels are vapor locked as a result of high pressure and low boiling points. The miscibility of low alcohols with gasoline is very limited, owing to the phase separation caused by the water content in the low alcohols. Compared to methanol, ethanol has a lesser vapor pressure, enhanced water tolerance, a higher heating value and better solubility with hydrocarbon liquids, which makes ethanol fuels better than blended methanol fuels. It has been shown that the increased oxygen concentration of alcohols can result in a better complete and cleaner combustion and that this can also lower the temperature inside the combustion chamber.[35,36] Methanol has a greater oxygen concentration than ethanol (approximately 50 and 35 by weight, respectively, as shown in Figure 1). Hence, methanol will provide less diluting power than other oxygenates. Due to the apparent oxygen and carbon contents in low alcohol and ether fuels,[37] their caloric value is less than that of gasoline.[38] The greater the oxygen concentration of the fuel, the lower the heating value; on the other hand, the higher the carbon level, the higher the heating value. As a result of these challenges, finding sustainable substitute energy sources is critical. However, some attempts are being made to explore and develop novel techniques for producing transportation fuels using non-petroleum resources (bioethanol feedstock) to replace the conventional method. Hence, the catalytic conversion (upgrading) of low alcohols offers the opportunity to transform low alcohols into value-added chemicals and higher hydrocarbons that can serve as petrochemicals and transportation fuels for industrial and automobile engine applications, respectively. The synthesis, properties and other applications of low alcohols are presented in Supplementary section 8.1.

3 | CATALYST FOR LOW ALCOHOL CONVERSION

Numerous catalysts have been applied in converting low alcohols, often classified based on their reaction phase. That is, systems in which the reactants and the catalyst are of the same phase are known as homogeneous.[39] In contrast, systems in which the reactant phase differs from that of the catalyst are known as heterogeneous.[40] Irrespective of the reaction phase, catalysts have significantly contributed to the production of chemicals in industry, and this has invoked interest in researchers to synthesize novel catalysts through various methods such as metal doping,[41] complex composites[42] and catalyst supports.[43] Interestingly, heterogeneous catalysts produce 85% of industrial chemicals, whereas homogeneous catalysts account for almost 15%.[40,44] As such, optimizing these catalysts has proved beneficial in the catalytic conversion of safe, renewable and readily available materials such as low alcohols (methanol, ethanol and propanol).

3.1 | Homogeneous catalyst

Biorefining of low alcohols has sparked interest recently due to their application as fuel blends for diesel engines, where blends can consist of alcohols as high as 30%.[45] The application of these low alcohols as blends have drawn criticism due to their low lubricating properties, which negatively affect the durability of internal combustion (IC) engines. Proposed solutions to overcome this bottleneck involve the catalytic conversion of low alcohols, such as bio-ethanol, into higher alcohols or hydrocarbons that are both linear and branched.[45]

Homogeneous catalysts with high catalytic activity and selectively have been applied in upgrading ethanol into advanced biofuels. Among these, ruthenium, iridium and manganese are the commonly used homogeneous catalysts to control yields and selectivity better.[45] These homogeneous catalysts use the Guerbet reaction to convert low alcohols into biofuels. They can be applied to various alcohol conversions; this reaction is also known as borrowed-hydrogen chemistry. An interesting study by Black et al.[46] used the Guerbet reaction to catalytically convert an alcohol substrate through the carbon-to-carbon bond formation to produce longer-chain alkanes. Although the Guerbet process has shown potential in the conversion of alcohols, the transformation of ethanol through homogeneous catalysts has faced challenges due to two drawbacks: (1) low alcohols (ethanol) tend to resist the dehydrogenation step. However, Carlini et al. (2003) have recommended creating alcohol mixtures (methanol/ethanol and methanol/ethanol/n-propanol) to alleviate this problem; (2) controlling the based-catalyzed aldol condensation of acetaldehyde is challenging, which leads to the formation of oligomeric and polymeric species.[47] It should be noted that these homogeneous catalysts require mild reaction conditions. Compared to the heterogeneous catalyst, they achieved higher control on selectivity and yield towards advanced biofuels.[45] A review of the homogenous catalysts for low alcohol conversion is presented in Supplementary section 8.2.

3.2 | Heterogeneous catalyst

The use of heterogeneous catalytic reactions in catalysis has enabled researchers to effectively and economically convert low alcohols into valuable chemicals and biofuels without any adverse environmental impacts.[48,49] Due to their traditional usage in the chemical industry, these heterogeneous catalytic reactions have shown potential in the application of biotechnology, nanotechnology and green chemistry.[50] Furthermore, compared to homogeneous catalysts, heterogeneous catalysts are responsible for producing the majority of chemicals and over 20% of all industrial products ([51]; Wang et al., 2021). Heterogeneous catalysts are water-insoluble, environmentally friendly, non-corrosive to equipment and reusable. Thus, they are considered a green sustainable alternative due to their ability to avoid using harmful substrates and producing toxic wastes ([52]; Zhang et al., 2019). The most commonly used heterogeneous catalysts include transition metal oxides, rare earth metals, supported metal catalysts, hydroxyapatites (HAP) (Wang et al., 2018[53];) and zeolites ([54,55]; Y.[56,57]). The choice of

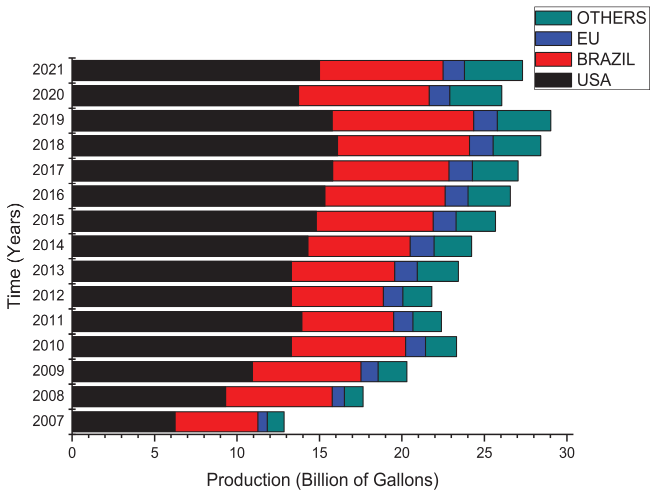

FIGURE 2 Global ethanol production from 2007 to 2021 (Source: References [58,59]).

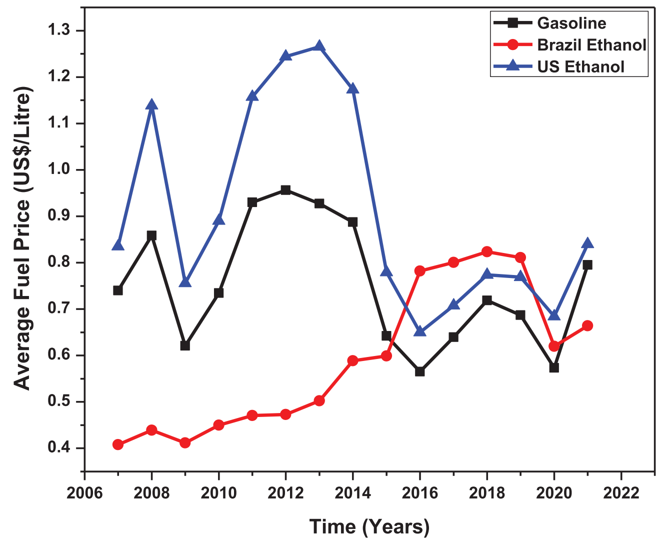

FIGURE 3 Comparison of the average retail fuel prices of Gasoline, Brazil ethanol and US ethanol in liter per gasoline-equivalent (LGE) from 2007 to 2021 (Source: Reference [63]; Brazil[64,65]).

catalyst used depends on the targeted products since each heterogeneous catalyst will have a specific reaction pathway to produce the targeted product. Various studies have been conducted to upgrade low alcohols into other valuable chemicals catalytically. For instance, Dagle et al.[60] reviewed the economic benefits of using low alcohol as a potential renewable feedstock for producing biofuels and chemicals. In contrast, (2020) used an ethanol steam reforming (ESR) reaction mechanism to develop a sustainable, carbon-neutral hydrogen production process. On the other hand, Eagan et al.[61] looked to address the growing demand for middle distillate fuels (diesel and jet fuel) by reviewing the technologies for upgrading low alcohols and their respective reaction chemistries. The Supplementary section 8.3 reviews the common heterogeneous catalysts used to upgrade low alcohols into fuels and petrochemicals, including metal oxides, zeolites and hydroxyapatite.

4 | TECHNO-ECONOMIC EVALUATION OF LOW ALCOHOL: CURRENT PRODUCTION, COSTS, AND ECONOMIC IMPACT

Due to the increasing depletion of the world's fossil-fuel reserves, there has lately been a surge in research in utilizing biofuel in compression-ignition engines. Environmental issues have indeed increased in the price of fossil fuels and regulations on exhaust emissions from internal combustion (IC) engines. Various nations, including the United States, have switched from fossil fuels to sustainable fuels.[62] As a result, low alcohol is essential to substitute fuels that can be employed in conjunction with gasoline in internal combustion engines, either as a blend or as an additive. The cost of producing low alcohols can vary significantly depending on the feedstock used, the transformation approach used, the production level, and the region in which the fuel is produced.[33] For this study, bioethanol production and cost will be discussed. Figure 2 illustrates global ethanol production by nation or area from 2007 to 2021. It can be observed that production climbed rapidly from 2007 to 2010, with the highest output occurring in 2019 after a dip in 2011 and 2012 and a further decline in 2020 due to the COVID-19 outbreak. The United States is the world's greatest manufacturer of ethanol, having synthesized over 13.7 billion gallons (BG) in 2020 despite the pandemic and 15.1BG in 2021, which represents 52% and 54% of the world's ethanol production, respectively. Brazil ranks second in world ethanol production with 7.9 and 7.5BG, representing 30% and 27.5% of world ethanol production in 2020 and 2021, respectively. The United States and Brazil manufacture 83% of the world's ethanol, while the European Union produced the remaining 17% (EU), 1.3BG and other countries in 2021.

To determine the market costs of biofuels, the most important factors to consider are labor and land expenses, feedstock, the oil market, and agricultural incentives. As of 2020, the cost of ethanol from sugar cane and corn is approximately US$0.60–US$0.70 per LGE (liter per gasoline equivalent), which is significantly higher than the cost of gasoline, with an average cost price of US$ 0.58/ L (US $2.40/gallon), making ethanol less competitive in the market (Figure 3).[59] Likewise, sugar beet or wheat ethanol may cost between US$ 0.6 and US$ 0.8 LGE. However, in 2021 the cost of sugarcane ethanol showed an appreciable competitive average cost of US$ 0.66 compared to corn ethanol and gasoline (US$ 0.80 and US$ 0.84 average cost, respectively), which shows that sugarcane ethanol can compete with gasoline in the fuel market. Considering the energy cost, ethanol is more costly than gasoline in all countries. Only ethanol generated in Brazil comes close to competing with gasoline in terms of price and performance. A significant price difference exists between the cost of ethanol from corn in the United States and that of sugar cane in Brazil, with ethanol made from grain and sugar beet in Europe being even more costly.[66] Owing to the significant production of corn

(USA) ethanol, its comparatively expensive cost is a considerable barrier to its widespread use and commercialization as an alternative energy source and gasoline additive. Consequently, ethanol has not been economically competitive with gasoline; however, with government subsidies, the cost of ethanol manufacturing will be reduced significantly.[67] Moreover, when compared to fossil fuels, the use of biofuels will reduce the net cost of fuel. The most significant difficulty is that increasing the use of biofuels will, in the short term, increase the overall fuel cost, making it more expensive than fossil fuels. On the other hand, the long-term savings in fuel expenditures may assist in mitigating this challenge.

These discrepancies in the cost of ethanol result from various parameters, including scale, operational efficiencies, biomass costs, capital and labor expenses, co-product accounting, and the form of estimates.[33] These parameters influence the cost, pricing, and profitability of biofuel synthesis. The price of biomass resources remains a significant factor in determining the cost of biofuel synthesis. The wide majority of U.S. ethanol is generated from corn, Brazil mainly utilizes sugarcane, while the EU employs wheat and sugar beet for ethanol production. The costs of these agricultural products are determined by factors such as planted area, outputs, harvest variables, and market characteristics, all of which are prone to year-to-year variations. The technological complexity of manufacturing facilities and the price of the fuels utilized for process energy have an impact on the cost of biofuel production. In Brazil, the cost of sugar cane ethanol varies according to the harvest period, with prices increasing during the inter-harvest season from January to March. Other factors influencing biofuel pricing include frequent modifications of current gasoline and diesel prices. The expense of commercial-scale bio-based product synthesis is now prohibitively expensive in developed nations. For instance, the price of producing biofuels may be three times greater than that of producing petroleum fuels without considering the non-market advantages. In contrast, the costs of manufacturing biofuels in developing nations are far lower than in Organization for Economic Co-operation and Development (OECD) countries and are quite close to the world market cost of petroleum fuel.[68]

5 | CHALLENGES OF LOW ALCOHOLS AS FEEDSTOCK FOR FUEL AND PETROCHEMICALS SYNTHESIS

Despite the potential of low bioalcohol as a renewable energy source, its production, conversion to higher hydrocarbons (for fuels and petrochemicals), and applications still face some challenges.

5.1 | Biomass and land availability; food and water security

Technologies for producing biofuels will only be effective and beneficial to the general public if there is an adequate supply of biomass feedstock available in a sustainable manner, taking into consideration ecological implications and the "food versus fuel" controversy.[69–72] A sustainable and environmentally favorable approach to developing oil crops has been proposed in one of the reviews by Groom et al.[73] They also urge that zero-carbon, more sustainable, and virtually entirely non-fodder feedstock are promoted so that biodiversity and the preservation of critical and native food crops are not jeopardized or compromised in any way. The issues associated with the long-term supply of biomass resources for biofuel synthesis have also been discussed in other publications,[74,75] in which the authors have specifically emphasized the dispute between food and biofuel. The need for food and water will continue to rise with the world's increasing population, and it is among the reasons that food costs have risen substantially worldwide. Historically, there was no substantial relationship between biofuel costs and food prices; however, the amount of food crops (sugarcane, maize, soybean, and rapeseed) used to make biofuels has increased, and this relationship has become stronger as well. The constant rise in and generation of biofuel, as well as the increased competitiveness of the biofuel industry, results in a spike in the costs of raw materials used to manufacture biofuel. In light of these rising tendencies, the food and biofuel industries will become increasingly intertwined in the coming years, which will almost probably impact food costs.[76]

As a result, the focus of biofuel study is changing away from fodder raw material and advancing biofuel synthesis from non-fodder biomass (like Jatropha, Karanja, Polanga oils etc., for biodiesel production and agro and forestry residue cellulosic biomass for bio-ethanol synthesis). For this purpose, much of the study on biofuel generation concentrates on the possible consequences on food security, land use variations, and water sources.[70–72] Farmers, especially in developing countries such as India, have begun to adjust their farming practices away from cultivating food crops and towards producing biofuel crops on agricultural land to increase their profit and job opportunities in the agricultural sector, even though humans do not consume the new crops. Consequently, food accessibility and security would deteriorate, while the price of food would rise.[70,71] Furthermore, several other impediments to the long-term development of present biofuel technology exist. The energy density of biomass-derived fuels is low, and the feedstock is expensive to gather and transport. Furthermore, increasing the development of biofuel-based crops without considering the quality and accessibility of water in each location could burden water resources, particularly in developing nations. Such agricultural transitions towards the production of biofuel crops can alter the supply of clean and potable water while drastically increasing the burden on regional water resources.[70,71] Aside from that, the high input requirements for biofuel synthesis (land use, water use, crops, energy use, etc.) are primarily fully liable for the poor economics related to these biomass-derived fuels, which is recognized as one of the significant barriers in their long term development.[71,77,78]

The above impediment can be summed up as follows:

1. Because biomass production is always dependent on various conditions, the development of biofuel synthesis may necessitate the acquisition of additional land to ensure long-term viability.

2. Increased water resource demand is due to the expansion of biofuel feedstock synthesis.
3. Biomass preservation has proven to be a significant challenge, as storage costs have reduced cost efficiencies.
4. Technological advancements in manufacturing equipment result in a cleaner, more consistent, and smoother output.
5. The applications of by-products should be adequately delineated and categorized.
6. The utilization of organic chemicals, which are damaging to the ecosystem, in the majority of procedures and green process development with substantial output has become an issue of great concern.

5.2 | Effect of low alcohol water content and catalyst deactivation in catalytic transformation

Several studies[15,79,80] showed that water and contaminants that are possibly present in low alcohols might influence the catalytic activity and stability of catalysts during the bioalcohol transformation into different chemicals and fuels. With bioethanol (10 wt% ethanol in water) as a substrate, it was discovered that water substantially impacted the ethanol's dehydration on alumina-based catalysts. Kochar and colleagues[81] found that the existence of water, mainly when the water level is substantial, considerably reduces the rate of ethanol transformation. Chen et al. discovered that in a microchannel reactor and at reduced temperatures (i.e., 380°C), ethanol transformation reduced from 86% to 65% as water content rises from 5 to 90 wt% over TiO_2/-Al_2O_3, while diethyl ether specificity improved at the cost of ethylene transformation. However, extreme temperatures (greater than 420°C) might completely remove the impact of water.[82] Several years of comprehensive research have revealed that the process temperature on alumina-based catalysts should be set high (>400°C, particularly in the presence of increased water content)[82,83] to prevent the synthesis of diethyl ether and obtain excellent ethylene selectivity.[81,82,84]

The distinct pore structure and acidic properties of H-ZSM-5 make it one of the most suitable catalysts for transforming ethanol into gasoline. On the other hand, coke formation (preventing active site accessibility) and dealumination lead to rapid deactivation (loss of acidity) of H-ZSM-5. The existence of water in the system has a complicated impact on the deactivation of the catalyst. Because water reduces the acid strength of the catalyst by hydrating Brønsted acid sites, since water and coke precursors compete for adsorption on the acid sites during coke accumulation, water can limit coke deposition at mild temperatures.[85] However, the presence of water at higher temperatures (above 450°C) can trigger the dealumination of the zeolite, leading to a significant reduction in the active sites of the catalyst.[86–88] It is suggested that catalyst development and tuning should focus on adjusting acidity and mesoporosity and incorporating metal promoters to develop ethanol conversion catalysts with excellent specificity and hydrothermal stability at appropriate temperatures.[15]

5.3 | Environmental and health impact

Global acknowledgement of the severe long-term consequences of climate change offers a critical premise for using low alcohol fuels, which implies that alcohol fuels should be ready to embrace opportunities to reduce greenhouse gas emissions (CO_2, CH_4, N_2O, etc.). Low bioalcohols have proven to be quite successful in lowering greenhouse gas emissions. Compared to pure gasoline, bioethanol derived from corn emits 43% fewer greenhouse gases than the latter. From a completely scientific perspective, ethanol can be manufactured from biomass generated from the CO_2 absorbed by plants during photosynthesis. As a consequence, it can be considered carbon neutral. In contrast to fossil fuels, which release a large quantity of CO_2 from their internal carbon atoms during combustion, ethanol can be considered carbon-neutral since it does not release nearly as much CO_2 from its internal carbon atoms during combustion. However, the growth of biomass crops and the production of alcohol fuels are responsible for many greenhouse gas emissions, both directly and indirectly. When alcohol fuels are employed, there is a wide range of potential CO_2 reduction. According to Alckmin–Governor and Goldemberg–Secretary,[89] the values range between 0.5 kg CO_2-equivalent/liter of ethanol for wheat-derived ethanol and as high as 2.24 kg CO_2-equivalent/liter of sugar cane-derived ethanol. Natural environments disintegrate ethanol at an alarmingly fast rate. Biodegradation of ethanol is quick in soil, groundwater and surface water, which can be retrieved within 10 days at most. As a result, it poses little threat to the environment and living organisms. However, there have been a few isolated instances in which the degradation of oxygen in surface water due to large amounts of ethanol has resulted in the death of fish in surface water. On the other hand, ethanol is not assimilated by soil particles.[90] Furthermore, it has been asserted that ethanol enhances air quality by assisting ozone formation.[91]

Methyl alcohol (methanol), on the other hand, is a toxin that is colorless and flammable. It is employed as a solvent, an alternative fuel for motors, as a feedstock for catalytic processes or as a primary fuel for picnic stoves, as an antifreeze (by decreasing the freezing point of water) for automobile radiators, and as a pesticide.[92,93] Methanol is a low-toxicity compound for aquatic and most terrestrial species, and adverse consequences from exposure to methanol in the environment are unlikely to be noticed except in the event of a spillage. Non-primate animals have low acute toxicity when exposed to methanol. However, methanol is associated with several health hazards, including blindness, mobility difficulties, and mortality.[93] The intake of 10 mm of methanol results in lifelong visual impairment, while the intake of 30 mm of methanol leads to death when consumed as part of a beverage. Methanol toxicity in humans (methanol poisoning) is a result of its metabolism (in the liver) via alcohol dehydrogenase which triggers the formation of formaldehyde,[94] and subsequently converted to formate (formic acid), a highly poisonous substance responsible for metabolic acidosis and end-organ toxicity.[95] These transformations cause damaging impacts on the central nervous system. Methanol can be absorbed into the human body through various routes (ingestion, inhalation, eye or skin contact). To be classified as renewable, a fuel or its source must be biologically recycled, which combines CO_2 and H_2O in photosynthesis. However, while H_2O and CO_2 are necessary for methanol production, a mechanism can be developed to supply CO_2 (a GHG) from the atmosphere or flue gases, both needed for methanol production. Because H_2 is required for initiating synthesis, water electrolysis is carried out to kick-start the renewable energy system. A substantial quantity of CO_2 is needed to synthesize methanol from various resources such as natural gas, coal, biomass, and flue gas. To generate methanol, natural gas and coal need less CO_2.[96]

6 | PROSPECTS AND FUTURE WORK CONSIDERATIONS

The use of low alcohols as a transportation fuel can enhance the reduction of greenhouse gas emissions. The effective exploitation of lignocellulose is anticipated to benefit the bioalcohol manufacturing sector. Technological improvements in this developing sector, especially the excellent performance of metabolically modified microbes at the pilot scale, are credible for optimistic predictions in the industry. Meanwhile, metabolic engineering (in combination with conventional methods including random mutagenesis) is being used to resolve the additional advancement of microbe functionality by incorporating attributes including tolerance to ethanol and inhibitors, hydrolysis of cellulose/hemicellulose, thermotolerance, a limited requirement for nutrient supplementation, and advancement of sugar transport.[97] Maintaining a reasonable viewpoint, on the other hand, is critical. The enhancement in the fermentation phase achieved with metabolic engineering is only one of the components of an incorporated processing system. To achieve an effective industrial design, certain elements must be assembled appropriately (and optimized) before completing the rest. Once in operation, it is predicted that the existing model techniques will require numerous cycles of enhancement and study before they will be optimized and competitive, as with other technologies.

Low alcohol valorization has become more appealing and promising due to bioethanol's growing supply and competitive price. It is possible to generate a wide variety of fuels and commodity chemicals by catalytically upgrading low alcohols, which reduces reliance on fossil fuels and, consequently, the environmental consequences of this reliance. In addition to process factors (including reaction temperature, feed component, and residence time), catalysts are critical in low alcohol transformation because they influence product specificity and distribution during the processes. In the 21st-century liquid fuel sector, several contenders have evolved that are directly competing with low-alcohol fuels. The most significant participants in this field are green hydrogen and green electricity. Suppose alcohol fuels can contend with these two players in the future. In that case, it will be determined by how far they have progressed in addressing the significant objectives of CO_2 decrease, environmental cleanness, ease in current facilities, and cost competitiveness, among others. Also of note are sustainability topics, eligibility for carbon-free (green energy) status, and the reduction of polluting elements such as fine dust, mainly emerging and ecologically significant areas in the energy sector today. The substitution of fossil fuels with viable, clean fuels will ultimately result in a sustainable society based on green energy. Although the technologies presently utilized can meet the economically viable criteria for public approval in terms of CO_2 emissions and fine dust, among other things, the existing state of the art must be improved substantially.

The synthesis of highly effective catalysts will be critical in the long-term manufacture of viable fuels and value-added chemicals from sustainable low-alcohol resources.[98] In recent years, basic study on bioethanol conversion to fuels and petrochemicals has been heavily focused on less expensive zeolite and metal-based catalysts, which have demonstrated interesting performance and selectivities at comparatively low temperatures. Because of their distinct structure and variable acidity, zeolite-based catalysts have demonstrated potential applicability in low-temperature environments. It has been claimed that using support with high oxygen mobility (e.g., CeO_2) can improve the gasification of carbon residues and, as a result, reduce the development of coke on some metal-based catalysts to tackle the deactivation problem.[99] CeO_2, on the other hand, has the potential to accelerate the oxidation of metals, resulting in decreased catalytic activity.[100] To develop longer chain hydrocarbon fuels/chemicals while reducing unwanted side reactions, it is necessary to devote more attention to the nature and degree of acidity, process temperature, pressure, and residence duration. Moreover, by varying the catalyst Si/Al ratios, doping the surface, the surface acidity of the catalyst may be modified to ensure high selectivity of target products. Generally, reduced temperatures (<573 K) favor the generation of ethyl ether and ethylene, while higher temperatures (573–723 K) enhance the production of C_3 and C_4 hydrocarbons under moderately acidic conditions. The synthesis of heavy hydrocarbons, such as aromatics, is typically accompanied by the production of strong acidic sites and the application of increased temperatures (623–723 K).[53] This shows that product selection and specificity can be achieved by adjusting the operational parameters of the catalytic conversion process of the low alcohols.

Due to the high concentration of water in low alcohols (bioethanol crude), the effect of water on the framework and activity of catalysts and catalytic processes must be tackled with great care and attention. The fabrication of catalysts that is effective at water dissociation and carbon species oxidation while also enhancing the process pathways is still needed for high product specificity and catalyst stability, notwithstanding thorough research into the basic knowledge of process mechanisms and advances in catalytic development.[101] However, although significant research has been carried out extensively to improve low alcohol transformation and specificity towards a preferred product, as also the catalyst stability, additional studies into catalyst structure–activity interactions and the associated process operations are still needed for the logical development of active catalysts and the effective conversion of low alcohols to value-added chemicals and fuels.[15] It is also necessary to constantly study and evaluate bioethanol valorization's economic and environmental consequences in contrast to alternative synthesis techniques to facilitate the transfer and commercialization of the newly established low alcohol conversion technologies. The use of life-cycle analysis (LCA) for any industrial output process that begins with biomass and ends with the generation of biofuels or bioproducts is strongly suggested. The economic and environmental impact assessment will enhance the establishment a list of all the inputs and outputs of a manufacturing system and analyzing their environmental impact (resource use, human health, and ecological effects) throughout the product's life cycle (cradle to grave) to ensure economic viability and, environmental compliance and sustainability. However, quantitative LCA is difficult to perform due to the extensive inventory needed and possible inconsistency in the impact assessment. It is recommended that LCA be used as a decision-making instrument at the beginning of the product design, and it may even be beneficial at the laboratory level.

7 | CONCLUSION

In the most advanced production routes, techno-economic analyses have revealed that additional reductions in manufacturing costs are required to design and actualize cost-competitive substitute production paths. The reinforcing of fuel policies with strict requirements for blending rates and sanctions for greenhouse gas emissions can spur research and development to enhance the production processes of renewable fuel substitutes. These policies will also serve as a vital motivation for the fuel sector to invest in innovations that are not yet competitive, thereby improving the relatively close feasibility of low alcohols as fuel constituents. A comprehensive understanding of the catalytic conversion process of low alcohols is required to facilitate the design of an efficient tunable catalyst that will be active in the conversion of low alcohols to fuels and petrochemicals. It has been demonstrated that a wide variety of possible production costs exist since several factors substantially impact the costs of low alcohol production that can be achieved. Feedstock costs, pretreatment, realistic yields, and capital constraints are the most important factors to consider when determining profitability. However, due to the sensitivity of specific technological and financial indicators, no single conversion pathway will be the most reliable and cost-effective globally; instead, the most suitable pathway must be selected and configured to fit the structure of specific regional, economic, and infrastructural parameters. Generally, low-alcohol fuels should be employed as an energy source that has an environmental impact that is as low as natural gas in all uses while offering more possibilities and making a cheaper liquid fuel that can be utilized in large quantities, even in developing nations where abundant but low-quality raw materials are available in abundance.

AUTHOR CONTRIBUTIONS

Ifeanyi Michael Smarte Anekwe: Data curation; formal analysis; investigation; methodology; validation; writing – original draft; writing – review and editing. **Nhlanhla Nyembe:** Data curation; formal analysis; writing – original draft. **Mbaliyezwe Madikizela:** Data curation; formal analysis; writing – original draft. **Loyiso Clemence Nqakala:** Data curation; formal analysis; writing – original draft. **Yusuf Makarfi Isa:** Conceptualization; funding acquisition; methodology; project administration; resources; supervision; validation; writing – review and editing.

FUNDING INFORMATION

This work is financially supported by an international collaborative project (BRICS2019-040) under the BRICS STI Framework Programme with government funding organizations of South Africa NRF (BRIC190321424123), Brazil CNPq (402849/2019-1), Russia RFBR (19-58-80016), India DST (CRG/2018/004610, DST/TDT/ TDP-011/2017) and China MOST (2018YFE0183600).

CONFLICT OF INTEREST STATEMENT

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 STATEMENT

Data available on request from the authors.

ORCID

Ifeanyi Michael Smarte Anekwe https://orcid.org/0000-0001-8582-5869
Nhlanhla Nyembe https://orcid.org/0000-0002-1001-2377
Loyiso Clemence Nqakala https://orcid.org/0000-0002-1028-2377
Mbaliyezwe Madikizela https://orcid.org/0000-0002-6096-283X
Yusuf Makarfi Isa https://orcid.org/0000-0001-8272-3402

REFERENCES

1. Adewuyi A. Challenges and prospects of renewable energy in Nigeria: a case of bioethanol and biodiesel production. *Energy Rep*. 2020;6:77-88.
2. Soni RA, Rizwan M, Singh S. Opportunities and potential of green chemistry in nanotechnology. *Nanotechnol Environ Eng*. 2022;7:1-13.
3. Thakur S, Chaudhary J, Singh P, Alsanie WF, Grammatikos SA, Thakur VK. Synthesis of bio-based monomers and polymers using microbes for a sustainable bioeconomy. *Bioresour Technol*. 2022;344:126156.
4. Antar M, Lyu D, Nazari M, Shah A, Zhou X, Smith DL. Biomass for a sustainable bioeconomy: an overview of world biomass production and utilization. *Renew Sust Energ Rev*. 2021;139:110691.
5. Lima M, Mendes L, Mothé G, et al. Renewable energy in reducing greenhouse gas emissions: reaching the goals of the Paris agreement in Brazil. *Environ Dev*. 2020;33:100504.
6. Stephanie, N. E. M. *The Transition of Fossil Fuel as a Source of Energy to Renewable Energy*. Centria University of Applied Sciences; 2022.
7. Alonso DM, Bond JQ, Serrano-Ruiz JC, Dumesic JA. Production of liquid hydrocarbon transportation fuels by oligomerization of biomass-derived C9 alkenes. *Green Chem*. 2010;12(6):992-999. doi:10.1039/c001899f
8. Alonso DM, Bond JQ, Dumesic JA. Catalytic conversion of biomass to biofuels. *Green Chem*. 2010;12(9):1493-1513.
9. Ennaert T, Van Aelst J, Dijkmans J, et al. Potential and challenges of zeolite chemistry in the catalytic conversion of biomass. *Chem Soc Rev*. 2016;45(3):584-611.
10. Yusaf T, Hamawand I, Baker P, Najafi G. The effect of methanol-diesel blended ratio on CI engine performance. *Int J Autom Mech Eng*. 2013;8(1):1385-1395.

11. Yilmaz N, Sanchez TM. Analysis of operating a diesel engine on biodiesel-ethanol and biodiesel-methanol blends. *Energy*. 2012; 46(1):126-129.
12. Kianfar E, Hajimirzaee S, Mousavian S, Mehr AS. Zeolite-based catalysts for methanol to gasoline process: a review. *Microchem J*. 2020; 156:104822. doi:10.1016/j.microc.2020.104822
13. Bin Samsudin I, Zhang H, Jaenicke S, Chuah GK. Recent advances in catalysts for the conversion of ethanol to butadiene. *Chem Asian J*. 2020;15(24):4199-4214.
14. Phung TK, Pham TLM, Vu KB, Busca G. (Bio)Propylene production processes: a critical review. *J Environ Chem Eng*. 2021;9(4):105673.
15. Xiang H, Xin R, Prasongthum N, et al. Catalytic conversion of bioethanol to value-added chemicals and fuels: a review. *Resources Chem Mater*. 2022;1(1):47-68. doi:10.1016/j.recm.2021.12.002
16. Khorsheed Zangana LM, Yaseen AH, Hassan QH, Mohammed MM, Mohammed MF, Alalwan HA. Investigated kerosene-diesel fuel performance in internal combustion engine. *Cleaner Eng Technol*. 2023; 12:100591. doi:10.1016/j.clet.2022.100591
17. Albayati N, Waisi B, Al-Furaiji M, Kadhom M, Alalwan H. Effect of COVID-19 on air quality and pollution in different countries. *J Transp Health*. 2021;21:101061.
18. Mohammed MK, Awad OI, Rahman M, et al. The optimum performance of the combined cycle power plant: a comprehensive review. *Renew Sustainable Energy Rev*. 2017;79:459-474.
19. Gad M, Ismail MA. Effect of waste cooking oil biodiesel blending with gasoline and kerosene on diesel engine performance, emissions and combustion characteristics. *Process Saf Environ Prot*. 2021;149: 1-10.
20. Baral B, Raine R. Performance and Emissions of a Spark Ignition Engine Running on Gasoline Adulterated with Kerosene (no. 2009-28-0014). SAE Technical Paper. 2009.
21. Yadav SR, Murthy V, Mishra D, Baral B. Estimation of petrol and diesel adulteration with kerosene and assessment of usefulness of selected automobile fuel quality test parameters. *Int J Environ Sci Technol*. 2005;1(4):253-255.
22. Bergstrand, P. *Effects on Combustion by Using Kerosene or MK1 Diesel (0148–7191)*. SAE International; 2007.
23. Pathak S, Aigal A, Sharma M, Narayan L, Saxena M. Reduction of exhaust emissions in a kerosene operated genset for electrical energy applications. SAE technical paper series. 2005.
24. Liu S, Clemente ERC, Hu T, Wei Y. Study of spark ignition engine fueled with methanol/gasoline fuel blends. *Appl Therm Eng*. 2007; 27(11–12):1904-1910.
25. Turner J, Pearson R, Dekker E, Iosefa B, Johansson K, Ac Bergström K. Extending the role of alcohols as transport fuels using iso-stoichiometric ternary blends of gasoline, ethanol and methanol. *Appl Energy*. 2013;102:72-86.
26. Kang R, Zhou L, Hua J, Feng D, Wei H, Chen R. Experimental investigation on combustion characteristics in dual-fuel dual-injection engine. *Energy Convers Manag*. 2019;181:15-25.
27. Sayin C. Engine performance and exhaust gas emissions of methanol and ethanol–diesel blends. *Fuel*. 2010;89(11):3410-3415.
28. Hassan QH, Shaker Abdul Ridha G, Hafedh KAH, Alalwan HA. The impact of methanol-diesel compound on the performance of a four-stroke CI engine. *Mater Today: Proc*. 2021;42:1993-1999. doi:10.1016/j.matpr.2020.12.247
29. Yilmaz N. Comparative analysis of biodiesel–ethanol–diesel and biodiesel–methanol–diesel blends in a diesel engine. *Energy*. 2012; 40(1):210-213.
30. Wu C-W, Chen R-H, Pu J-Y, Lin T-H. The influence of air–fuel ratio on engine performance and pollutant emission of an SI engine using ethanol–gasoline-blended fuels. *Atmos Environ*. 2004;38(40):7093-7100.
31. Niven RK. Ethanol in gasoline: environmental impacts and sustainability review article. *Renew Sust Energ Rev*. 2005;9(6):535-555.
32. Agarwal AK. Biofuels (alcohols and biodiesel) applications as fuels for internal combustion engines. *Prog Energy Combust Sci*. 2007; 33(3):233-271.
33. Awad OI, Mamat R, Ali OM, et al. Alcohol and ether as alternative fuels in spark ignition engine: a review. *Renew Sust Energ Rev*. 2018; 82:2586-2605.
34. Yanowitz, J., Christensen, E., & McCormick, R. L. *Utilization of Renewable Oxygenates as Gasoline Blending Components*. National Renewable Energy Lab (NREL); 2011.
35. Awad OI, Mamat RB, Ali OM, Yusri I. Effect of fuel oil-gasoline fusel blends on the performance and emission characteristics of spark ignition engine: a review. *J Sci Res Dev*. 2016;3(5):31-36.
36. Mittelbach MRC. *Biodiesel: the Comprehensive Handbook*. Martin Mittelbach; 2004.
37. Demirbas A. Combustion characteristics of different biomass fuels. *Prog Energy Combust Sci*. 2004;30(2):219-230. doi:10.1016/j.pecs.2003.10.004
38. Osten DW, Sell NJ. Methanol-gasoline blends: blending agents to prevent phase separation. *Fuel*. 1983;62(3):268-270. doi:10.1016/0016-2361(83)90079-0
39. Zhao F, Liu Y, Lu N, Xu T, Zhu G, Wang K. A review on upgrading and viscosity reduction of heavy oil and bitumen by underground catalytic cracking. *Energy Rep*. 2021;7:4249-4272. doi:10.1016/j.egyr.2021.06.094
40. García-Serna J, Piñero-Hernanz R, Durán-Martín D. Inspirational perspectives and principles on the use of catalysts to create sustainability. *Catal Today*. 2022;387:237-243. doi:10.1016/j.cattod.2021.11.021
41. Xu R, Yan C, Liu Q, et al. Development of metal-doping mesoporous biochar catalyst for co-valorizing biomass and plastic waste into valuable hydrocarbons, syngas, and carbons. *Fuel Process Technol*. 2022;227:107127. doi:10.1016/j.fuproc.2021.107127
42. Potemkin DI, Filatov EY, Zadesenets AV, et al. Bimetallic Pt-Co/η-Al2O3/FeCrAl wire mesh composite catalyst prepared via double complex salt [Pt(NH3)4][Co(C2O4)2(H2O)2]·2H2O decomposition. *Mater Lett*. 2019;236:109-111. doi:10.1016/j.matlet.2018.10.097
43. Marčeta Kaninski MP, Šaponjić ZV, Mudrinić MD, et al. Comparison of Pt and Pd anode catalysts supported on nanocrystalline Ru–SnO2 for ethanol oxidation in fuel cell applications. *Int J Hydrog Energy*. 2021;46:38270-38280. doi:10.1016/j.ijhydene.2021.09.088
44. Zecchina A, Califano S. *The Development of Catalysis: A History of Key Processes and Personas in Catalytic Science and Technology*. Vol 4. Wiley & Sons; 2017.
45. Cesari C, Gagliardi A, Messori A, et al. Boosting the guerbet reaction: a cooperative catalytic system for the efficient bio-ethanol refinery to second-generation biofuels. *J Catal*. 2022;405:47-59. doi:10.1016/j.jcat.2021.11.027
46. Black PJ, Edwards MG, Williams JMJ. Borrowing hydrogen: indirect "Wittig" olefination for the formation of C-C bonds from alcohols. *Eur J Org Chem*. 2006;19:4367-4378. doi:10.1002/ejoc.200600070
47. Pang J, Zheng M, He L, et al. Upgrading ethanol to n-butanol over highly dispersed Ni–MgAlO catalysts. *J Catal*. 2016;344:184-193. doi:10.1016/j.jcat.2016.08.024
48. Wang S, Wang J, Zhu M, et al. Molybdenum-carbide-modified nitrogen-doped carbon vesicle encapsulating nickel nanoparticles: a highly efficient, low-cost catalyst for hydrogen evolution reaction. *J Am Chem Soc*. 2015;137(50):15753-15759. doi:10.1021/jacs.5b07924
49. Xu X, Tang M, Li M, Li H, Wang Y. Hydrogenation of benzoic acid and derivatives over Pd nanoparticles supported on N-doped carbon derived from glucosamine hydrochloride. *ACS Catal*. 2014;4(9): 3132-3135. doi:10.1021/cs500859n
50. Wang C, Wang Z, Mao S, Chen Z, Wang Y. Coordination environment of active sites and their effect on catalytic performance of heterogeneous catalysts. *Chin J Catal*. 2022;43(4):928-955. doi:10.1016/s1872-2067(21)63924-4

51. Taketoshi A, Haruta M. Size-and structure-specificity in catalysis by gold clusters. *Chem Lett*. 2014;43(4):380-387. doi:10.1246/cl.131232
52. Ong HC, Chen WH, Farooq A, Gan YY, Lee KT, Ashokkumar V. Catalytic thermochemical conversion of biomass for biofuel production: a comprehensive review. *Renew Sustainable Energy Rev*. 2019;113:109266. doi:10.1016/j.rser.2019.109266
53. Sun J, Wang Y. Recent advances in catalytic conversion of ethanol to chemicals. *ACS Catal*. 2014;4(4):1078-1090.
54. Anekwe IMS, Isa YM. Catalytic conversion of low alcohol to hydrocarbons: challenges, prospects, and future work considerations. *Int J Energy Res*. 2023;2023:1648449. doi:10.1155/2023/1648449
55. Isa YM, Mohammed UA, Musamali R, Anekwe IM. Water treated promoted catalysts for the conversion of ethnol to hydrocarbons. *Sustainable Energy-Water-Environment Nexus in Deserts*. Springer; 2022.
56. Makarfi Y, Tretyakov V, Koval L, Erofeev V, Lermontov A. Ethanol conversion to toluene over HZSM-5. 2009 Proceedings of the 21 NAM, San Francisco, California.
57. Ndebele MS, Isa YM. Comparative performance of ZSM-5 and activated carbon supports in alcohol conversion over Fe, Zn and Ni based catalysts. *Int J Appl Eng Res*. 2018;13(12):10749-10752.
58. United State Department of Agriculture. *Biofuels Annual*. United State Department of Agriculture; 2020.
59. US Energy Information Administration. Global ethanol production. 2021 https://afdc.energy.gov/data/10331
60. Dagle RA, Winkelman AD, Ramasamy KK, Lebarbier Dagle V, Weber RS. Ethanol as a renewable building block for fuels and chemicals. *Ind Eng Chem Res*. 2020;59(11):4843-4853. doi:10.1021/acs.iecr.9b05729
61. Eagan NM, Kumbhalkar MD, Buchanan JS, Dumesic JA, Huber GW. Chemistries and processes for the conversion of ethanol into middle-distillate fuels. *Nat Rev Chem*. 2019;3(4):223-249. doi:10.1038/s41570-019-0084-4
62. Traver AE. Automated engine for determining the combustion quality of a fuel. Google Patents. 1967.
63. US Department of Energy. Energy efficiency and renewable: fuel prices. 2021 https://afdc.energy.gov/fuels/prices.html
64. Brazil Ethanol. (2019). Biofuel average consumer Price: ethanol hydrated: Brazil average consumer price: ethanol hydrated: Amapá. https://www.ceicdata.com/en/brazil/biofuel-average-consumer-price-ethanol-hydrated/average-consumer-price-ethanol-hydrated-amap
65. US Energy Information Administration. Petroleum and other liquids: retail prices for gasoline. 2022 https://www.eia.gov/dnav/pet/hist/LeafHandler.ashx?n=pet&s=emm_epm0_pte_nus_dpg&f=m
66. Anekwe IMS, Khotseng L, Isa YM. *The Place of Biofuel in Sustainable Living; Prospects and Challenges: Reference Module in Earth Systems and Environmental Sciences*. Vol 5. 2nd ed. Elsevier; 2021:226-256. doi:10.1016/B978-0-12-819727-1.00068-6
67. Yacobucci, B. D. *Fuel Ethanol: Background and Public Policy Issues*. Congressional Research Service Reports. Congress of United States; 2007.
68. Abbasi T, Abbasi SA. Biomass energy and the environmental impacts associated with its production and utilization. *Renew Sust Energ Rev*. 2010;14(3):919-937. doi:10.1016/j.rser.2009.11.006
69. Cheng JJ, Timilsina GR. Status and barriers of advanced biofuel technologies: a review. *Renew Energy*. 2011;36(12):3541-3549. doi:10.1016/j.renene.2011.04.031
70. Lin L, Cunshan Z, Vittayapadung S, Xiangqian S, Mingdong D. Opportunities and challenges for biodiesel fuel. *Appl Energy*. 2011;88(4):1020-1031. doi:10.1016/j.apenergy.2010.09.029
71. Luthra S, Kumar S, Garg D, Haleem A. Barriers to renewable/sustainable energy technologies adoption: Indian perspective. *Renew Sust Energ Rev*. 2015;41:762-776.
72. Painuly JP. Barriers to renewable energy penetration: a framework for analysis. *Renew Energy*. 2001;24(1):73-89. doi:10.1016/S0960-1481(00)00186-5
73. Groom MJ, Gray EM, Townsend PA. Biofuels and biodiversity: principles for creating better policies for biofuel production. *Conserv Biol*. 2008;22(3):602-609. doi:10.1111/j.1523-1739.2007.00879.x
74. Demirbas A. Biorefineries: current activities and future developments. *Energy Convers Manag*. 2009a;50(11):2782-2801. doi:10.1016/j.enconman.2009.06.035
75. Demirbas A. Political, economic and environmental impacts of biofuels: a review. *Appl Energy*. 2009b;86:S108-S117. doi:10.1016/j.apenergy.2009.04.036
76. Joshi G, Pandey JK, Rana S, Rawat DS. Challenges and opportunities for the application of biofuel. *Renew Sustainable Energy Rev*. 2017;79:850-866. doi:10.1016/j.rser.2017.05.185
77. Demirbaş A. Social, economic, environmental and policy aspects of biofuels. *Energy Educ Sci Technoly Part B: Soc Educ Stud*. 2010;2(2):75-109.
78. Escobar JC, Lora ES, Venturini OJ, Yáñez EE, Castillo EF, Almazan O. Biofuels: environment, technology and food security. *Renew Sustainable Energy Rev*. 2009;13(6–7):1275-1287.
79. Kyriienko PI, Larina OV, Balakin DY, et al. 1,3-Butadiene production from aqueous ethanol over ZnO/MgO-SiO2 catalysts: insight into H2O effect on catalytic performance. *Appl Catal A: Gen*. 2021;616:118081.
80. Wu J, Xia Q, Wang H, Li Z. Catalytic performance of plasma catalysis system with nickel oxide catalysts on different supports for toluene removal: effect of water vapor. *Appl Catal B: Environ*. 2014;156:265-272.
81. Kochar, N., Merims R, Padia AS. *Ethylene from Ethanol*. Scientific Design Co; 1981.
82. Chen G, Li S, Jiao F, Yuan Q. Catalytic dehydration of bioethanol to ethylene over TiO2/γ-Al2O3 catalysts in microchannel reactors. *Catal Today*. 2007;125(1–2):111-119.
83. Kagyrmanova A, Chumachenko V, Korotkikh V, Kashkin V, Noskov A. Catalytic dehydration of bioethanol to ethylene: pilot-scale studies and process simulation. *Chem Eng J*. 2011;176:188-194.
84. Pearson DE. Process for Catalytic Dehydration of Ethanol Vapor to Ethylene. Google Patents. 1983.
85. Gayubo AG, Alonso A, Valle B, Aguayo AT, Olazar M, Bilbao J. Kinetic modelling for the transformation of bioethanol into olefins on a hydrothermally stable Ni–HZSM-5 catalyst considering the deactivation by coke. *Chem Eng J*. 2011;167(1):262-277.
86. Aguayo AJ, Gayubo AG, Vivanco R, Alonso A, Bilbao J. Initiation step and reactive intermediates in the transformation of methanol into olefins over SAPO-18 catalyst. *Ind Eng Chem Res*. 2005;44:7279-7286.
87. Aguayo AT, Gayubo AG, Atutxa A, Olazar M, Bilbao J. Catalyst deactivation by coke in the transformation of aqueous ethanol into hydrocarbons. Kinetic modeling and acidity deterioration of the catalyst. *Ind Eng Chem Res*. 2002;41(17):4216-4224.
88. Aguayo A, Gayubo A, Atutxa A, Valle B, Bilbao J. Regeneration of a HZSM-5 zeolite catalyst deactivated in the transformation of aqueous ethanol into hydrocarbons. *Catal Today*. 2005;107:410-416.
89. Alckmin–Governor G, Goldemberg–Secretary J. *Assessment of Greenhouse Gas Emissions in the Production and Use of Fuel Ethanol in Brazil*. Government of the State of São Paulo; 2004.
90. National Research Council. *Measuring Lead Exposure in Infants, Children, and Other Sensitive Populations*. National Academies Press; 1993.
91. Vallinayagam R, Vedharaj S, Roberts WL, Dibble RW, Sarathy SM. Performance and emissions of gasoline blended with terpineol as an octane booster. *Renew Energy*. 2017;101:1087-1093. doi:10.1016/j.renene.2016.09.055

92. Goswami A, Vashist S, Nayyar A. Effect of compression ratio on the performance characteristics of spark ignition engine fueleod with alternative fuels: a review. 2015 SAE Technical Paper Series.
93. Sheng C, Azevedo JLT. Estimating the higher heating value of biomass fuels from basic analysis data. *Biomass Bioenergy*. 2005;28(5): 499-507. doi:10.1016/j.biombioe.2004.11.008
94. Gribble NR. Alcohols and other oxygenates in automotive fuels. Doctoral thesis, Aston University. 1989.
95. Polss, P. *What Additives Do for Gasoline*. Vol. 52. Hydrocarbon Processing; 1973.
96. Demirbaş A. Calculation of higher heating values of biomass fuels. *Fuel*. 1997;76(5):431-434. doi:10.1016/S0016-2361(97)85520-2
97. Zaldivar J, Nielsen J, Olsson L. Fuel ethanol production from lignocellulose: a challenge for metabolic engineering and process integration. *Appl Microbiol Biotechnol*. 2001;56(1):17-34.
98. Oakley JH, Hoadley AF. Industrial scale steam reforming of bioethanol: a conceptual study. *Int J Hydrog Energy*. 2010;35(16):8472-8485.
99. Song H, Ozkan US. Ethanol steam reforming over Co-based catalysts: role of oxygen mobility. *J Catal*. 2009;261(1):66-74.
100. Davidson S, Sun J, Wang Y. Ethanol steam reforming on Co/CeO2: the effect of ZnO promoter. *Top Catal*. 2013;56(18):1651-1659.
101. Mattos LV, Jacobs G, Davis BH, Noronha FB. Production of hydrogen from ethanol: review of reaction mechanism and catalyst deactivation. *Chem Rev*. 2012;112(7):4094-4123.

SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

How to cite this article: Anekwe IMS, Nyembe N, Nqakala LC, Madikizela M, Isa YM. Sustainable fuels: Lower alcohols perspective. *Environ Prog Sustainable Energy*. 2023;e14175. doi:10.1002/ep.14175