Alternative Liquid Fuels for Power Plants and Engines for Aviation, Marine, and Land Applications

Geniy Kuznetsov 1, Dmitrii Antonov 1, Maxim Piskunov 1, Leonid Yanovskyi 2 and Olga Vysokomornaya 1,*

1 Butakov Research Center, School of Energy & Power Engineering, National Research Tomsk Polytechnic University, 634050 Tomsk, Russia
2 Central Aviation Institute of Mechanical Engineering, 111116 Moscow, Russia
* Correspondence: wysokomornaya@tpu.ru

Abstract: The article considers the main tendencies of development of alternative liquid fuels used in aviation, land transport, and for the needs of power generation sector. An overview of the main constraints to the development of alternative fuel technologies in these technical areas was carried out. The main groups of the most promising components and fuel compositions capable of effectively replacing conventional liquid fuels have been generalized. The basic criteria for evaluating alternative fuels are formulated. Environmental indicators of fuel combustion are of paramount importance for aviation. Rheological characteristics, calorific value, and environmental friendliness are critical for land transport engines. The effectiveness of alternative fuels for the power generation sector needs to be assessed in terms of such factors as economic, environmental, rheological, and energy to find an optimal balanced formulation. The list of potential components of alternative liquid fuels is extremely large. For a comprehensive analysis of the efficiency and selection of the optimal composition of the fuel that meets specific requirements, it is necessary to use multicriteria evaluation methods.

Keywords: aircraft engine; alternative liquid fuel; automobile engine; energy efficiency; power generation system

1. Introduction

The main difficulties of the global scientific community in sequestering greenhouse gases and other anthropogenic emissions (oxides of sulfur, nitrogen, chlorinates, aromatics, and solid particles) consist in a different understanding of the essence of the problems and, accordingly, the lack of compromises in finding ways to effectively solve them. Statistics and forecasts on anthropogenic emissions from aircraft engines, ground transport engines, and stationary power plants differ dramatically in international analytical agencies [1–5]. In particular, some agencies point to annual steady growth of emissions, while others are aimed at stabilization and even reduction [1–3]. In the global energy sector, the share of generated capacity relative to the actual demand using alternative sources (water, wind, and solar) does not exceed 20% [1,6]. In such conditions, the main solution to global environmental problems is to increase the efficiency of using hydrocarbon fuels [1,6]. An analysis of global climate change shows that it is important to comprehensively address the problem of anthropogenic emissions from the combustion of hydrocarbon fuels [7,8].

Global targets for reducing carbon monoxide emissions are close to zero. At the same time, humanity’s energy needs require increasing the volume of its production and not reducing the productivity of the industrial sector of the economy. Moreover, despite strict environmental requirements, it is impossible to prevent the occurrence of problems in the field of logistics and transport; achieving the target environmental indicators should not negatively affect the efficiency and power of aircraft and transport engines [3,9–11].
problem of disposal of solid and liquid industrial waste remains equally important. Thus, the problem is the need to reduce the carbon footprint while maintaining production capacity and engine performance in the aviation industry and in transport (Figure 1).

![Figure 1. Modern challenges on the topic of advanced fuel formulations.](image)

There are known attempts to create eco-friendly multicomponent fuels by mixing traditional fuels with plant materials, industrial carbon-containing substances, and flammable liquids [8,11,12]. This approach makes it possible to reduce anthropogenic emissions and dispose of solid and liquid waste. At the same time, significant changes in the modes and characteristics of the operation of power equipment are possible, which lead to a deviation from the regulated standards. Aviation fuels are subject to the highest requirements for a group of categories: environmental friendliness, high calorie content, and strict compliance with quality standards. The requirements for fuels for ground transport engines are less strict, but the conditions for using such fuels impose a number of significant restrictions: fuels should be able to develop the required power with acceptable rheological properties and high environmental performance. The potential of the raw material base for alternative fuels in the field of stationary energy is much more extensive: as much solid and liquid waste as possible should be involved in this area, while environmental and economic indicators should be monitored.

The purpose of this work is to review the main problems and areas of development of promising components and formulations of liquid fuels for aviation, land transport engines (automotive and marine), and stationary power plants.

2. Promising Fuel Formulations for Aviation

For aircraft engines, as a rule, from 30 to 50 basic fuel indicators are allocated (Figure 2) [12]. For the development of alternative liquid fuels, a systematic approach is used with simultaneous monitoring of approved indicators and their change within acceptable ranges [13,14]. This makes it possible to optimize the work on creating new-generation synthetic liquid fuels for aviation.
The improvement of existing fuel technologies and the creation of new ones with the use of advanced synthetic liquid fuels require knowledge of the physics of processes occurring during their movement in a high-temperature gas environment, as well as requirements for their operational characteristics. To date, the general theory of heat–mass transfer and phase changes for such conditions has not been developed. Moreover, there are no uniform regulations on the required performance characteristics of new fuels for engines in the aviation and space industries. Synthetic fuel (SAF) is a term approved by the International Civil Aviation Organization [15]. In recent years, experimental [9,16–19] and theoretical results [20–22] have been obtained, which are certain prerequisites for creating such a theory, but it is necessary to attract large resources and time for research. It is essential to control a set of regulatory requirements applicable to alternative fuels with a significantly different nature of these requirements, as well as corresponding to current ecological trends. Synthetic liquid fuels are one of the solutions for reducing anthropogenic emissions during engine operation in the aviation and space industry [23]. Alternative fuels should not contribute to climate change and should ensure low concentrations of anthropogenic emissions throughout the entire life cycle. For example, the use of synthetic liquid fuels, which are a mixture of certified alternative fuel and traditional Jet A-1 fuel, allows the reduction in the concentration of anthropogenic emissions by 50–70% compared to the pure Jet A-1 [23]. There are known initiatives that are aimed at finding new solutions, including the use of biofuels as an alternative liquid fuel for engines and power plants in the form of hybrid electric systems [24,25], as well as solar-powered aircraft [26]. The undoubted advantage of advanced synthetic fuels in comparison with other alternative methods of energy production is their use without the need to change the design of the engine and fuel infrastructure.

Over the past 10 years, more than 200,000 flights have been made using alternative fuels [27]. The first biofuel-powered flight was made in 2008 from London to Amsterdam by Virgin Atlantic Airways. This flight was carried out on a mixture of 80% traditional fuel and 20% alternative synthetic fuel from coconut oil [28]. Promising alternative synthetic fuels for engines and power plants are currently also obtained from microalgae...
[13], sugar cane [29], liquid hydrocarbons (diesel and biodiesel [19]), sewage sludge [16], animal fats and vegetable oils [30,31], municipal solid household waste [30], genetically modified organisms [14], etc. International commitments indicate that, by 2050, greenhouse gas emissions should be twice as low as in 2005 [15]. According to forecasts, the need for fuel, for example, for aviation, will amount to 852 million tons in 2050 [32]. To handle these challenges, measures are being taken both to improve the design of engines and power plants and to switch to alternative fuels in order to achieve the goals adopted for 2050. To meet strict emission requirements for CO₂ reduction in the long term, large-scale use of alternative synthetic fuels will be required. The challenge is to create high-quality, reliable, and safe alternative synthetic fuels that meet a wide range of performance requirements. There are known attempts to create methods for optimizing all requirements based on multi-attributive optimization [13] and new hybrid multi-criteria decision-making (MCDM) methods for selecting alternative synthetic fuels to replace Jet A-1. The main areas of research in the world science in the field of synthetic liquid fuels cover the entire cycle composed of preparation, stabilization, storage, transport, spraying, combustion, and emission capture.

In addition, liquid fuels for aviation based on a combination of components and additives must meet the required complex indicators, taking into account availability, economic, environmental, energy, technological, and other changing indicators using digital fuel planning, production, and testing systems [33,34]. In this case, the most promising components of alternative liquid fuels are products and waste from the processing of biomass, oil, gas, coal, agricultural waste, waste water, gas hydrates, tall oils, etc. [33,34]. Raw material composition changes with due account for the indicators selected based on the results of test experiments and assessments of environmental, economic, energy, technological, and other criteria. Almost all of the above-mentioned promising raw materials are multicomponent. This is the main scientific interest and complexity at the same time. It is advisable to adjust the fuel formulation due to changes in the composition of the involved flow products of oil, coal, gas, biomass, and other raw materials processing. For this purpose, it is important to develop mathematical models of the mixing process of components that allow calculation of the optimal ratio of components, taking into account their properties and characteristics of the resulting fuels. It is reasonable to develop a set of such models for the required types of fuel formulations for aircraft engines, using neural networks to build digital twins.

The preparation of typical fuels in the oil refining industry is characterized by a complex multi-stage scheme for the production and mixing of hydrocarbon flows (products of such processes as catalytic reforming and isomerization, alkylation, etc.), including the deep refining of petroleum raw materials, such as catalytic cracking and hydrocracking (Figure 3).
The non-additivity of the main chemical and technological indicators of the quality of the obtained fuels and the content of the main regulated substances is not taken into account. This leads to a deterioration in product quality and a decrease in economic indicators due to the overspending of expensive components. Fuel formulations should be calculated based on the parameters and properties of the mixing components, which reduces the output of substandard fuel batches, as well as saves on expensive components, such as alkylates, isomerizates, and high-octane additives. Physical and chemical properties of mixed flows are determined by the operating modes of oil recycling units and the quality indicators of the corresponding products [35,36]. Optimization of the compounding is due to the rational involvement of flows and the accurate calculation of fuel mixtures. This leads to savings of expensive fuel components and reduction in excess octane reserve, which gives a direct economic effect for the enterprise. Fuel compounding is a sequential process involving mixing the base with high-octane components and additives [37]. After addition into the mixing reactor of all components, according to the established recipe, an analysis of the mixture sample is made. If the product in the tank does not meet the regulatory requirements, an amendment is made to the formulation in order to adjust the operational quality indicators. This operation requires a lot of time and does not allow correcting the composition of the mixture during the mixing process, since the quality parameters of the final product can only be obtained after all the components are fed into the tank and properly mixed. To conduct a complete qualitative and quantitative analysis of compounding efficiency, it is necessary to establish the relationship between the production facilities and the operating modes of the plants, and their impact on preparation productivity. In this case, recommendations for changing formulations to improve the efficiency of the preparation stage will be correct and fully justified. The solution of the multi-factor problem of predicting the composition and quality indicators of fuel components obtained in the processes of secondary oil refining is most effective when using the method of mathematical modeling on a physicochemical basis [38–40]. The key aspect of constructing mathematical models is sensitivity to changes in the composition of raw materials and the activity of catalysts for oil recycling processes [41,42]. Only in this case, the model is universal and it can be used to optimize and predict production indicators. One of the ways to increase the energy and resource efficiency of high-octane fuel production, taking into account the physicochemical laws of each stage of the produced intermediate product, is to optimize and predict the technological modes of multi-stage processes with the application of an integrated system of technological modeling of oil processing processes and apparatuses. This system includes mathematical models of basic oil refining technologies [42,43]. At the same time, an important function
of the integrated modeling system is the ability to take into account the nonadditive properties of hydrocarbons that form flows entering the compounding stage. In particular, the non-additivity of the detonation properties of these flows is due to the effect of chemical interaction between individual components of the mixture (hydrocarbons of different fractions of reforming, alkylation, isomerization, catalytic cracking, as well as anti-knock additives and oxygenates) [42,44,45]. To create a flexible system for efficient fuel production, it is necessary, firstly, to develop a single platform that represents a bank of mathematical models of secondary oil refining processes and, secondly, to develop a scientifically grounded approach based on the mathematical prediction of the detonation resistance indicator. The latter is manifested in two- and multicomponent fuel mixtures. The development of such an approach will ensure the development of optimal formulations for the preparation of aviation fuels, accounting for the chemical interaction between individual components of the mixture (hydrocarbon flows, additives, high-octane components of motor fuels, etc.).

3. Promising Fuel Formulations for Land and Marine Engines

It is important to note that there is no standard engine for any application, e.g., for the industrial one in power generation and as pumps for cargo vehicles or marine transport. Industrial engines, usually diesel, can be adapted to operate on marine vessels [46,47]. There are differences between industrial and shipping engines due to the duration of operation before major repairs, which is determined by the usage profile consisting of hours of operation at a given speed, the number of revolutions and gears, and the nature of gear changing [48]. The usage profile sets out the technical differences between industrial and shipping engines. This review will not directly address the technical features of the engines. Attention will be focused on current trends in fuel formulations and the technological challenges they generate. To a lesser extent, the environmental effects of using such formulations will be addressed.

3.1. Fuel Mixtures for Dual-Fuel Engines

The pursuit of a carbon-neutral goal leads to the development of marine fuels with low or zero carbon content [47,49,50]. Natural gas is currently one of the most competitive low-carbon fuels for gas and dual-fuel engines [51–53]. However, the low compression ratio used to control detonation combustion limits the increase in thermal efficiency of natural gas engines [52]. Another potential marine fuel of the future is methanol, the use of which contributes to the reduction in air pollutants, including particulate matter emissions [54].

The advantage of using synthetic gas in the engine with compression ignition in dual-fuel mode lies in implementing an energy system with “flexible” fuel, especially for autonomous stationary applications. Figure 4 shows a schematic flow diagram of a dual-fuel engine with an exhaust gas separation and cooling system as part of EGR and a preheating system for fuel and air. The gas–liquid mixture preparation system provides for the supply of syngas and traditional liquid fuels or mixtures with the addition of liquid biofuels, as well as heterogeneous emulsion liquids. In the dual-fuel mode, due to the pre-injection of jet fuel (e.g., diesel), there is an additional difficulty, which consists in poorly understood physicochemical interactions during combustion between syngas and atomized liquid fuel. To date, the operation of dual-fuel engines using methane or natural gas is fairly well covered in the literature [55–58] but to a lesser extent for syngas. Similar to compressed natural gas (CNG) and liquefied petroleum gas (LPG) [59], the synthetic gas is also a good candidate for use in dual-fuel engines due to its variable composition, flexibility regarding the feedstock for its production, and the ability to produce directly on board the vehicle [60,61]. Paykani et al. [62] showed a significant influence of the synthetic gas composition on the combustion characteristics. In particular, the increase in hydrogen in syngas plays an important role in improving combustion. In addition, changing the pre-injection strategy seems to be a promising way to expand the prospects
of dual-fuel syngas engines. It is noted that research in the field of synthetic gas production and combustion in internal combustion engines is mainly focused on stationary operating conditions, and very few studies have been conducted in the context of transient processes [62]. For correct optimization of a dual-fuel engine with compression ignition running on syngas, the effect of its composition should be carefully investigated. This problem was successfully solved in a recently published study [63]. The examination of the effect of the composition of synthetic gases on the characteristics of a dual-fuel engine consists not in providing the engine with real synthetic gas, but in optimizing compositions that are representative from the point of view of what can be obtained as an input parameter as a result of gasification. In parallel, the problem of determining the effect of each gas component on engine performance and harmful emissions is solved.

Recently, ammonia has become increasingly popular as a carbon-free alternative fuel in the field of freight transport [64], especially in the maritime transport sector [65]. Yousefi et al. [65] studied the effect of the strategy of separate diesel fuel injection (two-pulse diesel fuel injection) on the indicator thermal efficiency (ITE) of ammonia–diesel dual-fuel (ADDF) engine under medium-load operating conditions. The results show that a dual-fuel combustion mode with a single diesel fuel injection strategy provides a lower value of ITE compared to the corresponding combustion mode of diesel fuel only. However, using a separate diesel fuel injection strategy increases the value of ITE for dual-fuel combustion mode up to 39.72%, which is higher than for diesel-only combustion mode (maximal ITE\text{diesel} = 38.62%). In addition, the split-injection strategy reduces unburned ammonia emissions in the dual-fuel combustion mode by 83.5% compared to the unburned ammonia emissions typical of the single-injection strategy. However, the lowest concentration of unburned ammonia achieved in study [65] still exceeds the recommended threshold and, therefore, the possibility of using appropriate devices for subsequent processing should be considered in the future. The higher auto-ignition temperature of ammonia has a negative impact on combustion and performance, which, however, can be improved by implementing advanced injection strategies [64].

A recent bibliometric study of the use of gas–liquid fuels [66–68] proved that biodiesel, biogas, and hydrogen have been most frequently studied in the last 15–20 years. Hydrogen is considered as the fuel of the future, representing a renewable, inexhaustible, and environmentally friendly source of energy [68]. The results of these studies are closely related to the characteristics of the engine [69], combustion [70,71], and harmful emissions [72], leaving out many issues related to the direct implementation of a dual-fuel system, such as infrastructure availability, policy, cost, cargo transport applicability, life cycle assessment, and public acceptance. All of these issues require further attention in the future; at the moment, the research area under examination is considered as a relatively new one.
Figure 4. Schematic flow diagram of a dual-fuel engine running on mixtures of syngas and conventional liquid fuels with the addition of biofuels or heterogeneous emulsion liquids.
Nevertheless, currently appearing experimental [73,74] and numerical [74] studies show that, in general, the technology of dual-fuel engines, taking into account modifications (mainly gas–liquid fuel mixture preparation systems) and optimization works (compression ratio and injection strategy), contributes to achieving competitive engine performance characteristics. Among them are the brake thermal efficiency (BTE), brake-specific fuel consumption (BSFC), specific energy consumption (SEC), and exhaust gas temperature (EGT). Chockalingam et al. [73] reduced the diesel fuel consumption by up to 73% at the tested compression ratios (12–18) due to its replacement with generator gas obtained from the cocoa pod husk. Based on the results of the analysis of operational characteristics and the composition of harmful emissions, it is concluded that the biomass used can become a promising raw material for the production of biogas and the replacement of diesel fuel in internal combustion engines. However, additional optimization work is required to predict the most appropriate engine operation parameters in dual-fuel mode with the proposed biogas. Another example of a gas–liquid fuel formulation used in a dual-fuel engine with a Common Rail injection system is a mixture of polyoxymethylenedimethyl ethers (PODE) with methanol [74]. The study found that, as the injection time and inlet temperature increase, the rate of generation of H and OH radicals during dual-fuel combustion increases, the emissions of NO and NO₂ rise, and the emissions of methanol, HCHO, C₂H₆, CH₄, and C₃H₈ reduce. On the other hand, as methanol increases during combustion, the emissions of NO and NO₂ decrease, while the emissions of methanol, HCHO, C₂H₆, CH₄, and C₃H₈ increase. The problem associated with increasing the level of control of unregulated emissions of NO₂, HCHO, and methanol in a dual-fuel engine operating on the mentioned fuel mixture has been highlighted.

Summarizing the information presented in this section, it should be noted that it is not so much the modification of engines for dual-fuel operation or the introduction of additional devices for fuel processing [52], as optimization studies for certain fuel mixtures.

### 3.2. Fuel Mixtures for Flex-Fuel Engines

Flexible fuel engines (FFE) are designed to work on one or several fuel formulations, such as mixtures based on gasoline and ethanol [75]. The use of ethanol-based mixtures requires modification of FFE, including the use of other materials to ensure a longer service life of components and achieve maximum power output [76]. This is due to the varying chemical composition of ethanol, higher anti-knock characteristics, and lower calorific value. In addition, the ignition timing and high energy density of spark plugs and batteries must be calibrated and optimized for various ethanol mixtures [77]. Other modifications and optimization works related to the fuel supply system are also required [77]. However, for FFE with the addition of ethanol and appropriate calibration of the operating parameters, it is possible to achieve improved combustion characteristics, productivity, and harmful emissions [78]. However, fuel consumption always increases as the proportion of ethanol increases under static and dynamic test conditions. The influence of the ethanol fraction on unregulated emissions, in particular, aldehydes, methane, ethane, propane, ammonia, and unburned ethanol, is considered by many researchers [78]. Future research highlights the development of a hybrid powertrain with “flexible” fuel, adapted to a wide range of ethanol-based mixtures, in order to reduce fuel consumption. In addition, the research related to FFE technology can develop in the direction of material compatibility, corrosion inhibitors, additives for sediment control, and advanced combustion management strategies for various ethanol fractions [78].

Review study [79] devoted to alternative liquid fuels for transport identifies two major areas, such as bio-oils and plastic oils. It is concluded that it is necessary to conduct fuel efficiency studies by adding various nanoadditives and oxygen-containing additives that can catalyze combustion. In addition, quite serious modifications in the piston chamber and combustion chamber and optimization works within injection and
supercharging systems are proposed. They should eventually lead to life-cycle analysis when using bio-oil and plastic oil to gain access to improved engine efficiency and fuel economy.

Esters are considered as a potential fuel in the transport sector, including road, sea, and air transport, to control greenhouse gas emissions [80]. Moreover, esters with longer aliphatic carbon chains reduce soot formation and particulate emissions. On the other hand, a comprehensive analysis of the presence of soot particles at the nanoscale is appropriate, taking into account a wide range of experimental conditions. The physicochemical properties of esters and the use of esters in engines indicate that they can compete with ethanol and petroleum fuels [80]. Nevertheless, experiments on the driving of vehicles running on esters on roads are appropriate to establish the effect of using esters on engine power output and interaction with engine parts and petroleum-based fuel.

Currently, there are studies [81] that show that the characteristics of diesel fuel made from algae are compatible with petroleum diesel fuel, and the performance and emissions parameters are close to diesel fuel. Thus, algal biodiesel and its mixtures can be used as fuel for diesel engines without any modifications in existing diesel engines. This area of research is certainly less studied in terms of FFE technologies. However, along with the preparation of mixtures with the addition of algae diesel fuel, it seems appropriate to conduct studies of the physicochemical properties of mixtures and the effect of a small amount of algae biodiesel admixture on the performance and emissions of a compression ignition engine.

Other potential candidates for the right to be considered a biofuel that can replace petroleum-based fuels are 2,5-dimethylfurural (DMF) and ethoxymethylfurfural (EMF) [82]. These fuels have physical and chemical properties comparable to those required for the operation of gasoline engines, but they have more favorable properties than bioethanol. Two types of initial substrates are used for their production: hydroxymethylfurfural (HMF) and fructose-based raw materials, due to their higher production efficiency. The implementation of these biofuels is at the stage of developing production optimum strategies [82]. Thus, these biofuels can currently also be considered as potential candidates for research within the FFE technology.

### 3.3. Heterogeneous Fuel Formulations: Emulsion Fuel

Emulsions and emulsion fuels. The main advantage of using emulsion fuel in internal combustion engines with compression ignition is emulsions play an important role in a number of industrial and domestic applications [83–85]. The use of emulsions covers a wide field, starting with the lubrication and cooling of equipment involved in metalworking processes and ending with a more delicate application in cosmetics [85]. Emulsions are also found at various stages of oil production and processing of raw materials, namely in the processes of oil separation and treatment, flotation plants, crude oil transportation equipment, etc. [86]. Currently, emulsions are also of great importance for the food industry [87]. Special mention should be made of research in the field of development and improvement of emulsified fuels [88], in particular, in the form of water-in-oil emulsions [89–93]. In most of these applications involving the use of emulsions, it is often necessary to predict and reliably control their viscosity.

Promising emulsified fuel can be used without preliminary modification of engines [94]. The possibility of using complex fuel compositions of two or more immiscible liquids has led to a wide range of experimental and theoretical studies, mainly devoted to the study of water–diesel emulsions in relation to maintaining or increasing the performance of engines with compression ignition or electric ignition, as well as reducing emissions of harmful substances (NOx, SOx, CO2, and soot) during combustion. Generalizations based on the results of these studies are presented in review articles, e.g., [89,90,95].

Currently, the most complete theoretical base is being compiled, potentially containing detailed information about the puffing and microexplosion of various emulsified fuel compositions in internal combustion engines. Moreover, it includes the
results of fundamental studies on the influence of the concentration of emulsion components, their rheological properties, initial temperatures of the environment and emulsion, viscosity of the latter, and others on meaningful target characteristics (puffing and microexplosion) under heating and ignition conditions [89,90,96–102]. In addition, the results of experimental and numerical studies of the factors affecting the origin and intensity of puffing and microexplosion processes of single drops of emulsions are presented separately. Among these factors are the size of particles (droplets) of the dispersed phase, the size of drops of emulsions, the ambient pressure, the type and percentage of surfactants that stabilize emulsions, the type of compression ignition engine, and the conditions of engine operation [102].

As noted earlier, when studying the impact of the use of emulsified water–diesel fuel on the performance of internal combustion engines with compression ignition, great attention is paid to reducing emissions of harmful substances from fuel combustion. An important advantage of meeting puffing and microexplosion conditions is the production of water vapor in the combustion area, which helps to reduce the flame temperature and, consequently, reduce emissions NO [97]. The presence of free radical OH released due to water vaporization also contributes to the reduction in soot formation [97].

There are a number of works devoted to the study of the effect of the microexplosion phenomenon on the flame characteristics, in which the spray-cone angle during the combustion of emulsified water–diesel fuel is relatively much wider and larger than that of pure diesel fuel [103].

Water-diesel micro-emulsions. Comparison of the potential capabilities of emulsions and micro-emulsions. Micro-emulsion fuel was first created in 1976 [104]. Lif and Holmberg [104] and many others afterwards (e.g., [105–107]) demonstrated the use of the water-in-diesel micro-emulsion as a fuel. The diameter of droplets of the dispersed phase in the micro-emulsion varies in the range from 5 to 20 nm, while the same parameter in the water-in-diesel emulsion is 1–10 microns. The main advantage of micro-emulsions is their thermodynamic stability, unlike conventional emulsions, which are unstable in nature. However, micro-emulsions have a number of critical disadvantages. The main one is the need for a large amount of stabilizer during emulsification, usually up to 10% [108]. This is quite a lot in comparison with conventional emulsions, which require an average of about 2% of stabilizer [108]. When a micro-emulsion is injected into the combustion chamber, it penetrates further than a conventional emulsion. This is due to the lower volatility of micro-emulsions due to the addition of a significant amount of surfactant, which leads to a relatively greater reduction in the surface tension of liquids. The increased content of stabilizing additives affects the final price of the product and may limit the commercialization of this type of fuel (especially in large-scale production). However, attempts to commercialize micro-emulsified fuel have been made, e.g., in one discussed in Ref. [109].

Three-phase emulsions. This type of emulsified fuel is the least studied one. Unlike a conventional emulsion, the physical structure of a three-phase emulsion assumes the presence of internal, dispersed, and external phases. The dispersed phase (water) is located in the middle of the system. Diesel droplets are located inside the dispersed phase, and the dispersed phase itself is distributed in the form of droplets in the volume of the surrounding diesel. It was found that the viscosity of the three-phase emulsion is higher than that of the conventional emulsion [110]. When forming a three-phase emulsion, hydrophilic (e.g., Tween 80 with a hydrophilic–lipophilic balance (HLB) of 15) and lipophilic (e.g., Span 80 with HLB = 4.3) surfactants are used.

A small number of research results on the effect of three-phase emulsions on internal combustion engine performance and reducing emissions of harmful substances have been published. Nevertheless, the first attempts to apply three-phase emulsions in diesel engines have been performed relatively recently [111]. When using a three-phase emulsion, BSFC was reduced when compared with a conventional emulsion. In addition, the three-phase emulsion usage promotes lower CO and NO emissions. However, even
taking into account some improvements in such indicators as engine performance and the amount of harmful emissions, this type of fuel still receives little research interest due to the labor intensity and high cost of the three-phase emulsion formation process.

Prospects and existing problems of water-in-diesel emulsion fuel. An extremely limited number of studies are carried out during long-term operation of a diesel engine on water-in-diesel emulsion fuel; here, the so-called durability check or strength tests of the corresponding internal combustion engine components and assemblies [112] are meant. Ithnin et al. [102] revealed potential research areas with regard to studies on the long-term interaction of emulsified fuel and diesel engine parts. Among them are friction analysis of piston sealing rings and piston blocks, analysis of carbon deposits in fuel injectors, analysis of the water content in lubricating oil, and corrosion analysis. Studies [103,110] proved the expediency of using emulsified fuel instead of the common method of direct injection of water into the combustion chamber. Direct contact of water and engine parts leads to negative consequences. Thus, there is still a serious question about the scalability of the results of the above studies obtained in laboratory conditions, taking into account the long-term operation of the diesel engine.

Another pressing issue is the stability of water-in-diesel emulsion fuel. The stability period of a conventional water-in-diesel emulsion is relatively short, i.e., after this period, water and diesel fuel are separated. The disadvantages of thermodynamically stable micro-emulsions were mentioned earlier. Due to the current difficult (in terms of commercial expediency) situation, a mechanical approach was proposed to solve the problem of stabilizing emulsions, which involved the development, patenting, and use of special devices for forming emulsified liquids (see, e.g., [113–115]). Subsequently, such devices helped to reduce the dependence on the high cost of forming emulsions, since the need for using stabilizers was significantly reduced or completely eliminated. Although these devices, to some extent, solve the problems associated with the stability of water-in-diesel emulsions, the potential, definitely high degree of complexity of such fuel supply systems is a huge obstacle to the commercialization of such a fuel preparation method. Nevertheless, in this area of research, it is rational to solve the problems of optimizing and simplifying such devices and, accordingly, increasing the efficiency of fuel preparation.

4. Promising Fuel Formulations for Power Systems

4.1. Main Features of Utilization of Liquid Fuel Compositions at Power Industry Facilities

An important feature of using liquid composite fuels for stationary power plants is that the fuel preparation process can be carried out continuously. This fact makes it possible to significantly expand the potential raw material base of components for use in power plants. Water-based fuel suspensions (coal–water slurry (CWS) and coal–water slurry with petrochemicals (CWSP)) have shown their efficiency for use in power engineering facilities [116–118]. The main fuel component of such slurries is low-grade solid fuels (most often coal processing waste), water as a binding agent, and specific additives (petrochemical waste and surfactants) that allow regulating energy, rheological, and environmental characteristics. This approach makes it possible to involve the huge potential of carbon-containing industrial and household waste in the energy sector and to reduce the anthropogenic load on the environment by deep recycling of a wide group of pollutants [119–121].

The limited storage time stability of fuel mixtures is of little importance if they are burned in stationary boilers and furnaces. It is enough to have all the necessary and prepared components at your disposal, and the mixture can be prepared on their basis immediately before being fed into the heat exchange chamber. The low energy potential relative to fossil fuels can always be compensated by including additional burners or boilers operating on a high-calorific fuel in the thermal scheme of the enterprise to cover peak loads.
The possibility of a relatively simple transition of stationary power plants to alternative fuels with minimal investment in the equipment or without any changes at all is confirmed by studies in Refs. [118,122–125]. In general, changes should be made to the fuel storage, preparation, transportation, and injection systems [126,127] (Figure 5). If the fuel compositions do not have sufficient stability for long-term storage, it is necessary to organize landfills for storing solid components and containers for specific fuels and stabilizing liquid components. Since most of the basic solid components of mixed fuels for the energy industry are low-caloric, the specific fuel consumption per unit of energy generated increases significantly relative to traditional fuels [126]. This results in the need to increase the area of the corresponding fuel depots and landfills for ash disposal.

**Figure 5.** Basic technological scheme of a thermal power station: 1—fuel storage; 2—fuel preparation; 3—steam boiler; 4—steam turbine; 5—electric generator; 6—ash catcher; 7—smoke exhauster; 8—chimney; 9—blower fan; 10—ash removal; 11—high-pressure heater; 12—low-pressure heater; 13—pump; 14—condensate pump; 15—heat consumer; 16—return condensate pump; 17—condenser; 18—technical water supply; 19—chemical water treatment; 20—cooling water pump; Qc—fuel heat consumption per station; Qe—heat loss with cooling water; Do—steam flow to the turbine; No—electrical power transmitted to consumers.

The combustion temperature of composite liquid fuels is slightly lower than that of traditional fuels, which is a favorable factor for reducing the intensity of slagging of boiler heating surfaces. At the same time, it is necessary to take into account the increased ash content of low-grade fuels [128–130].

The most important aspect of the use of composite liquid fuels based on water is the environmental characteristics of combustion products [131,132]. Due to microexplosion phenomena, the proportion of mechanical underburning decreases during heating of inhomogeneous drops of fuel suspensions. Moreover, the presence of a vapor in the furnace chamber initiates additional chemical reactions with intermediate oxidation products, which is a favorable factor for reducing the proportion of sulfur and nitrogen oxides in flue gases [133].

Thus, a joint analysis of the positive and negative aspects of the use of liquid fuel compositions at energy facilities suggests that the use of alternative fuel slurries based on low-grade fuels and water is economically, environmentally, and energetically feasible [134].
4.2. Components of Alternative Fuel Compositions

The main fuel component of composite liquid fuels is most often a solid component—low-grade coal of substandard fractions, filter cake, coal sludge, coke ash, etc. [122,135,136]. The use of such components in fuel mixtures is currently a priority in some countries with actively growing economies and is encouraged at the state level [137,138]. Li et al. [137] analyzed the main results of research on the use of solid carbon-containing industrial waste in the electric power industry and heat supply. The conclusion, based on the results of an impressive literature review, is that it is necessary to conduct a comprehensive study of the combustion characteristics of potentially profitable components of fuel suspensions, taking into account environmental and energy aspects, in order to identify possible environmental risks.

The proportion of the solid carbon-containing component in the fuel composition is usually from 40 wt% to 50 wt%. The content of solids of more than 60% leads to a deterioration in the rheological properties of the slurry. The compositions with a high content of solids become usually unsuitable for injection into the combustion chambers of power plants [139–141].

In Ref. [134], an attempt was made to generalize data on the energy properties and environmental aspects of combustion of a wide group of fuel suspensions based on combustible industrial and household waste. The characteristic temperatures and ignition delay times of composite fuel drops were determined experimentally. Moreover, the maximum stable combustion temperatures were determined for liquid fuel mixtures with different compositions and ratios of combustible components, such as coal sludge and filter cake of different grades of coal, wastewater, liquid petrochemical waste, solid plant biomass, and specialized additives. The results of study [134] confirm the high ability of fuel suspensions based on waste from a wide group of industrial sectors to compete with traditional fuels when used in power plants [134]. In addition to reducing economic costs by eliminating expensive and scarce fossil fuels, well-chosen formulations of liquid fuel compositions allow the required energy performance to be reached with more favorable environmental characteristics of combustion products. It is worth noting that the environmental aspects of the use of CWS and CWSP become the object of research quite often [133,137,142]. At the same time, the results allow us to conclude that the environmental characteristics of the combustion products of fuel slurries are more favorable compared to the similar characteristics of the combustion of components in pure form or when using traditional solid and liquid fuels.

The main liquid component of CWS and CWSP is water. It serves as the basis and binding component. However, municipal and industrial effluents of a wide variety of compositions can be used for slurrying [135,143–145]. Relying on the results of comparing the thermogravimetric characteristics of CWS, a slurry based on coal and waste water from coke production, and a slurry based on coal, water, and coke sludge, Zhao et al. [135] concluded on minor differences in the ignition and combustion mechanisms of these fuels. Since the highest combustion temperatures were recorded in the case of coke waste water slurry, it is likely that the composition contains components with catalytic properties. At the same time, the composition of the combustion products of waste-based mixtures was more toxic (this is indirectly indicated by a reduced content of heavy metals in the ash). In Ref. [135], the revealed effect is justified by the probable presence of chlorine compounds in wastewater and sludge, which reacts with heavy metals when the temperature rises. These results once again confirm the need for a detailed study of the environmental aspects of involving combustible waste in the energy sector [137].

Rheological characteristics of fuel suspensions based on coke wastewater and coke ash were studied in Ref. [144]. The studied fuel compositions are classified by their characteristics as non-Newtonian pseudoplastic fluids. To manage the rheological properties of such slurries and to provide for the possibility of using them in the energy industry, it is necessary to introduce special dispersants into the composition. The coke ash content should not exceed 66% in coke waste water slurry and 75% in coke ash and
water-based formulations. Recommendations on the choice of dispersants for more stable slurring of the studied compositions are also formulated.

Domestic wastewater can also be effectively used to form promising energy fuels [146]. However, the substances dissolved in them, as well as the composition of silt sediment, can vary significantly in different regions. Therefore, recommendations on the optimal composition and feasibility of using effluents for energy needs should be formulated for specific conditions. At the same time, taking into account the environmental indicators of burning fuel suspensions, including municipal effluents, is no less important.

To increase the energy potential of CWS, it is advisable to introduce various combustible organic liquids into their composition. Such components can include waste to be disposed of (heavy oil fractions and sludge, used motor, turbine, and compressor oils, and cooking oils) [11,117,133,134] and highly reactive fuels (alcohols and mixtures of light oil fractions) [147].

Vershinina et al. [11] researched combustion characteristics of drops of the slurry based on coal sludge and coal dust with the addition of the used turbine oils up to 15 wt%. The share of the coal component varied in the range of 40–60%. Ignition and combustion characteristics of fuel suspension drops of different diameters were recorded. It was shown in Ref. [11] that the addition of waste turbine oil to the suspension intensifies the ignition and burnout of drops. As the temperature in the combustion chamber increased, the burnout rates of fuel compositions with oil were lower than those of CWS without additives. Vershinina et al. [11] demonstrated that to significantly improve the process, it is sufficient to use no more than 5 wt.% of oil. Higher concentrations of oils or other highly reactive components lead to an increase in the viscosity of the suspension, which makes it difficult to use it in power plants. In addition, an increase in the proportion of oils in CWS has a negative impact on the environmental performance of flue gases.

Jianzhong et al. [125] prepared the fuel suspension on the basis of hard coal and liquid waste from petrochemical production. The composition with the addition of petrochemical waste showed a higher reactivity during ignition initiation and during combustion. The combustion temperature of the slurry with waste in a semi-industrial furnace [125] was higher by 50–100 °C compared to fuel without oil additives. A more complete burnout of CWS compared to CWS was justified, as evidenced by the results of chemical analysis of ash (lower carbon content in the unburned residue). At the same time, more intensive slagging of heating surfaces was recorded relative to the combustion of CWS. A likely explanation for this effect is the increased combustion temperatures in the furnace.

Staroñ et al. [133] investigated the effect of spent glycerol on the rheological and energy characteristics of CWS. The suspension with glycerol is characterized by a higher viscosity and density (184.2 mPa·s at a shear rate of 100 rpm, 1.11 g/cm³) than the slurry without glycerol (45.5 MPa·s at a shear rate of 100 rpm, 1.08 g/cm³). This makes it easier to spray the slurry. In addition, thanks to glycerol, the calorific value of the fuel composition increases. The emissions of SO2 and NOx are reduced by half compared to the release of these gases when burning hard coal.

At the same time, it should be taken into account that, along with the positive effect of petrochemical additives on the rheological, energy, and environmental characteristics of composite fuels, their use can significantly increase economic costs. Therefore, for each specific operating conditions, it is necessary to choose the optimal proportion of the valuable but rather expensive petrochemical component of the fuel slurry.

Various specialized stabilizers are used to regulate the rheological characteristics of fuel suspensions based on low-grade fuel components [144,148,149]. Usually, their share in the fuel composition is small (up to 10 wt%), since the use of such additives increases the cost of fuel and increases the risk of formation of harmful combustion products with inorganic impurities. However, the use of surfactants can increase the stability of fuel suspensions and increase the efficiency of their injection into the combustion chambers,
so, in specific conditions, it is necessary to take into account possible benefits from the use of surfactants.

Another important group of components of fuel suspensions for the energy industry are different grades of biomass. Most often, wood processing waste (sawdust) is attracted to the energy sector [122,142]. Sawdust can be attributed to components with a high calorific value but, due to its absorbent properties, this type of fuel can be characterized by high ignition inertia. The combustion of sawdust in its pure form is not effective, including due to the intensive formation of ash and slag deposits. Gasification of woodworking waste is more profitable; however, it requires the use of complex technological systems. In Ref. [142], the selection of the optimal ratio of sawmill waste, oil sludge, and water in the fuel suspension gives high profitability from the use of such mixtures in the energy sector. Research [142] presents the experimental results of the main temporal characteristics of fuel combustion (ignition delay and duration of combustion), the amount of heat release, and man-made emissions. The optimal ratios of sawdust and oil were determined as follows [142]. A total of 30–50 wt.% of sawdust and 30–50 wt.% of oil promote the minimization of the ignition delay and ignition temperature (minimum ignition costs); 30 wt.% of sawdust and 50 wt.% of oil are needed for the maximum calorific value; 50 wt.% of sawdust, 25 wt.% of oil, and 25 wt.% of water is required for the minimum concentration of man-made emissions into the atmosphere and economic costs. For the best overall fuel efficiency, the optimal ratio of components in the fuel is 50 wt.% of sawdust, 25 wt.% of oil, and 25 wt.% of water. With this ratio, an efficiency factor of about 2.6 can be achieved relative to coal and about 12.9 relative to fuel oil [142].

A promising direction in the development of alternative liquid fuels for the energy industry is deep processing of the initial carbon-containing raw materials to produce the so-called bio-oil [148,150]. Johansson et al. [148] researched the combustion of bio-oil produced by pyrolysis of wood waste. The fuels were burned in a tube furnace in a normal atmosphere and with an excess of oxygen (40% and 60% O₂). Bio-oil was pre-mixed with 40 wt.% of methanol to reduce the viscosity and facilitate injection into the combustion chamber. The oxygen-saturated atmosphere did not affect the release of inorganic substances during the combustion of bio-oil. The use of this fuel is very environmentally friendly, since it reduces the amount of solids in flue gases. Another positive aspect of bio-oil combustion is the almost complete absence of slagging of heating surfaces. However, the process of obtaining bio-oil itself is very complex, time-consuming, and costly, and, in most cases, is much less cost-effective for use in stationary power plants than, e.g., in transport engines.

When injecting liquid fuels into the combustion chambers of power plants, it is important to ensure optimal atomization parameters. At the same time, too small droplets are subject to reversal and entrainment from the flame control zone by turbulent gas flows. When using CWS and CWSP, it is often not possible to provide optimal spraying parameters due to nozzle devices [139,151]. Thus, the use of the so-called secondary atomization of fuel droplets directly in the furnace due to microexplosion phenomena is advisable. Similar phenomena occur in fuel droplets, in which thermophysical properties of components differ significantly. Microexplosion requires low-boiling and high-boiling components. From this point of view, the use of water–oil emulsions is advantageous. Ismael et al. [152] studied the regularities of the occurrence of microexplosion sites in water-in-diesel drops. The water content in the drops was 10 vol.%. Experiments were performed for single drops with varying injection pressure. Based on the results of the study, a conclusion is formulated about the need to choose the optimal injection pressure to ensure stable conditions for the occurrence of microexplosion.

Summarizing the review of promising components and development vectors of alternative liquid fuels for the energy industry, it is important to note that stationary power plants make it possible to use almost any type of combustible materials. Low-grade combustible waste cannot be used for the needs of aviation and land transport, but they can be involved in the energy sector. At the same time, the search for the optimal ratio of
CWS and CWSP components for specific operating conditions is very important. To identify the best formulation of fuel emulsions and suspensions the method of multi-factor analysis is successfully applied [153,154]. As criteria for evaluating a particular fuel composition, it is possible to use energy characteristics (calorific value, ignition and combustion temperature, ignition delay time, and ash content), rheological characteristics (viscosity, density, and stability), spraying and fragmentation characteristics (critical Weber and Reynolds numbers, injection pressure, increase in droplet area after fragmentation, and breakup time), environmental indicators (concentrations of harmful emissions), and cost.

5. Conclusions

(i) The main vector of development of fuel formulations for aircraft engines is the search for synthetic fuels, the use of which would allow environmental benefits to be obtained. Highly reactive biofuels and multicomponent mixtures are considered as alternatives to traditional aviation kerosene. At the same time, the characteristics of aviation fuels are strictly regulated for safety reasons. In this regard, it is extremely important to develop mathematical models of mixing and combustion of alternative fuels for aviation.

(ii) The requirements for fuels for land transport engines are less stringent, but the primary characteristics of alternative fuels are their rheological properties (stability), high reactivity, and environmental friendliness. “Flexible” compositions, bio-oils, multicomponent mixtures, and emulsion fuels are considered as alternative fuels in this area.

(iii) The potential raw material base of alternative fuels for stationary power generation is very extensive. For this industry, it is advisable to use low-reactive components together with high-calorific and specific ones for managing rheological and energy characteristics. The optimal formulation of the fuel mixture should be developed for each specific operating conditions, taking into account energy, environmental, rheological, and economic indicators.

(iv) In order to achieve the target environmental and technological indicators, it is necessary in the future to investigate in detail the possibility and feasibility of using fuel compositions and their components in various combinations. The results of such studies will make it possible to create an appropriate database that allows the most effective use of known alternative fuel compositions considering the specific operating conditions of power plants.

Author Contributions: G.K., Conceptualization, Supervision; D.A., Conceptualization, Visualization, Writing—original draft; M.P., Conceptualization, Visualization, Writing—original draft; L.Y., Conceptualization; O.V., Conceptualization, Visualization, Writing—original draft, Project administration. All authors have read and agreed to the published version of the manuscript.

Funding: The study was supported by National Research Tomsk Polytechnic University development program Priority 2030 (Priority-2030-NIP/038-1308-2022).

Conflicts of Interest: The authors declare no conflict of interest.

Nomenclature

\[ D_0 \] steam flow to the turbine;
\[ N_0 \] electrical power transmitted to consumer;
\[ Q_c \] fuel heat consumption per station;
\[ Q_w \] heat loss with cooling water.
References


