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FTIR Analysis for Determining Stability of Methanol–HVO Blends for Non-Road Engine Application

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Abstract: The Green Deal targets, along with tightening emissions legislation, foster research on alternative propulsion systems. In non-road mobile machinery (NRMM), these efforts largely rally around sustainable fuels while keeping the benefits of energy security (multi-fueling) high. In this context, the blends of Hydrogenated Vegetable Oil (HVO) and Methanol (MEOH) are amongst the most promising yet under-researched alternatives and, as such, need dedicated methods for determining their suitability in engine applications. In this paper, we evaluate the feasibility of Fourier transform infrared (FTIR) analytics for determining the stability of MEOH-HVO mixtures. The research considers temperature effects during storage by conditioning the test samples at −20 °C and +20 °C. The stability of the blends and different co-solvents is analysed after six weeks, and FTIR spectra are used to identify the chemical bonds. From FTIR analysis, blending MEOH20 with 1-dodecanol results in stable homogenous alkyl-ether fuels, while the MEOH20 blend with methyl-butyrate results in ester fuels. There are observable differences in the blend samples according to their storage temperatures. In conclusion, both fuel blend samples formed different fuel types, which are stable and homogenous at room temperature, posing great potential for their applicability in different NRMM types.

Keywords: bioenergy; biofuels; co-solvents; FTIR; fuel blend; GHG emissions; internal combustion engines; NRMM; methanol; hydrogenated vegetable oil; spectroscopy analysis

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1. Introduction

Alternative fuels are considered the present and, in fact, the future of the world's energy sources. The transition from fossil fuel continues to be on the rise for zero carbon emission solutions and energy security. Long-term sustainability, which encourages a circular economy, is another important reason for the transition. Most of these alternative fuels are already known chemicals with outstanding features, such as their inherent potential as energy carriers (i.e., relatively high heating values) [1]. Alternative fuels, or biofuels, can be classified based on the level of evolution, fuel source, production processes, biofuel types, advantages, and disadvantages. First-generation biofuels are produced from edible crops. Hence, they are now outdated as they allow energy production to compete with food security. The second-generation biofuels are considered the most feasible. They enable a circular economy, which results from their advantages in agricultural and food waste recycling. They have been proven to aid in lowering greenhouse gas (GHG) emissions [2]. Besides plant and animal waste, algae also form a good biofuel source as it is one of the most important carbon-sequestrating methods [3]. Pathways for the synthesis of second-generation biofuels include thermochemical, biochemical, and chemical conversion of raw non-food feedstock. Biofuels have wide applicability in the transportation sector, and their employability in non-road mobile machinery (NRMM) is being explored.

NRMM covers a wide range of applications and is employed for purposes other than the transportation of passengers and goods on the road. They are also installed

with an internal combustion engine (ICE). They include both off-road equipment and vehicles. According to EPA (2016), off-road engines can be classified into four types (based on size, purpose, and engine concept type) [4]. They include small-sized spark–ignition (SI) engines (typically found in light-duty industrial and agricultural equipment such as light logging machines, lawnmowers, garden tractors, etc.), large-sized SI engines (including industrial generators, forklifts, and compressors generating no more than 19 kW of power), compression ignition (CI) engines (with power between 19 and 560 kW used for agricultural and industrial machines such as farm tractors, heavy forklifts, excavators), and other recreational vehicles (including off-highway motorbikes, snowmobiles). The use of conventional fossil fuels on these engines contributes greatly to GHG emissions. Due to growing concern for carbon footprint reduction, the suitability of second-generation biofuels (SGB) for powering NRMM is being investigated. Research results on this issue have shown that the use of biofuels for off-road applications is technologically possible [5]. However, it requires advanced technology, that is, the engine technology advancement to the low-temperature concepts (LTC) and/or biofuel blending (either as neat biofuels or blended with fossil fuels) [6,7].

1.1. Methanol–HVO Blends in NRMM

Hydrotreated vegetable oil (HVO), otherwise known as renewable or green diesel, is an SGB produced by high temperature/pressure hydrocracking and catalytic hydrogenation of feedstocks, causing oxygen sequestration from the triglycerides and fatty acids in the feedstocks, resulting in a straight chained paraffins as seen in Figure 1. According to ETIP Bioenergy (2020), the properties and molecular size of the resulting paraffin may vary depending on the feedstock type and the process's initial conditions [8]. HVO is sulphur-free, oxygen-free, and free from aromatic hydrocarbon, therefore resulting in a supercritical reduction of GHG emissions when used to power NRMM. European standard EN590:2009 [9] for diesel fuel has not stipulated the blending ratio of HVO with fossil diesel as long as resulting fuel properties meet up to standard [10]. HVO has chemical compositions and properties similar to fossil diesel (although it has lower energy content and density) and, therefore, can be used as a drop-in fuel in State-of-the-Art off-road diesel engines.

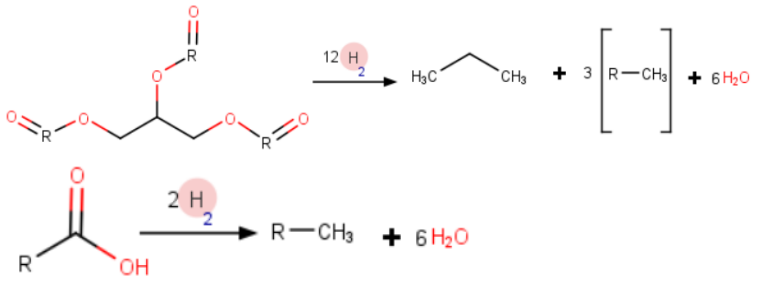


Figure 1. Hydrotreatment reaction for (**top**) triglycerides and (**bottom**) fatty acids. R is an alkyl group.

Methanol (MeOH) is an example of oxygenated biofuel and one of the potential e-fuels. According to European standard EN 228:2012+A1:2017 [11], 3% methanol can be added in methanol/gasoline fuel blends for use in existing SI engines. The suitability of methanol fuels for CI engines is currently being investigated due to their poor auto-ignition properties [12]. Production of methanol may either be through the thermochemical pathway, where the biomass is gasified into synthesis gas under favorable thermodynamic conditions as presented in Figure 2, or through the biochemical pathway with microbes' anaerobic digestion of methane biogas [13]. At ambient temperature, methanol is a polar liquid miscible with petrol, water, and other organic compounds. Its toxicity is comparable to gasoline and even more biodegradable. Methanol burns with an almost invisible flame. Table 1 shows the comparison of the different ICE fuel properties.

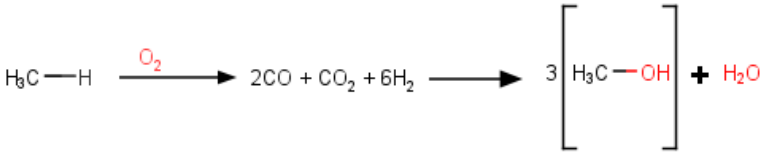


Figure 2. Gasification reaction of methane to methanol.

Table 1. Fuel specifications comparison (median values are used; refer to standards for value range; missing values are represented with a '–' sign).

Fuel Properties	Units	Fossil Diesel [1]	HVO [1]	Gasoline [1]	Methanol [1]	MeOH20/HVO [2]
Cetane number	–	50	>80	–	–	–
Octane number	–	–	–	92	>110	–
Oxidative stability	–	>48 h	25 g m^{-3}	>60 h	–	–
Density (20 °C)	kg L^{-1}	0.83	0.78	0.74	0.79	0.78
Lower heating value	MJ kg^{-1}	43.1	44.4	43.9	19.7	–
IBP	°C	162	217	160	65	63
flash point	°C	67.5	82	−45	9	9
Kinematic viscosity (40 °C)	mm^2 s^{-1}	3.33	3.14	0.7	0.55	2.64
GHG [3]	$kgCO_2eq$ $gallon^{-1}$	10.21	3.5	8.78	4.11	–
Molecular weight	g mol^{-1}	~203	~222	~100	~32	–

[1] Data according to ETIP Bioenergy fact sheet [8]; [2] Data according to research studies [14]; [3] Data according to the United States Environmental Protection Agency, EPA [15].

For employment of biofuels in the ICEs (particularly multifuel low-temperature combustion concepts), there have been documented reports on research for MeOH/diesel fuels, both fossil and green diesel (HVO) [12–14]. Blending methanol with HVO offers several advantages. One of the arguments is that methanol, as a renewable fuel, when blended with HVO, increases the share of renewable resources and lowers dependence on fossil fuels. Methanol also burns cleaner, leading to reduced emissions of particulate matter and other pollutants [13]. Secondly, methanol has a lower viscosity compared to HVO. Blending methanol can help reduce the overall viscosity of the fuel blend. This can help to improve fuel spray atomization and combustion characteristics, thereby enhancing engine performance, overall efficiency, and emission reduction [12]. Thirdly, HVO has poor cold flow properties at low temperatures. Blending with methanol (which has better cold flow properties) and co-solvent may enhance their performance at low temperatures [14]. This may also help with issues such as filter plugging. Also, depending on the type of reaction that occurs, the resulting fuel blend may have enhanced operability in cold weather. Lastly, the fuel blend can lower the overall cetane index (reactivity) and heat of evaporation, allowing for the use of less exhaust gas recirculation to achieve proper combustion phasing in low-temperature combustion (LTC) technologies [14].

Although HVO is a renewable fuel and has properties that are good for traditional diesel engines, blending with methanol can offer potential benefits and suitability for different combustion engine technologies, including NRMM, while offering a more sustainable path for renewable fuel utilization and fostering energy security. Table 1 shows the fuel properties of Methanol/HVO blends as presented in the study of Wang-Alho et al. (2023) [14]. MeOH/diesel blend is not feasible as this fuel blend forms visible separate layers, presenting that the fuels are not readily miscible despite the polarity of methanol. Nashte et al. (2021) investigated the use of co-solvent as additives to stabilize the resulting diesel–methanol fuel blends on existing heavy-duty genset engines and revealed that without additives, specific fuel consumption (SFC) improved with a decrease in carbon oxides (CO) and particulate matter (PM) while nitrogen oxides (NOx) emission level increased; however, with the additives, PM was reduced but SFC, NOx, and CO increased [12]. The research concluded that MeOH/fossil diesel is promising without additives, although this

conclusion may be generic as the chemical composition of the additive used may also influence the resulting engine performance and combustion characteristics.

1.2. InfraRed Spectroscopy for Fuel Analytics

Infrared spectroscopy involves the absorption, emissions, and reflection of electromagnetic light in the wavelength region of 780 nm to 1 mm [16]. The infrared region may be further divided into three according to increasing wavelength: near-infrared (NIR), mid-infrared (MIR), and far-infrared (FIR). The FIR is less discussed since it is less commonly applied in quality control processes due to its ineffectiveness compared to other IR spectroscopy methods. In fuel research, NIR spectroscopy is majorly applied for probing chemical compositions of fuel samples (including blends, additives, and impurities), although there is also a technically modified version, such as the Fourier transform (FT-) NIR spectroscopy, which utilizes the NIR light waves for a more rapid method for determining the chemical composition concentrations in a sample [17]. MIR light waves are typically referred to as IR spectroscopy. IR spectroscopy uses the vibrational properties of chemical compounds since the vibrational frequencies of molecular compounds correlate with those of MIR light, allowing stronger absorption peaks than those in the NIR spectral (which uses overtones and combination bands). These molecular vibrations may include symmetric or asymmetric stretch, in-plane rotation (bending or rocking), and out-of-plane rotation (wagging or twisting) [18]. Like the FTNIR, the FTIR technique is likewise more rapid and more accurate with a better signal-to-noise ratio. Depending on the sample to be measured, NIR, FTNIR, and FTIR have found applicability in fuel quality control, although they both have strengths and weaknesses in different areas of quality control. Table 2 shows the comparison between the FTIR and NIR. The Attenuated total reflectance (ATR-) FTIR with the partial least square (PLS) method was used for biodiesel blends research, and the result from the study indicates that the predictions of fatty acid methyl esters (FAME) biodiesel concentration in diesel fuel can be obtained but with restrictions on the concentration from 1% to 20% by volume. The study also reported that the concentration range could be increased to 100% with proper ATR accessories; however, precision data above 20% FAME are unavailable. Additionally, the prediction was only applicable to FAME, as biodiesel in the form of fatty acid ethyl ester (FAEE) will lead to wrong predictions [19].

Table 2. Comparison of NIR and FTIR spectroscopy methods.

NIR	FTIR
No sample preparation	Requires sample preparation for immiscible or solid samples
Inexpensive detectors	More expensive detectors that respond to variations in temperature
Excellent for samples with food samples and other samples with high water content	Highly sensitive to water signals, muddling up other useful spectral information in samples with high water content
Non-destructive penetration into bulky samples (solids)	Cannot probe beyond the surface of samples
Ideal for heterogeneous samples	Not ideal for heterogeneous samples
Accurate. Takes static and representative measurements.	Stronger absorption peaks than those in the NIR spectral. It can be used for chemical reaction monitoring

Other analytical methods, such as dielectrometric methods and impedance spectroscopy methods, have significant advantages for studying fuel storage stability. However, the complexity of setup, high-temperature sensitivity, fuel homogeneity requirements, additive interference, and, lastly, non-specific chemical data interpretation (unlike in FTIR methods) are all limitations necessitating these methods' elimination as plausible solvers for this study. However, discussion of these other analytical methods may provide a diverse overview of the available techniques for fuel analysis. However, with respect to the presented scope and aim of the research study, infrared spectroscopy was identified from the literature as the most plausible analytical tool for the research objectives. Therefore, to avoid redundancy, infrared spectroscopy is presented as a type of solver capable of being

used for this fuel blend analytical study. Table 2 presents a comparison of FTIR and NIR as plausible solvers and analytical tools for the current study. This comparison gave a premise to support the need for mid-infrared (FTIR) technology rather than NIR technology.

The suitability of FTIR and NIR in the measurement of methanol either as a fuel component or as impurities in fuel samples has been investigated and proven feasible. Faraguna et al. (2019) concluded in their study that ATR-FTIR can be used to successfully determine the quantitative amount of different fatty acid alkyl esters (FAAE) in biodiesel/diesel fuel blends [20]. Nevertheless, the study reported that FAAE cannot be quantitatively analyzed with the ATR–FTIR in blends of lower alcohols (methanol, ethanol, propanol) with FAAE/diesel due to their miscibility problems. However, blends of butanol and higher alcohols with FAAE/diesel can be quantitatively analyzed for blends up to 50 vol% alcohol and 9 vol% FAAE using a different calibration method, although with less accurate results. Two other studies investigated the use of ATR–FTIR for the analysis and quantification of methanol content in biodiesel washing wastewater and quantification of methanol in a methanol gasoline fuel blend. The studies reported remarkable results from the analysis with a coefficient of determination (r^2) greater than 0.99 [21,22]. Liu et al. (2022) presented a study on the use of NIRS for the determination of alcohol–diesel fuel blends. The study proposed the use of Gramian angular field (GAF) image coding and convolution neural network (CNN) for the evaluation of the NIRS spectra to distinguish ethanol/diesel, methanol/diesel, and diesel [23]. Another study by Czechlowski et al. (2019) proposed the use of NIRS as a quality control method for the prediction of methanol content in fatty acid methyl ester (FAME) with the aid of a partial least square (PLS) regression model for the evaluation of the NIR spectra [24].

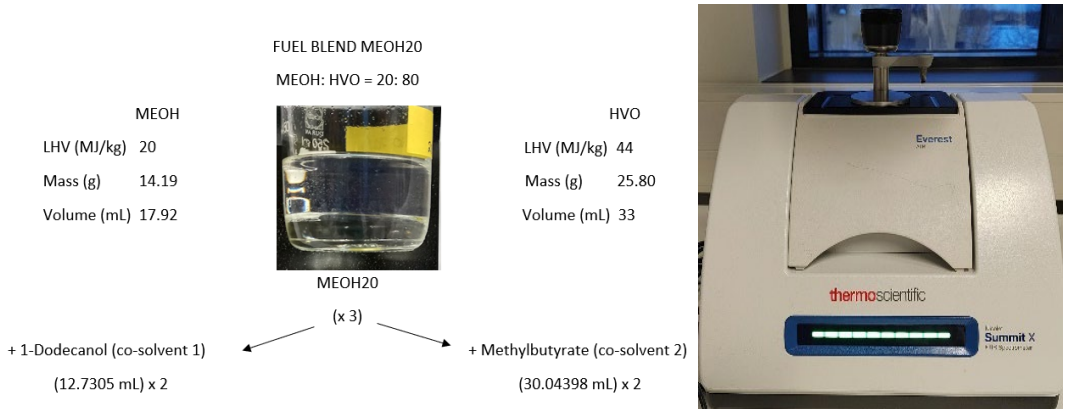
Oxygen-rich fuels or additives pose the potential to act as co-solvents in the stabilization of methanol–diesel fuel blends. The fatty alcohol 1–dodecanol is industrially produced from coconut oil or palm kernel oil, commonly used as a surfactant for various application purposes, including lubrication, emulsification, and even as a co-solvent to enhance solubility. Methyl butyrate or methyl butanoate, on the other hand, is an ester naturally present from vegetable origin that can be used as an additive in diesel fuel and has a history of being used as surrogate diesel in combustion studies [22]. FTIR analysis of diatomite/dodecanol composite material was presented by Fort et al. (2018), with spectra lines showing the interaction of both substances [25]. This study shows the suitability of FTIR in the measurement of dodecanol in a sample. Cunliffe et al. (2021) conducted NIRS studies for the quantification of unsulphured alcohol in sodium lauryl sulphate (ethoxylated dodecanol). With PLS regression methods, NIRS was successfully applied as an alternative technique to gas chromatography for impurities determination in the surfactant [26]. There are also FTIR and NIRS studies on methyl esters [20,24]. The practicality of FTIR and NIR can also be seen in understanding the solvent effect and intermolecular interaction in physical chemistry, although Bec et al. (2019) study reported that, compared to FTIR, NIR is relatively less sensitive to the chemical environment (e.g., co-solvent) and intermolecular interaction [27]. For this reason, this research work's proposed IR spectroscopy method is the ATR-FTIR, as it is focused on understanding the intermolecular interactions of the co-solvents in stabilizing methanol/HVO fuel blend as a single fuel.

Only a few investigations have focused on the utilization of methanol-HVO blends in diesel engines for agricultural vehicles. The reason might be that the fuels are not homogeneously miscible together, and blending them leads to phase separation. However, all the fuel and fuel blend options to enable carbon-neutral agriculture need to be investigated. Agricultural engine applications, in particular, would benefit from single-fuel solutions. As both methanol and HVO are potential fuels to reduce the dependence on fossil energy and be utilized in agricultural engines, this study focuses on investigating their feasibility in those applications by analysing the methanol-HVO blends stability after co-solvent (1–dodecanol and methyl butyrate) addition. Furthermore, the research of new additives requires the proper knowledge of the blends and additives chemistry. Hence, in addition to storage stability studies, this research work takes novelty in the use of Fourier-transform

infrared (FTIR) spectroscopy as an analytical tool to identify the resulting fuel compositions and fuel properties for viability in NRMM use.

2. Materials and Methods

Fuel blends of methanol and HVO were prepared using the energy ratio of 20:80 and denoted as MEOH20. According to the Lower Heating Value (LHV) of methanol and HVO, which are 20 MJ kg^{-1} and 44 MJ kg^{-1}, respectively, the fuel blend composition was 14.194 g/25.806 g and 17.922 mL/33 mL (on the mass and volume basis, respectively). Three separate samples of the same fuel blend composition were prepared. 1–dodecanol (co-solvent 1, solid at room temperature) was melted slightly to the liquid state and added to the first MEOH20 sample. Methyl butyrate (co-solvent 2, liquid at room temperature) was added to the second MEOH20 sample. The third MEOH20 sample (with no co-solvent) was left as a baseline reference sample for comparison with the two others. Two samples of each category were prepared (a total of six samples) to facilitate different storage temperatures (−20 °C and +20 °C) for the stability experiment. All six fuel samples were stored for 6 weeks. Figure 3 shows a flow diagram of the fuel sample preparation and the blend composition.



(**a**) (**b**)

Figure 3. (**a**) Flow diagram of fuel sample preparation and fuel blend compositions with co-solvents (**b**) ATR–FTIR spectrometer used for analysis.

ATR–FTIR Spectroscopy as Experimental Method

ATR–FTIR measurements of the six samples were conducted to generate spectra lines to identify the intermolecular interaction for the blend samples and the co-solvents, and perhaps the storage temperature would influence the results. Three samples were collected from the cold storage at −20 °C, and the remaining three samples were collected from the fume hood storage at +20 °C. Table 3 shows the visible physical properties of the fuel blend samples. Fuel samples were transferred with a small-sized (1 mL) disposable transfer pipette to the top of the measurement crystal slab (made of zinc selenide) of the Thermo Scientific^{TM} Nicolet^{TM} Summit^{TM} X Spectrometer as seen in Figure 3b. Each measured sample size was controlled by adding about four drops (0.2 mL) of the sample to the sensory plate. A small sample size was used to avoid the sample smearing all over the zinc selenide crystal sensory slab, as this may cause detector saturation and, consequently, a higher signal-to-noise ratio. Table 3 shows the basis parameters of the spectrometer in Figure 3b. This spectrometer is useful in chemical identification, contaminant analysis, purity, changes in chemical bonds, quantification, and mixture analysis [28]. The measurement was conducted by the spectrometer in less than 60 s. After each sample measurement, the spectrometer measurement crystal slab was cleaned with ethanol wipes and allowed to dry before the next measurement. This is to avoid any error in the generated spectra for each sample. Since the analysed samples with co-solvent already formed homogeneous blends, they were easy to transfer to the FTIR sensory slab for analysis. However, the control methanol-HVO

sample with no co-solvent formed a double layer. To analyse these heterogeneous phase blends, the sample was first mixed rigorously. During this rigorous mixing, there was a dispersion of one liquid into tiny droplets within the other, which eventually separated back into distinct layers when the sample was left standing. During the temporary formation of this emulsion, the sample was transferred using a 1 mL disposable transfer pipette to the FTIR sensory slab for analysis. Once the spectra were generated, they were opened in the OMNIC Paradigm Software v2.5 for analysis.

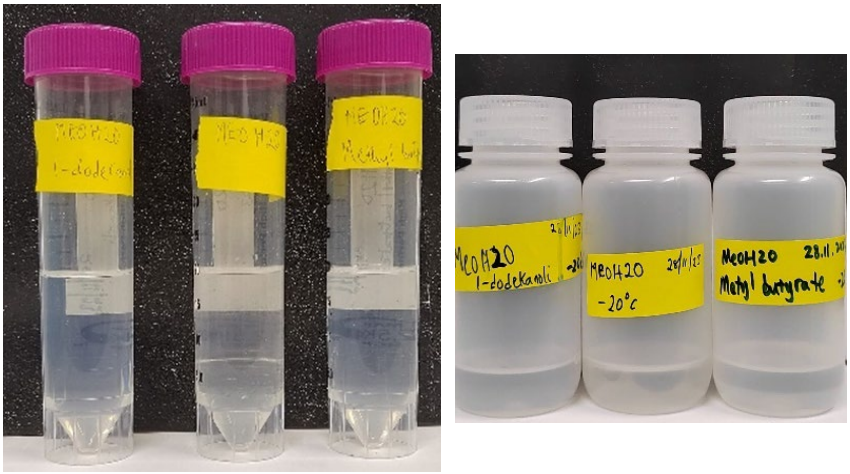
Table 3. Parameters of the Thermo Scientific™ Nicolet™ Summit™ X Spectrometer [1].

Parameter	Specification
Detector type	Thermoelectrically cooled DTGS for maximum detector response linearity
Source type	Standard: single-point source with a non-migrating hotspot for unmatched data reproducibility
Spectral range	8000–350 cm^{-1} optimized, mid-infrared KBr beamsplitter
Spectral resolution	Better than 0.45 cm^{-1}
Analysis software	OMNIC Paradigm Software Version v2.5

[1] Data from ThermoFisher Scientific (2023) [28].

3. Results

Samples were investigated exactly six weeks after preparation. Figure 4a,b shows pictures of the samples at +20 °C and −20 °C, respectively. The sample's visible physical properties are presented in Table 4.



(**a**) (**b**)

Figure 4. (**a**) Fuel blend samples stored at room temperature for six weeks; (**b**) Fuel blend samples stored at −20 °C for six weeks. Samples are placed in the order of MEOH20/1–dodecanol, MEOH20, and MEOH20/methyl butyrate.

Table 4. Visible physical effects of additives on MEOH20 at room and cold temperatures at six weeks storage period.

Samples	+20 °C	−20 °C
MEOH20	Formed separate liquid layer (baseline sample), No temperature effect	Did not solidify No temperature effect, formed separate layer still
MEOH20 + 1–dodecanol	Formed a stable, single-phase fuel mixture. Slightly soapy after mix (presence of a surfactant)	Solidified at this temperature but went to a molten state within five minutes at room temperature. Formed a stable, single-phase liquid fuel mixture after being left standing at room temperature
MEOH20 + methyl butyrate	Formed a stable, single-phase liquid fuel mixture	Did not solidify Formed separate liquid layer Formed a single-phase liquid fuel after an additional three days of storage at room temperature

3.1. Effect of Stabilizing Agent on FTIR Spectra

The FTIR spectra of MEOH20 after six weeks of storage at +20 °C and −20 °C are presented and compared in Figure 5. It can be observed that the characteristic wavenumber of the molecules existent in the sample did not change with temperature. However, the number of molecules with particular energy levels changed with respect to temperature and hence reflected in the relative absorption intensity. As presented in the graph, wavenumbers representing the functional group signify obtainable products that may be generated from the reaction between HVO and methanol. From Figure 5, functional groups found in the samples are the alkyl ether functional group, more methylene than methyl bending in the alkane functional group (a ratio of 2:1), a strong alkyl stretching, and a weak hydroxyl stretching, which could be from water formation. Ethers containing more than three carbon atoms are insoluble in water, with a decrease in solubility as the number of carbon increases [29]. The governing chemical reaction presented in (Equation (1)) explains the insolubility of the MEOH/HVO fuel blend.

$$3CH_3OH + CH_3(CH_2)_nCH_3 = CH_3O(CH_2)_{4+n}CH_3 + 2H_2O + H_2$$
$$\text{(Methanol)} + \text{(HVO)} = \text{(AlkylEther)} + \text{(Water)} + \text{(Hydrogen)} \quad (1)$$

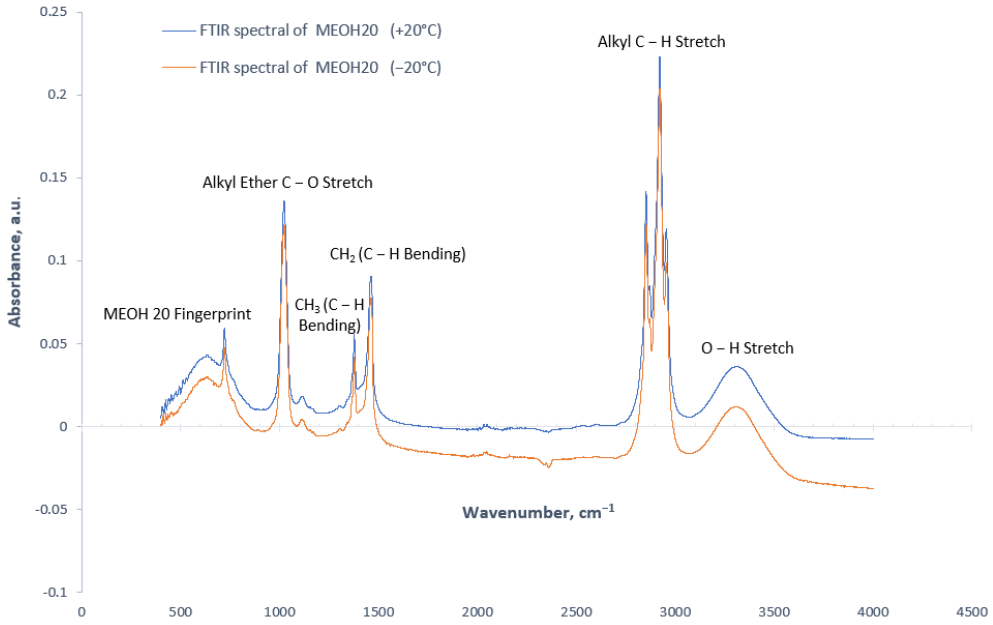


Figure 5. FTIR spectra of MEOH20.

Spectral analysis is performed according to the infrared spectroscopy absorption table labelled as Table 5 (an extract) [30]. With the addition of a 1–dodecanol as a co-solvent for stabilizing the miscibility of MEOH20, there was relatively not much changes in the FTIR spectra absorbance nor wavelength with respect to the spectra of MEOH20 at the same temperature of +20 °C as seen in Figure 6, despite the visible miscibility of the additive containing MEOH20 sample. However, there was a slight increase in the absorbance intensity of the alkyl ether C–O stretch and the alkyl C–H stretch. This was indicative of a lower number of carbon atoms in the molecule since the stretching frequency of the C–O bond and C–H bond is inversely proportional to the mass of surrounding carbon atoms in the molecule [31]. Additionally, there was a relatively slight decrease in the O–H stretching, which is more intensified in water than in alcohol. The reaction of the fuel blend with dodecanol may result in an ether with another alcohol. Hence, as presented in Figure 6, there is still a presence of an ether functional group but with better solubility due to the

presence of a new alcohol (not water) in the product. (Equation (2)) presents the predicted governing chemical reaction equation.

$$CH_3OH + CH_3(CH_2)_nCH_3 + C_{12}H_{25}OH = CH_3O(CH_2)_{4+n}CH_3 + C_{10}H_{21}OH + H_2$$
$$\text{(Methanol) + (HVO) + (Dodecanol) = (AlkylEther) + (Decanol) + (Hydrogen)} \quad (2)$$

Table 5. Infrared spectroscopy absorption table [30].

Wavenumber (cm^{-1})	Absorbance Signal Type	Molecule	Vibration Type	Functional Group
3500−3200	medium/broad	O−H	stretching	alcohol/phenol
3000−2840	medium/sharp	C−H	stretching	alkane
1750−1735	strong/sharp	C=O	stretching	ester
1465	medium	C−H	bending	methylene (alkane)
1450−1375	medium	C−H	bending	methyl (alkane)
1275−1200, 1075−1020	strong	C−O	stretching	alkyl ether
1210−1163	strong	C−O	stretching	ester
<1300	weak	–	–	Sample fingerprints

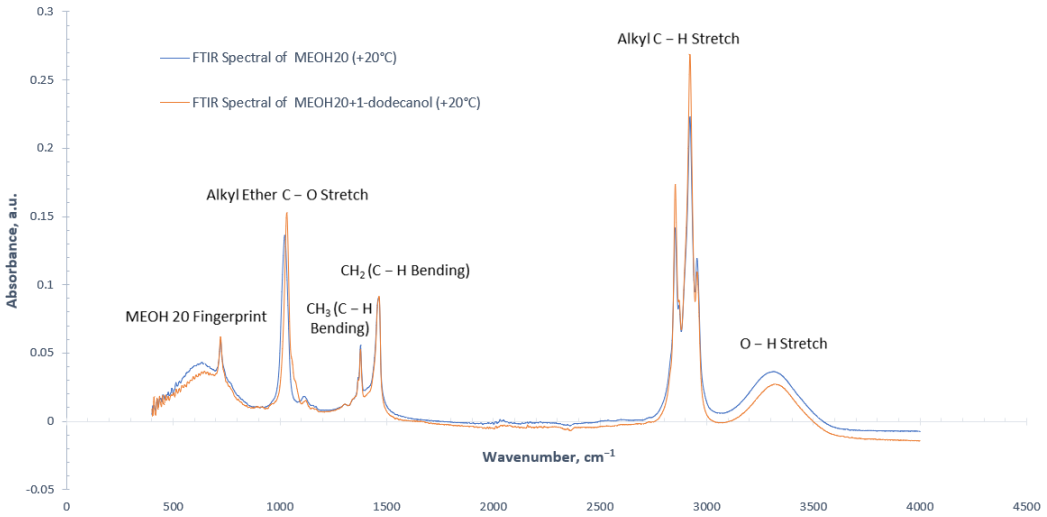


Figure 6. FTIR spectra of MEOH20 versus MEOH20/1–dodecanol stored at +20 °C.

From Figure 7, there was a significant difference in the FTIR spectra of the MEOH20 sample and the methyl butyrate−containing MEOH20 sample, both collected from storage of +20 °C after six weeks. From the co-solvent−containing fuel sample, it was obvious that there was a formation of new chemical bonds as reflected by the spectra. Functional groups identified include ester C–O and C=O stretching and a relatively higher carbon alkyl C–H stretching compared to that in the MEOH20. There was an absence of the strong ether C–O stretch and the weak alcohol O–H stretch. Hence, (Equation (3)) presents a predicted chemical equation.

$$2CH_3OH + CH_3(CH_2)_nCH_3 + C_5H_{10}O_2 = 2CH_3COO(CH_2)_{2+n}CH_3 + 6H_2$$
$$\text{(Methanol) + (HVO) + (methyl butyrate) = (Ester) + (Hydrogen)} \quad (3)$$

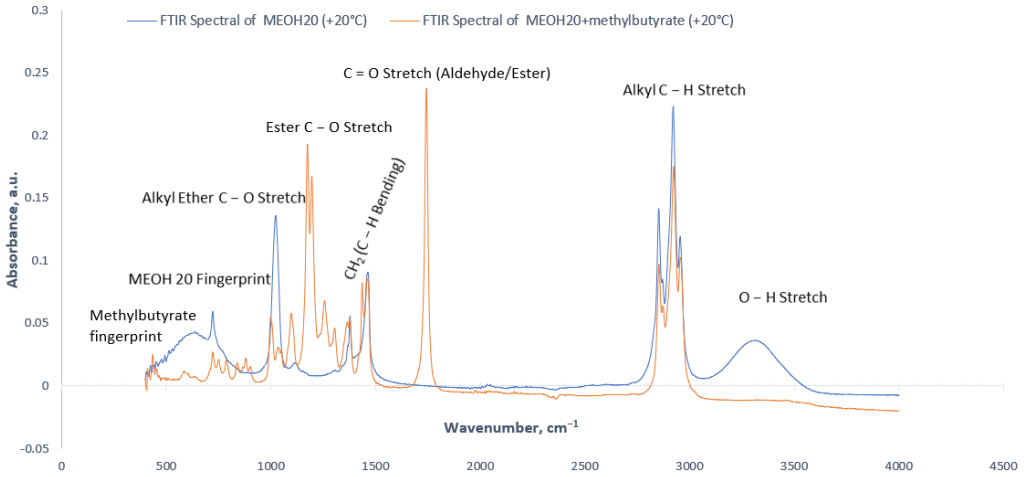


Figure 7. FTIR spectra of MEOH20 versus MEOH20/methyl butyrate stored at +20 °C.

3.2. Effect of Temperature on FTIR Spectra

A comparison of FTIR spectra of MEOH20/1–dodecanol samples, collected after six weeks from storage of +20 °C and −20 °C, was conducted. Figure 8 shows relatively significant changes in the spectra intensities of both samples. For the cold storage MEOH20/1–dodecanol sample, there was an increase in the intensity of the alkyl ether C–O stretch (at an approximate ratio of 1.5:1), indicative of a lower number of carbon atoms around the alkyl ether bond. Simultaneously, there was a noticeable decrease in the alkyl C–H stretch. Likewise, the methyl and methylene group bending in the alkane was reduced, resulting from a higher amount of carbon atoms around the functional group. Overall, Figure 8 presents that the MEOH20/1–dodecanol sample stored at −20 °C temperature had a lower carbon alkyl ether and a higher carbon alcohol than its counterpart stored at +20 °C. Hence, the sample solidified by recovery from cold storage, which is similar to the original physical state of 1–dodecanol, which was melted before use as a co−solvent. The governing chemical reaction presented in (Equation (4)) explains the temperature effect.

$$CH_3OH + CH_3(CH_2)_nCH_3 + C_{12}H_{25}OH = CH_3O(CH_2)_{2+n}CH_3 + C_{12}H_{25}OH + H_2$$
$$\text{(Methanol)} + \text{(HVO)} + \text{(dodecanol)} = \text{(AlkylEther)} + \text{(dodecanol)} + \text{(Hydrogen)} \quad (4)$$

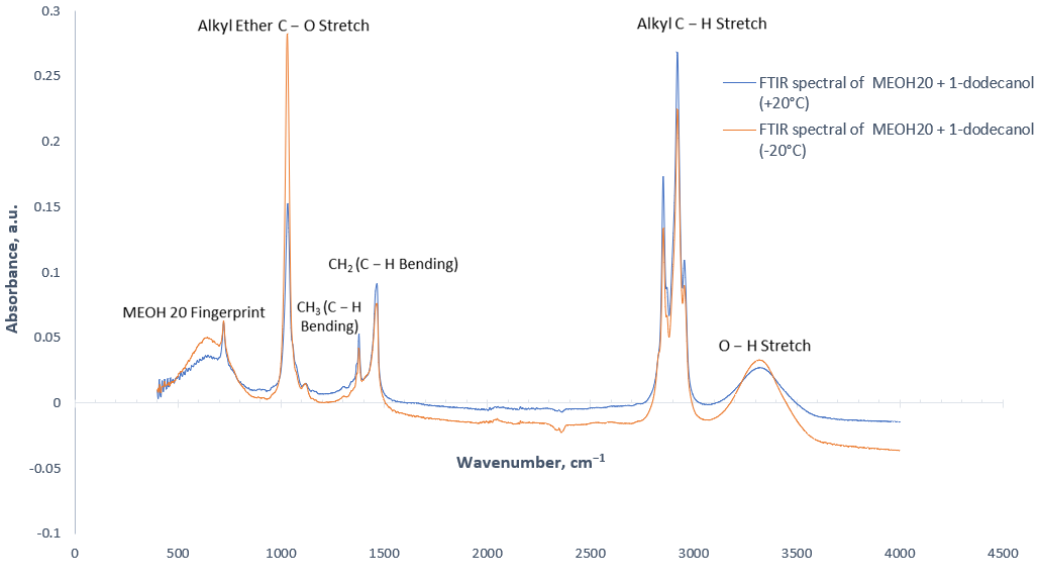


Figure 8. FTIR spectra of MEOH20/1–dodecanol.

A significant change observed in the physical state of the MEOH20/methyl butyrate sample after recovery from −20 °C storage was a separation of the fuel blend into two immiscible layers, as can be seen in Figure 4b, although the fuel blend was soluble in methyl butyrate at +20 °C storage. From Figure 9, the absorbance intensity of the product ester C–O, C=O, and C–H stretch were relatively lower for the cold temperature-stored sample than that of the room temperature-stored sample, indicative of the formation of a relatively higher carbon ester. Esters are polar molecules that can engage in hydrogen bonding, and hence, at cold temperatures, there is a formation of higher carbon esters, which are invariably denser and less soluble in comparison with lower carbon esters [32]. Nevertheless, the sample, which formed separated layers after cold storage, became miscible again and formed a homogenous fuel blend after an additional three days of further storage at room temperature.

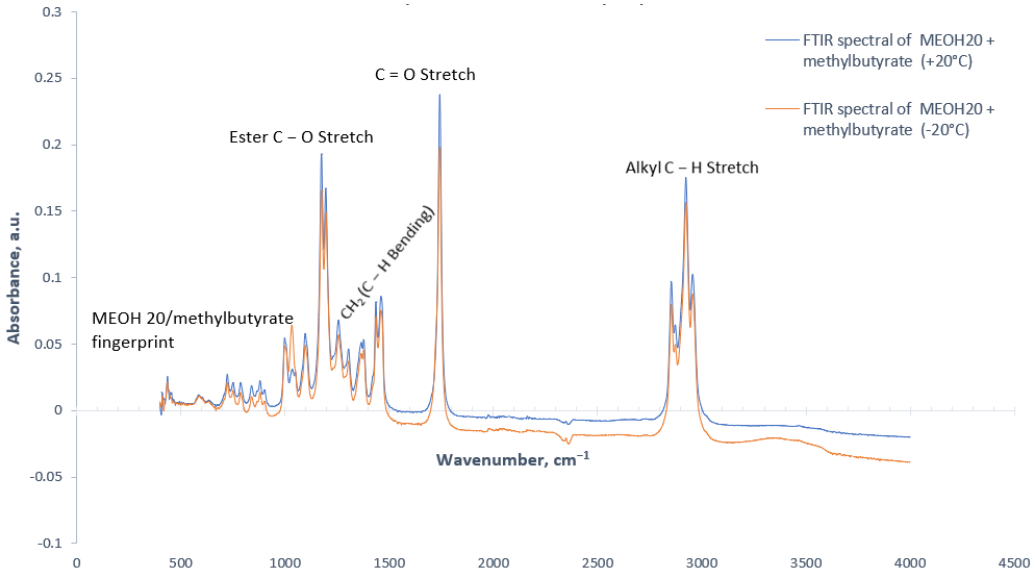


Figure 9. FTIR spectra of MEOH20/methylbutyrate.

Following precedence in the discussion of results, blending MEOH20 with 1−dodecanol resulted in stable homogenous alkyl ether fuels, while the MEOH20 blend with methyl butyrate resulted in ester fuels. Ether fuels, depending on the number of carbons, may have potential major use as fuel surrogates (e.g., dimethyl ether as a substitute for propane in liquified petroleum gas) or even as fuel blend components to enable cleaner burning in SI engines [33]. In comparison, ethers have higher oxygen content than ester and, consequently, a lower heating value. Hence, ethers are more appropriate for small−sized agricultural SI engines such as light logging machines, lawnmowers, and garden tractors. Esters are commonly used as fuel surrogates, especially in CI engines [34]. They may also find potential applications in small-sized non-road CI engines such as farm tractors, heavy forklifts, excavators, and so on.

The storage of the fuel blends at both cold and room temperature for six weeks was performed to carry out a fuel stability test. The blend samples stored at room temperature maintained their visible physical properties over the period of six weeks. Samples stored at cold temperatures had obvious changes in their physical appearances. The blend sample containing MEOH20 and 1−dodecanol solidified at cold temperature but melted in approximately five minutes of standing at room temperature. The second fuel sample containing MEOH20 and methyl butyrate formed separate layers of fuels at cold temperatures. Since both fuel blend samples formed different fuel types, they both have applicability in different ICE types. Hence, the shelf life at room temperature of both fuel blend samples may exceed six weeks; however, additives may be needed to improve the fuel blend's stability at cold temperatures.

4. Discussion

As presented in the research background, the research gap highlights that new fuels substituting fossil diesel in NRMM are necessary for climate neutrality, tightened emissions legislations, and also energy security. This study aimed to investigate the feasibility of FTIR analytics for determining the stability of methanol-HVO fuel blends. The stability referred to here is the storage stability. Majorly, the factors governing storage stability include storage conditions (temperature, humidity, and exposure to light), type of storage container (material, seal integrity, and the presence of stabilizers and biocides. In this study, we investigated the storage stability of the fuel blend based on storage condition (temperature) and the effect of stabilizers for a period of 6−week storage time using FTIR analytics. The innovative nature of the research lies in several key aspects. First is the exploration of the potential use of second-generation biofuels (methanol-HVO) blends as an alternative to fossil fuels in agricultural engine use. This represents an innovative approach to addressing the need for sustainable and climate-friendly fuel sources for ICEs. Second is the addition of co-solvents; as these fuels have different properties and the almost inert nature of alkanes (HVO), the fuel blend does not mix properly to form a single-phase homogenous fuel. This research investigated the impacts of co-solvents in stabilizing the biofuel blends, thereby addressing the practical application of the fuel blends. Third is the use of FTIR spectroscopy as an analytical tool to identify the resulting fuel blend chemical compositions, thereby offering a novel method for evaluating their suitability for off-road engine use. Overall, the combination of the specific fuel blend (methanol-HVO), the inclusion of the respective co-solvent (as additives/stabilizers), the storage temperature study (both extreme cold and ambient temperature), and the emphasis on off-road engine use collectively distinguishes this study from similar research in the field of alternative fuels and biofuel stability. The concentration of the fuel blend is arrived at by using the energy ratio of methanol to HVO as 20:80. Since pure HVO has been used as a drop-in fuel in State-of-the-Art off-road diesel engines, this study focused on the blend of only 20% methanol to HVO as without co-solvents the fuel blend is immiscible. This means that the higher the blending ratio of methanol to HVO, the higher the amount of co-solvents required to stabilise the fuel blend. Therefore, from an economic point of view, a blending ratio higher than 20% may not be viable. Fuel homogeneity is important for complete combustion, and as such, the amount of co-solvents required to homogenize the fuel blend was used. The basis for selecting +20 °C and −20 °C for conditioning the test samples in the FTIR analytics study was to capture the phase behaviour and stability of methanol-HVO blends mixtures under both extreme cold and ambient storage conditions. This approach allows for the simulation of extreme cold storage conditions while the ambient temperature serves as a baseline for comparison. This approach gives an understanding of the fuel blend stability, ensuring its reliability and performance across a range of real−world scenarios. This study focused on qualitative and analytical assessments using FTIR as a tool to identify chemical compositions and intermolecular interactions rather than statistical analyses. The scope of the research informed the choice of analytical methods over statistical evaluations. Following this premise, general conclusions regarding the feasibility of FTIR spectroscopy for assessing the storage stability of MEOH/HVO blends are presented in two parts. The study draws the following conclusions regarding the effect of storage temperature on FTIR Spectra:

- MEOH/HVO blends with stabilizing agents form stable homogenous fuel blends at room temperature for at least 6 weeks of shelf−life.
- MEOH/HVO blend with 1−dodecanol solidifies at cold temperature but melted in approximately five minutes of standing at room temperature
- MEOH20 and methyl butyrate formed separate layers of fuels at cold temperatures.

Considering the effects of stabilizing agents, the study concludes:

- MEOH/HVO blend with 1−dodecanol results in stable homogenous alkyl ether fuels
- MEOH/HVO blend with methyl butyrate results in stable homogenous ester fuels.

As the study does not determine the permissible long-term storage time, it could not simulate real-world large storage (fuel tanks and storage tanks). However, the 6−week storage period for the laboratory samples (simulating portable fuel storage containers) provided initial insights into the storage stability of the fuel blends with respect to storage temperature and the effect of stabilizers. Therefore, studies taking account of long-term storage are good recommendations for future research. Chemical reactions between methanol and HVO fuels are less studied in the literature. Predicted reactions from this study can be further investigated and verified using more sophisticated reaction mechanism generators to give better insights about bond cleavages and formations, determine the exact carbon atoms formed in the resulting ethers and esters, and ultimately recognize the potentials of the fuel blends as a single homogenous fuel for non-road engine. In addition, the corrosive effects of the fuel blends on engines and the fuel combustion in engines may be further investigated for applicability in agricultural equipment and vehicles.

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References

1. Stančin, H.; Mikulčić, H.; Wang, X.; Duić, N. A Review on Alternative Fuels in Future Energy System. *Renew. Sustain. Energy Rev.* **2020**, *128*, 109927. [CrossRef]
2. Pramanik, A.; Sinha, A.; Chaubey, K.K.; Hariharan, S.; Dayal, D.; Bachheti, R.K.; Bachheti, A.; Chandel, A.K. Second−Generation Bio−Fuels: Strategies for Employing Degraded Land for Climate Change Mitigation Meeting United Nation−Sustainable Development Goals. *Sustainability* **2023**, *15*, 7578. [CrossRef]
3. Karwacka, M.; Ciurzyńska, A.; Lenart, A.; Janowicz, M. Sustainable Development in the Agri−Food Sector in Terms of the Carbon Footprint: A Review. *Sustainability* **2020**, *12*, 6463. [CrossRef]
4. EPA Emission Standards for Nonroad Engines and Vehicles. US EPA. Available online: https://www.epa.gov/emission-standards-reference-guide/epa-emission-standards-nonroad-engines-and-vehicles (accessed on 25 May 2024).
5. De Poures, M.V.; Sathiyagnanam, A.P.; Rana, D.; Babu, R.K.; Subramani, S.; Sethuramasamyraja, B.; Damodharan, D. Using Renewable N−Octanol in a Non−Road Diesel Engine with Some Modifications. *Energy Sources A* **2018**, *41*, 1194–1208. [CrossRef]
6. Heidari−Maleni, A.; Gundoshmian, T.M.; Karimi, B.; Jahanbakhshi, A.; Ghobadian, B. A Novel Fuel Based on Biocompatible Nanoparticles and Ethanol−Biodiesel Blends to Improve Diesel Engines Performance and Reduce Exhaust Emissions. *Fuel* **2020**, *276*, 118079. [CrossRef]
7. Hunicz, J.; Mikulski, M.; Shukla, P.C.; Gęca, M.S. Partially Premixed Combustion of Hydrotreated Vegetable Oil in a Diesel Engine: Sensitivity to Boost and Exhaust Gas Recirculation. *Fuel* **2022**, *307*, 121910. [CrossRef]
8. Fact Sheets & Guidelines. Home. Available online: https://www.etipbioenergy.eu/fact-sheets (accessed on 25 May 2024).
9. *EN590:2009*; Automotive Fuel-Diesel-Requirements and Test Methods. 2009. Available online: https://standards.iteh.ai/catalog/standards/cen/c3d8c75c-ea89-4b8a-afc3-0fb533afbc14/en-590-2009 (accessed on 10 November 2023).
10. Holzer, A.; Günthner, M.; Jung, P. Performance of Pure OME and Various HVO–OME Fuel Blends as Alternative Fuels for a Diesel Engine. *Automot. Engine Technol.* **2022**, *7*, 369–383. [CrossRef]
11. *EN228:2012+A1:2017*; Automotive Fuels—Unleaded Petrol—Requirements and Test Methods. 2017. Available online: https://standards.iteh.ai/catalog/standards/cen/81cde377-aac3-4a49-9bde-bb71e02c4585/en-228-2012a1-2017 (accessed on 10 November 2023).
12. Nashte, A.; J, S.P.S.; Rathod, D. Investigations of Emission Reduction Potential of Diesel−Methanol Blends in a Heavy−Duty Genset Engine. In *Symposium on International Automotive Technology*; SAE International: Warrendale, PA, USA, 2021. [CrossRef]
13. Domínguez, V.M.; Hernández, J.J.; Ramos, Á.; Giménez, B.; Rodríguez-Fernández, J. Exploring the Effect of Methanol and Ethanol on the Overall Performance and Substitution Window of a Dual-Fuel Compression-Ignition Engine Fueled with HVO. *Fuel* **2024**, *359*, 130529. [CrossRef]
14. Wang-Alho, H.; Sirviö, K.; Hissa, M.; Mikulski, M.; Niemi, S. Methanol-HVO Blends for Efficient Low-Temperature Combustion: Analytical Research on Fuel Properties. *Agron. Res.* **2023**, *21*, 994–1004. [CrossRef]

15. U.S. Environmental Protection Agency. US EPA. 2015. Available online: https://www.epa.gov/sites/default/files/2015-07/documents/emission-factors_2014.pdf (accessed on 25 May 2024).
16. ICNIRP. Infrared (780 Nm-1mm). ICNIRP. 2023. Available online: https://www.icnirp.org/en/frequencies/infrared/infrared.html (accessed on 25 May 2024).
17. NIR Spectroscopic Method vs. FTIR/FT-NIR | Allied Scientific Pro. Allied Scientific Pro | Global Leader in Photonics Solutions. 2023. Available online: https://www.alliedscientificpro.com/blog/welcome-to-our-blogs-1/comparing-the-nir-spectroscopic-method-withftir-ft-nir-132 (accessed on 25 May 2024).
18. Guide to FT-IR Spectroscopy. High-Value Life Science and Material Research and Diagnostics Solutions. Bruker. 2023. Available online: https://www.bruker.com/en/products-and-solutions/infrared-and-raman/ft-ir-routine-spectrometer/what-is-ft-ir-spectroscopy.html (accessed on 25 May 2024).
19. Standard Test Method for Determination of Biodiesel (Fatty Acid Methyl Esters) Content in Diesel Fuel Oil Using Mid Infrared Spectroscopy (FTIR-ATR-PLS Method). ASTM International—Standards Worldwide. 2023. Available online: https://www.astm.org/standards/d7371 (accessed on 25 May 2024).
20. Faraguna, F.; Racar, M.; Jukić, A. Test Method for Determination of Different Biodiesels (Fatty Acid Alkyl Esters) Content in Diesel Fuel Using FTIR-ATR. *Renew. Energy* **2019**, *133*, 1231–1235. [CrossRef]
21. Gomes, T.; Ramos, R.; Garcia, F.; Sousa, D. Atr-Ftir and Uv-Vis as Techniques for Methanol Analysis in Biodiesel-Washing Wastewater. *Quim. Nova* **2023**, *46*, 698–705. [CrossRef]
22. Xia, Q.; Yuan, L.-M.; Chen, X.; Meng, L.; Huang, G. Analysis of Methanol Gasoline by ATR-FT-IR Spectroscopy. *Appl. Sci.* **2019**, *9*, 5336. [CrossRef]
23. Liu, S.; Wang, S.; Hu, C.; Bi, W. Determination of Alcohols-Diesel Oil by Near Infrared Spectroscopy Based on Gramian Angular Field Image Coding and Deep Learning. *Fuel* **2022**, *309*, 122121. [CrossRef]
24. Czechlowski, M.; Marcinkowski, D.; Golimowska, R.; Berger, W.A.; Golimowski, W. Spectroscopy Approach to Methanol Detection in Waste Fat Methyl Esters. *Spectrochim. Acta Part A* **2019**, *210*, 14–20. [CrossRef] [PubMed]
25. Fořt, J.; Trník, A.; Pavlíková, M.; Pavlík, Z.; Černý, R. Fabrication of Dodecanol/Diatomite Shape-Stabilized PCM and Its Utilization in Interior Plaster. *Int. J. Thermophys.* **2018**, *39*, 137. [CrossRef]
26. Cunliffe, S.; Martin, P.; Baker, M.; Mihailova, O.; Martin, P. Near Infrared Absorption Spectroscopy for the Quantification of Unsulfated Alcohol in Sodium Lauryl Ether Sulfate. *J. Near Infrared Spectrosc.* **2020**, *29*, 11–23. [CrossRef]
27. Beć, K.B.; Grabska, J.; Ozaki, Y.; Czarnecki, M.A.; Huck, C.W. Simulated NIR Spectra as Sensitive Markers of the Structure and Interactions in Nucleobases. *Sci. Rep.* **2019**, *9*, 17398. [CrossRef] [PubMed]
28. Nicolet™ Summit™ FTIR Spectrometer. Access Denied. 2023. Available online: https://www.thermofisher.com/order/catalog/product/912A0972 (accessed on 25 May 2024).
29. Ensing, B.; Tiwari, A.; Tros, M.; Hunger, J.; Domingos, S.R.; Pérez, C.; Smits, G.; Bonn, M.; Bonn, D.; Woutersen, S. On the Origin of the Extremely Different Solubilities of Polyethers in Water. *Nat. Commun.* **2019**, *10*, 2893. [CrossRef] [PubMed]
30. Libretexts. Infrared Spectroscopy Absorption Table. Chemistry LibreTexts, 30 November 2014. Available online: https://chem.libretexts.org/Ancillary_Materials/Reference/Reference_Tables/Spectroscopic_Reference_Tables/Infrared_Spectroscopy_Absorption_Table (accessed on 25 May 2024).
31. Libretexts. 11.5: Infrared Spectra of Some Common Functional Groups. Chemistry LibreTexts, 9 February 2016. Available online: https://chem.libretexts.org/Bookshelves/Organic_Chemistry/Map:_Organic_Chemistry_(Wade)_Complete_and_Semesters_I_and_II/Map:_Organic_Chemistry_(Wade)/11:_Infrared_Spectroscopy_and_Mass_Spectrometry/11.05:_Infrared_Spectra_of_Some_Common_Functional_Groups (accessed on 25 May 2024).
32. Libretexts. Properties of Esters. Chemistry LibreTexts, 3 October 2013. Available online: https://chem.libretexts.org/Bookshelves/Organic_Chemistry/Supplemental_Modules_(Organic_Chemistry)/Esters/Properties_of_Esters (accessed on 25 May 2024).
33. Semelsberger, T.A.; Borup, R.L.; Greene, H.L. Dimethyl Ether (DME) as an Alternative Fuel. *J. Power Sources* **2006**, *156*, 497–511. [CrossRef]
34. Oppong, F.; Xu, C.; Li, X.; Luo, Z. Esters as a Potential Renewable Fuel: A Review of the Combustion Characteristics. *Fuel Process. Technol.* **2022**, *229*, 107185. [CrossRef]

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