



Article

The Initial Boiling Point of Lubricating Oil as an Indicator for the Assessment of the Possible Contamination of Lubricating Oil with Diesel Oil

Leszek Chybowski

Department of Machine Construction and Materials, Faculty of Marine Engineering, Maritime University of Szczecin, ul. Willowa 2, 71-650 Szczecin, Poland; l.chybowski@pm.szczecin.pl; Tel.: +48-91-48-09-412

Abstract: This article provides a brief introduction to the indicators of the volatility and flammability of lubricating oils and fuels. It is proposed that the initial boiling point be used as an indicator of the contamination of lubricating oil with distillate fuel (i.e., diesel biofuel oil) in the context of the rapid detection of explosion risks in the crankcase. Detailed tests were carried out on lubricating oil samples (SAE 30 and SAE 40 grades, which are most commonly used in the lubrication systems of marine trunk engines) diluted with diesel oil at selected mass concentrations (0, 1, 2, 5, 10, 20, 50, and 100%). The oils were tested to determine their relevant properties: the flash point temperature and the initial boiling temperature. The flash point was determined in a closed crucible using the Pensky–Martens method, which is in accordance with PN-EN ISO 2719. The differences between the initial boiling point and the flash point of the tested lubricating oils were determined for different dilution levels of lubricating oil in diesel fuel. An approximate method for the calculation of the flash point of the oil based on the initial boiling point is proposed. The results of oil flash point measurements are compared with values calculated as a function of the boiling point for both lubricating oils tested. An evaluation of how well models fit the experimental results is reported. Conclusions are presented on the applicability of the proposed method during operational practice.

Keywords: trunk piston marine engine; crankcase explosion; marine diesel engine; crankcase oil dilution; diesel oil; flash point temperature; initial boiling temperature

Boiling Point of Lubricating Oil as an Indicator for the Assessment of the Possible Contamination of Lubricating Oil with Diesel Oil. *Energies* **2022**, *15*, 7927. https://doi.org/10.3390/en15217927

Citation: Chybowski, L. The Initial

Academic Editor: Mohammad Yunus Khan Tatagar

Received: 22 September 2022 Accepted: 23 October 2022 Published: 25 October 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the author. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

1. Introduction

One of the hazards that can lead to possible explosions during the operation of marine trunk engines is the ingress of unburned fuel into the crankcase [1]. This occurs when the piston rings, the piston, and the sleeve are excessively worn or damaged and/or when the fuel injection system is not functioning properly [2]. Fuel has a lower flash point than lubricating oil (minimum 60 °C), and its presence could theoretically contribute to a crankcase explosion (CCE) that would not have occurred otherwise. Some authors have pointed out that fuel in oil is among the factors increasing the risk of a crankcase explosion [3–5]. For safety, the circulating oil is subjected to periodic laboratory measurements of its viscosity and flash point [5]. In practice, a 2–5% fuel dilution is considered excessive and calls for immediate maintenance [6]. This does not mean, however, that higher concentrations of diesel oil in lubricating oil are not encountered under operating conditions. In this article, to present a new method for determining lube oil contamination with distillate fuel, measurements for a full range of concentrations (0–100%) were carried out, which enables a complete picture regarding the possibility of mapping the change in the flash point and boiling point of lube oil to different degrees of lube oil contamination with distillate fuel. The causes of lubricating oil contamination with fuel and recommended corrective actions are shown in Table 1.

Energies **2022**, 15, 7927 2 of 15

Table 1. Fuel inflow caused by mechanical effects (based on [7]).

Action	Effect	What to Do		
Continued operation with stops and starts.	The fuel does not burn off completely.	Reduce the mileage change interval to the strictest change interval indicated by the manufacturer.		
Starting in the cold.	The fuel does not burn off well because the combustion temperature is low.	Wait for the engine to increase in temperature before accelerating.		
Problems in the injection system.	The droplets of fuel being injected into the chamber are big, leading to poor combustion.	Incomplete combustion is occurring; inspect the injectors.		
Poor combustion.	The fuel does not burn off completely.	Incomplete combustion is occurring. Check that the combustion chamber and the injection system are working properly.		
Worn-out engine parts: valve guides, injectors, and wear.	Conditions change in the combustion chamber, meaning it is no longer optimized.	Inchect the engine and in		
Excessive acceleration.	Excess inflow of fuel.	Incomplete combustion is occurring; adjust the control system.		
Mixture of rich fuels.	Excess fuel.	Incomplete combustion is occurring; inspect the injection system.		
Faulty injectors.	Can produce excessive inflow of fuel or inadequate fuel injection.	It does not burn fuel as well, resulting in deposits. Inspect the injection system.		

There are several methods to detect the presence of fuel in engine lubricating oil. The most important of these are summarized in Table 2. In operational practice, the lubricating oil circulating in marine engines is periodically checked for changes in its viscosity and flash point [8].

Table 2. Advantages and disadvantages of the main methods for detecting fuel in lubricating oil (prepared on the basis of Ref. [8]).

Method	Advantages	Disadvantages		
		Can only be carried out in a		
	Widely accepted industry	lab.		
	standard.	Requires costly equipment and		
Gas Chromatography	Highly precise.	gases.		
	Suited for high-volume labs.	Takes significant time to		
	Can detect biodiesel and etha-	achieve the best results.		
	nol.	Requires expensive equipment		
		and gases.		
Vicaccity Analysis	Availability of portable instru-	Inability to definitively indicate		
Viscosity Analysis	ments and lab instruments.	a fuel dilution issue.		

Energies **2022**, 15, 7927 3 of 15

	Accepted routine test for testing the lubricant condition. Optimal screening test for probable fuel dilution. Ability to detect ethanol and biodiesel.	
Flash Point Testing	A pass/fail result is sufficient in the case of most applications. Ability to detect ethanol. Very little sample required (i.e., 1–2 mL).	Requires knowledge of the oil/fuel type mandatory for
FTIR Spectroscopy	Low cost per sample after initial equipment purchase. Test can be carried out quickly.	Mandates the use of costly equipment. Calibrations are mostly specific to a narrow sample type.
Surface Acoustic Wave Sensing	Easy to use. Portable. Requires only 0.5 mL of a sample. Less expensive than gas chromatographs. Can complete the test quickly. Easily adaptable to different oil/fuel types.	Inability to measure biodiesel. Mandates calibration with a reference fluid.

Among the methods for the analysis of fuel dilution in lubricants is Gas Chromatography (GC) [9] based on ASTM methods D3524, D3525, and D7593 [8]. Such an approach can be aided by quantitation, which is achieved via the integration of the area under fuel peaks measured with a Flame Ionization Detector (FID) [10]. Fourier-Transform Infrared (FTIR) Spectroscopy [11] can also be used to detect fuel oil contamination, which enables the user-friendly and fast measurement of fuel dilution. However, this method does not accurately distinguish the base material from which specific hydrocarbons are derived. Another detection method is the Spectro Q6000 Fuel Dilution Meter (FDM), which includes a Surface Acoustic Wave (SAW) sensor [12] that responds particularly to the presence of fuel vapor [8].

The oil viscosity (the change in the viscosity of used oil relative to fresh oil) can be quickly determined under shipboard conditions with the use of portable test kits. In parallel, the lubricating oil samples are periodically sent to a laboratory, where the viscosity of the oil and other oil characteristics are determined. However, the change in the viscosity of the oil circulating within the engine is influenced by factors such as the aging of the oil, the gradual depletion of the supply of oil-improving additives, and the types of contaminants that enter the oil. Contaminants can include diesel oil (DO), heavy fuel oil (HFO), water, and combustion products [13,14]. Thus, depending on the operating conditions of the oil and the nature of the impurities, the viscosity of the oil may decrease or increase.

The flash point of a material is the lowest liquid temperature at which, under certain standardized conditions, a liquid emits vapors in such quantity that it can form an ignitable vapor–air mixture (standard EN IEC 60079-10-1). The flash point is an important parameter for classifying flammable liquids and is the lowest temperature of an analytical sample, corrected for an atmospheric pressure of 101.3 kPa, at which the application of an

Energies **2022**, 15, 7927 4 of 15

ignition source will momentarily ignite the vapors above the surface of the liquid under test [15]. There are several methods for determining the flash point.

The selection of a method for determining the flash point is dependent on several factors. First, the method of choice is imposed by the product specifications. In addition, the manner in which the method is selected may be determined by legislation. If regulations or specifications enable a choice of procedures among several, then it is advisable to use the most accessible method. There are two classes of flash point test methods [16]: closed-crucible ones, which require the use of a Pensky–Martens device [17], the Abel procedure [18], or the Tag method [19,20], or open-crucible ones that employ a Tagliabue device [21] or the Cleveland method [22]. The test method is selected depending on the type of substance to be tested and its physicochemical properties. For example, highly volatile substances, such as some alcohols or some hydrocarbons, can be tested using both the Abel method and the equilibrium method [23], but not the Pensky–Martens and Cleveland methods. On the other hand, petroleum substances such as diesel, fuel oil, or gasoline should be tested by non-equilibrium methods, such as the Penksy-Martens, Abel, or Cleveland methods [15].

There are diverging views in the literature about how the flash point of the oil affects the risk of ignition of oil vapors [24–26]. However, there is no doubt that the flash point is an indicator of the contamination of the lubricating oil with fuel, since the flash point of the oil is lowered by such contamination [27]. The flash point of oil under ship conditions is not commonly determined, and the results are obtained by the appropriate testing of oil samples sent to a specialized laboratory [5]. This has led the author to develop an alternative method for indirectly determining the change in the flash point based on another oil characteristic that can be determined under ship conditions, namely, the initial boiling point of the oil. Attempts have been made to use and evaluate this indicator for spark ignition engines [28,29]. With the exception of small vessels, spark ignition engines are not commonly used as marine engines on ocean-going vessels.

The initial boiling point is one of the characteristics of oils and fuels that relates to their volatility and, thus, indirectly to their tendency to be ignited by an external heat source. The volatility of an oil or fuel depends on its chemical composition. There are many indicators for assessing the volatility and the autoignition properties of a fuel, which are determined from the results of the fuel distillation. For example, from the percent by volume of fuel that vaporizes at 70 °C, a vapor lock index (VLI) is determined for petrol, which is also known as the flexible volatility index (FVI) [30]. This can be expressed by:

$$VLI = FVI = 10 \cdot VP + 7 \cdot E70, \tag{1}$$

where VP is the petrol vapor pressure determined using the Reid method (kPa), and E70 is the amount of petrol that distills up to 70 °C (% v/v).

There are a number of standards and indices that describe the volatility of fuels [31], which include those based on the recovery temperatures of a specific quantity of fuel during its distillation, e.g., 10, 50, and 90% v/v fuel. The volatility index can be determined from the following formula [32]:

$$VI = \frac{t_{10} + t_{50} + t_{90}}{100},\tag{2}$$

where t_{10} , t_{50} , and t_{90} (in units of °C) are the 10, 50, and 90% recovery temperatures, respectively.

The autoignition temperature or the kindling point of a substance is the lowest temperature at which it will spontaneously ignite in a normal atmosphere without an external source of ignition, such as a flame or a spark. An important indicator that describes the autoignitability of a substance is the autoignition delay, which, in the case of compression-ignition engine fuels, is defined as the time elapsing between the moment that the fuel is injected into the engine combustion chamber and the point when the fuel–air mixture ignites [33].

Energies **2022**, 15, 7927 5 of 15

As indicated by Formula (2), the temperatures t_{10} , t_{50} , and t_{90} of the recovery of a specific amount of fuel during the distillation are also used to calculate the empirical indicators of the fuel autoignition delay (which is an alternative to a measured parameter, the cetane number (CN)). One such indicator is the calculated cetane index (CCI), which is interpreted in the same way as the cetane number (the cetane rating) [34]. The CCI can be determined using an equation with two or four variables described in the respective standards. According to ASTM D976, the CCI value is [34]:

 $CCI = 454.74 - 1641.416 \cdot \rho_{15} + 774 \cdot \rho_{15}^2 - 0.554 \cdot t_{50} + 97.803 \cdot (\log t_{50})^2$ where ρ_{15} (g/cm³) is the density at 15 °C.

The CCI value based on ASTM D4737 is [34]:

$$CCI = 45.2 + 0.0892 \cdot (t_{10} - 215) + \{0.131 + 0.901 \cdot [e^{-3.5 \cdot (\rho_{15} - 0.85)} - 1]\} \cdot (t_{50} - 260) + \{0.0523 - 0.420 \cdot [e^{-3.5 \cdot (\rho_{15} - 0.85)} - 1]\} \cdot (t_{90} - 310) + 0.00049 \cdot [(t_{10} - 215)^2 - (t_{90} - 310)^2] + 107 \cdot [e^{-3.5 \cdot (\rho_{15} - 0.85)} - 1] + 60 \cdot [e^{-3.5 \cdot (\rho_{15} - 0.85)} - 1]^2.$$

$$(4)$$

The calculation of the ratios described by Formulas (3) and (4) requires distillation to determine the temperatures at which the corresponding percentage of the test substance is recovered. When analyzing lubricating oil contaminated with distillate fuel, recovery temperature values can only be determined at a very high diesel fuel content in the lubricating oil, i.e., at around 50% [35]. At a lower diesel fuel content (as occurs in practice) in the lubricating oil, recovery temperatures cannot be determined (but they are very high) due to the relatively homogeneous hydrocarbon composition of the lubricating oils and additives other than hydrocarbons. Furthermore, in practice, the derived cetane number (DCN) [36] can only be measured for pure fuels with special instruments, as these devices are not calibrated to the conditions required for the ignition of the lubricating oil. In summary, for lubricating oils potentially contaminated with diesel fuel, the quantity that can at least indirectly describe their ignition properties always remains the flash point.

As already indicated, the determination of the flash point t_{MFP} requires a suitable measuring instrument, which, in practice, does not occur under operating conditions. With the initial boiling point t_{IBP} , which is much easier to determine compared to the flash point, the latter can be approximated. The calculated flash point t_{CFP} can be described by the general formula proposed by the author:

$$t_{CFP} = t_{IBP} + \Delta t, \tag{5}$$

where Δt is a constant temperature difference that depends on the chemical composition of a substance.

If the substance tested is the lubricating oil contaminated with the diesel oil, with the latter corresponding to C (% m/m), the temperature difference Δt can be provided as a function of the contamination of the lubricating oil with diesel fuel, i.e.,

$$\Delta t = f(C). \tag{6}$$

This value can be estimated as the average difference, *K*, of the values of the flash point and the initial boiling point measured—for a specific lubricating oil and diesel fuel and for varying contents of diesel fuel in the lubricating oil—so that:

$$\Delta t \approx K = \frac{\sum_{i=1}^{n} (t_{IBP} - t_{MFP})}{n}, \tag{7}$$

where n is consecutive pairs of measurements for different diesel fuel contents in the lubricating oil in the interval $C \in [0,100]$ (% v/v).

After substituting Equation (7) into Formula (5), the approximate flash point of the oil can be determined using the measured initial boiling point with the following formula:

$$t_{CFP} \approx t_{IBP} + K. \tag{8}$$

To assess the feasibility of using the initial boiling point as an indicator to describe the contamination of the lubricating oil with diesel fuel, an experiment was conducted to determine the average value of the constant K for selected types of lubricating oils and their mixtures with diesel fuel. Subsequently, the flash point t_{CFP} calculated in this way can be compared with the flash point t_{MFP} determined in a closed crucible using the Pensky-

Energies **2022**, 15, 7927 6 of 15

Martens method according to PN-EN ISO 2719. The final step is to evaluate how well t_{CFP} fits t_{MFP} and, on this basis, to assess the suitability of using the model described by Formula (5) and thus determine the suitability of measuring the initial boiling point of the lubricating oil to assess its possible contamination with diesel fuel.

2. Materials and Methods

Detailed tests were carried out on lubricating oil samples (SAE 30 and SAE 40 grades) diluted with diesel oil at selected mass concentrations (i.e., 0, 1, 2, 5, 10, 20, 50, and 100%). The oils were tested to determine their properties:

- Flash point temperature *t*_{MFP};
- Initial boiling point *tibp*.

This experiment used the *Flash Point Pensky–Martens Semi-Automatic* device (Walter Herzog GmbH, Lauda-Königshofen, Germany), as shown in Figure 1, to measure both quantities. The flash point was determined in the closed crucible using the Pensky–Martens method, and the initial boiling point was measured in the open crucible (atmospheric conditions). According to the latest certification results of the mentioned apparatus, the measurement accuracy is 0.35% and the repeatability is 0.05 K (0.05 °C) for a range of 268.15–383.15 K (–5–110 °C), and the measurement accuracy is 0.10% and the repeatability is 0.10 K (0.10 °C) for a range of 363.15–643.15 K (90–370 °C).

For research conducted in specialized laboratories, a number of distillation methods can be used, an overview and detailed description of which are provided in the literature [37,38]. Approximate methods are also known that enable the determination of the average boiling point value based on knowledge of the exact chemical composition [39]. However, when complete information about the substance under test is absent, there can be a significant limitation in the use of these methods. In the present experiment, an apparatus from Walter Herzog GmbH, Lauda-Königshofen, Germany, that allows for the realization of flash point measurements according to ISO 2719 [17] was used to determine the boiling onset temperature.

Similarly, oil baths available on ships equipped with thermostats or specialized plate heaters, used as a standard for heat bearings, shafts, and bushings prior to assembly during repair work, can be used to conduct such a test. To increase the accuracy of the measurement, it is advisable to take several measurements of the boiling onset temperature and use the average value in the calculations. In this experiment, 5 measurements were taken for each sample, and the values presented in the article are averages. The maximum measured temperature difference obtained in a given measurement series for each sample did not exceed 1 K (1 °C).

Energies **2022**, 15, 7927 7 of 15

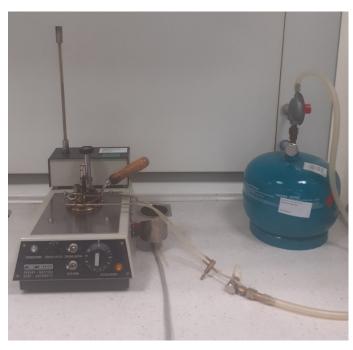


Figure 1. Flash Point Pensky–Martens Semi-Automatic camera from Walter Herzog GmbH used in the study (photograph by M. Szmukała).

Lubricating oils with SAE 30 and SAE 40 viscosity grades (Appendix A), which are among the most common oils in marine and industrial engines, were used in the experiment. The test used Orlen Efecta Diesel Biofuel (designated CN27102011D), the nominal parameters of which are listed in Table 3. This fuel belongs to the ISO-F-DMX category (Appendix B). The lubricating oils used in the test were Agip Cladium 120 SAE 30 CD and Agip Cladium 120 SAE 40 CD, the characteristics of which are listed in Table 4.

Table 3. Physical and chemical properties of Orlen Efecta Diesel Biofuel declared by the manufacturer [40].

Specification	Parameter
Cetane number	≥51
Initial boiling point	75–180 °C
Boiling point range	95% vol. distillates to 360 °C
Flash point (determined in a closed crucible)	>56 °C
Autoignition temperature (according to DIN51794:2003-05)	approx. 240 °C
Kinematic viscosity (acc. to PN-EN ISO 3104)	1.5–4.5 mm ² /s (2.549 mm ² /s) at 40 °C approx. 2.151 mm ² /s at 50 °C
Density	820–845 kg/m³ at 15 °C
Relative vapor density	approx. 6 (for air = 1)
Cloud point	-7 °C
Cold filter plugging point	-8 °C

Table 4. Physical and chemical properties of the Agip Cladium 120 CD lubricating oils used in the tests declared by the manufacturer [41–43].

Specification	Parameter				
Oil	Agip Cladium 120	Agip Cladium 120			
Oli	SAE 30 CD	SAE 40 CD			

Energies **2022**, 15, 7927 8 of 15

Kinematic viscosity (acc. to PN-EN ISO	108 mm ² /s at 40 °C	$160 \text{ mm}^2\text{/s}$ at $40 ^{\circ}\text{C}$	
3104)	12.0 mm ² /s at 100 °C	15.7 mm ² /s at 100 °C	
Viscosity index	100	100	
Total base number	12 mg KOH/g	12 mg KOH/g	
Flash point (determined in closed crucible) 225	235 °C	
Pour point	−18 °C	−15 °C	
Density	895 kg/m³ at 15 °C	900 kg/m³ at 15 °C	

Agip Cladium SAE 30 CD and Agip Cladium SAE 40 CD oils are high-quality engine oils of API CD grade (supercharged marine, traction, and industrial compression-ignition engines) from AGIP-ENI. The additive batch allows engines to operate on lower-grade fuels, i.e., marine fuels and fuels with higher sulfur content, while maintaining a high engine performance [41,42]. These oils meet the following specifications: Deutz MWM, Dorman Diesel, Fincantieri-Divisione Grandi Motori, Isotta Fraschini, MAN B&W, Mirrlees, MTU marine oil, New Sulzer Diesel, Nohab, S.E.M.T. Pielstick, SKL, VM, and Wärtsilä.

3. Results and Discussion

Figures 2 and 3 show the experimental results for the diesel fuel mixed with SAE 30 and SAE 40 grade oils, respectively. Detailed information on measured temperatures is presented in Appendix C. The functional relationships described by Formula (6) for both of the tested lubricating oils are shown in Figure 4.

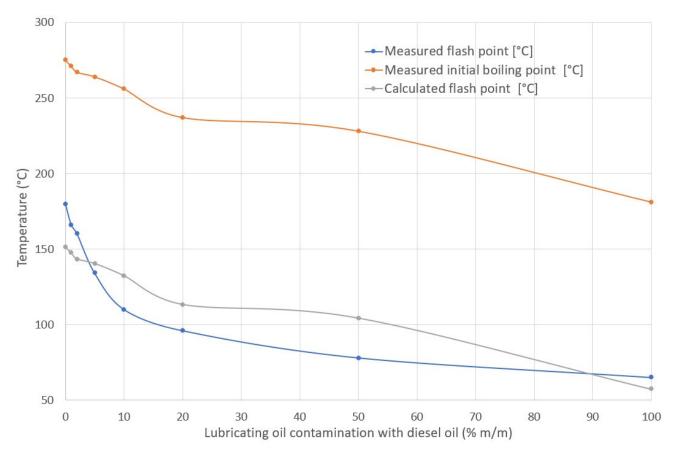


Figure 2. Measured values of the initial boiling point and the flash point and the calculated flash point of the tested SAE 30 oil at different levels of lubricating oil dilution with diesel fuel.

Energies **2022**, 15, 7927 9 of 15

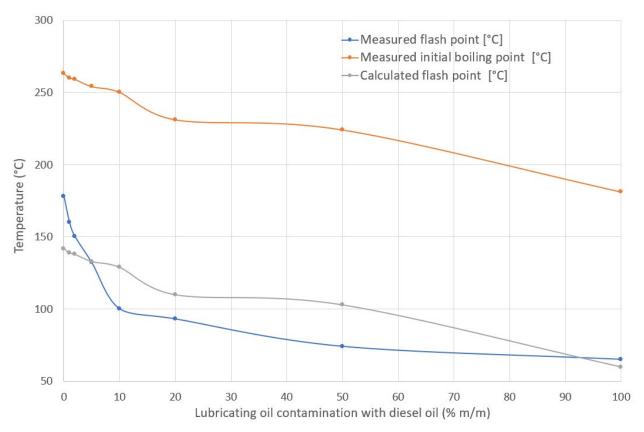
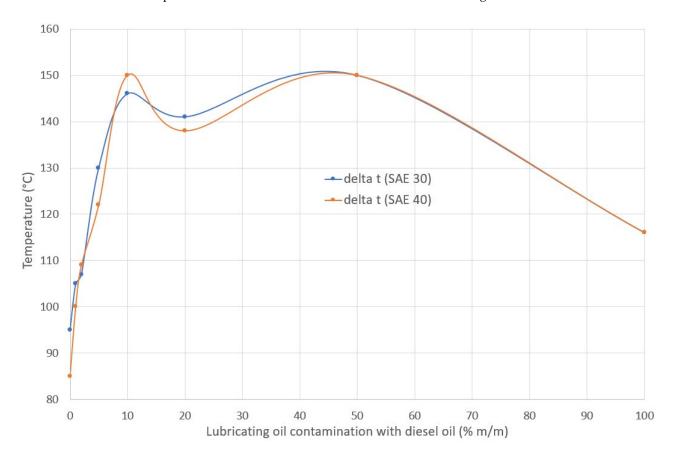


Figure 3. Measured values of the initial boiling point and the flash point and the calculated flash point of the tested SAE 40 oil at different levels of lubricating oil dilution with diesel fuel.



Energies **2022**, 15, 7927 10 of 15

Figure 4. Differences determined between the initial boiling point and the flash point of the tested lubricating oils for lubricating oil with different dilution levels of diesel fuel.

The values of the K factor were determined using Formula (7) for the concentrations tested in the present experiment. The K factor for the case studied, when lubricating oil of SAE 30 class was diluted with diesel fuel, was 123.75 °C (396.90 K). The accuracy of the model fit (as the difference between the calculated model and the flash point temperature) for the SAE 30 oil ranged from 95 to 146 °C (K). In contrast, the K factor for the case studied was 121.25 °C (394.40 K) when the SAE 40 lubricating oil was diluted with diesel fuel. The accuracy of the fit (as the difference between the calculated model and the flash point temperature) for the SAE 40 oil ranged from 85 to 150 °C (K).

The goodness of fit of the model was evaluated by determining the relative error δ_{max} (%) for the differences expressed on an absolute scale in units of Kelvin, alongside which MSE and RMSE were used to determine the estimator bias. In addition, the values of the Pearson correlation coefficient R and coefficient of determination R^2 were determined for sets of measured and calculated flash point values. The above indicators are summarized in Table 5.

Specification	Lubricating Oil Meeting Vis	cosity Grade Requirements
Oil grade	SAE 30	SAE 40
$\delta_{ ext{max}}$ (%)	7.47	8.28
MSE (K ²)	379.93	484.68
RMSE (K)	19.49	22.01
R (-)	0.89	0.85
R^2 (-)	0.78	0.72

Table 5. Indicators describing the model's goodness of fit to the experimental results.

The relative estimation error does not exceed 10%, while the MSE does not exceed 484.68 K² (the RMSE value does not exceed 22.01 K), which can be considered sufficient for the engineering applications in question. With the assumption that an *R* coefficient ranging between 0.7 and 0.9 indicates a strong correlation [44], both oils that were tested meet this criterion, and the direction of change is positive. The model fit described by the determination coefficients can, in turn, be classified as being at the borderline between good and satisfactory.

4. Conclusions

The results presented here are highly promising and prove that it is possible to use the initial boiling point of the oil to evaluate its potential contamination with fuel. Moreover, if the appropriate benchmark characteristics of lubricating oils from the relevant viscosity classes are available, the flash point can be estimated based on the measured initial boiling point.

This article characterizes the relationship between the initial boiling point and the flash point for oils of viscosity grades SAE 30 and SAE 40 [45] at different levels of dilution with distillate fuel of the ISO-F-DMX category. The next step should involve similar tests carried out on lubricating oils of viscosity grades other than those presented in this article and for fuels of other categories. Additionally, in a further investigation into the possibility of using the initial boiling point to assess the contamination of lubricating oils, similar experiments should be carried out for heavy fuel oils.

Funding: This research was funded by the Ministry of Science and Higher Education (MEiN) of Poland, grant number 1/S/KPBMiM/22. The APC was funded by MDPI.

Data Availability Statement: The dataset supporting the paper is Chybowski, Leszek (2022), "Lube oil-diesel oil mixes-dataset", Mendeley Data, V2, doi:10.17632/scbx3h2bmf.2.

Energies **2022**, 15, 7927 11 of 15

Acknowledgments: Laboratory tests were performed on behalf of the author at the Center for Testing Fuels, Working Fluids, and Environmental Protection (CBPCRiOS) of the Maritime University of Szczecin. The author would like to thank Magdalena Szmukała and Barbara Żurańska for their technical support.

Conflicts of Interest: The author declares no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

Abbreviations

ASTM American Society for Testing and Materials

CCE Crankcase explosion
CCI Calculated cetane index
CII Calculated ignition index

CN Cetane number

DCN Derived cetane number

DO Diesel oil

FDM Fuel dilution meter
FID Flame ionization detector
FTIR Fourier-transform infrared
FVI Flexible volatility index
GC Gas chromatography
HFO Heavy fuel oil

IEC International Electrotechnical Commission
ISO International Organization for Standardization

SAE Society of Automotive Engineers

SAE 30, SAE 40 Viscosity grades of lubricating oils according to SAE J300-2021

standard

SAW Surface acoustic wave VLI Vapor lock index VI Volatility index

Symbols

C Percentage lubricating oil contamination with the diesel oil

K Average temperature difference

 Δt Temperature difference

*t*₁₀, *t*₅₀, *t*₉₀ 10, 50, and 90% recovery temperatures

 t_{CFP} Calculated flash point t_{IBP} Initial boiling point

*t*_{MFP} Measured flash point temperature ρ_{15} Density of the substance at 15 °C

Energies **2022**, 15, 7927

Appendix A

Table A1. SAE J300-2021 classification based on viscosity for engine oils for SAE 30 and SAE 40 grades (based on [46]).

Paramo	eter ^b	Low-Temperature Cranking Viscosity (mPa·s) at Temp. (°C)	Low-Temperature Pumping Viscosity (mPa·s) at Temp. (°C)	Low-Shear- Rate Kine- matic Viscos- ity (mm²/s) at 100 °C	Low-Shear- Rate Kine- matic Viscos- ity (mm ² /s) at 100 °C	High-Shear- Rate Viscos- ity (mPa·s) at 150 °C
Lim	iit	Max.	Max. with No Yield Stress	Min.	Max.	Min.
	30	-	-	9.3	<12.5	2.9
CAE	40	-	-	12.5	<16.3	3.5 (0 W-40, 5 W-40, and 10 W-40 grades)
SAE Grade	40	-	-	12.5	<16.3	3.7 (15 W-40, 20 W-40, 25 W-40, 40 grades)

Appendix B

Table A2. Characteristics of Marine Distillate Fuels in Accordance with ISO 8217:2017 [47].

Domonoston	Limit		Category ISO-F-						Test Methods						
Parameter	DMX DMA DFA DMZ DFZ		DFZ	DMB	DFB	and References									
Kinematic viscosity at 40 °C	Max.	5.500	6.00	0	6.000		6.000		6.000		6.000		11.	00	- ISO 3104
(mm²/s) ^a	Min.	1.400	2.00	0	3.0	3.000		00	150 5104						
Density at 15 °C (kg/m³)	Max.	-	890.	0	890.0 900.0		ISO 3675 or ISO 12185								
Micro carbon residue at 10% volume distillation residue (% m/m)	Max.	0.30	0.30)	0.30		-		ISO 10370						
Micro carbon residue (% m/m)	Max.	-	-		-	-		30	=						
Sulfur (% m/m) ^b	Max.	1.00	1.00)	1.00		1.00		1.5	50	ISO 8754 or ISO 14596; ASTM D4294				
Water (% <i>v/v</i>)	Max.	-			-	0.3	0 с	ISO 3733							
Total sediment by hot filtration (% m/m)	Max.	-	-		-		0.1	0 с	ISO 10307-1						

Energies **2022**, 15, 7927 13 of 15

Ash (% m/m)	Max.	0.010	0.010	0.010	0.010	ISO 6245	
Flash point (°C)	Min.	43.0	43.0 60.0 60.0		60.0	ISO 2719	
Page 10 sint d (%C) in winter	Max.	-	-6	-6	0	ICO 2017	
Pour point d (°C) in summer	r Max.	-	0	0	6	- ISO 3016	
Claud naint d (%C) in winter	Max.	-16	Report	Report	-	ICO 2015	
Cloud point d (°C) in summer	r Max.	-16	-	-	-	- ISO 3015	
Cold filter plug- in winter	Max.	-	Report	Report	-	ID 200 on ID (12	
ging point d (°C) in summe	r Max.	-	-	-	-	– IP 309 or IP 612	
Calculated cetane index	Min.	45	40	40	35	ISO 4264	
Acid number (mg KOH/g)	Max.	0.5	0.5	0.5	0.5	ASTM D664	
Oxidation stability (g/m³)	Max.	25	25	25	25 e	ISO 12205	
Fatty acid methyl ester	Max.		- 7.0	- 7.0	- 7.0	ASTM D7963	
(FAME) (% v/v)	wax.	-	- 7.0	- 7.0	- 7.0	or IP 579	
Lubricity, corrected wear sca	May	520	520	520	520	ISO 12156-1	
diameter (WSD) at 60 °C (µm) f (11111X.	320	320	320	320	150 12156-1	
Hydrogen sulfide (mg/kg)	Max.	2.00	2.00	2.00	2.00	IP 570	
Appearance	-		Clear and brig	ht ^g	_ c	<u>-</u> _	

a—1 mm²/s = 1 cSt. b—Notwithstanding the limits given, the purchaser shall define the maximum sulfur content in accordance with relevant statutory limitations. c—If the sample is not clear and bright, the total sediment by hot filtration and water tests shall be required. d—Pour point cannot guarantee operability for all ships in all climates. The purchaser should confirm that the cold flow characteristics (pour point, cloud point, cold filter, and plugging point) are suitable for the design of the ship and intended voyage. c—If the sample is not clear and bright, the test cannot be undertaken, and, therefore, compliance with this limit cannot be shown. c—This requirement is applicable to fuels with a sulfur content below 500 mg/kg (0.050 % m/m). c—If the sample is dyed and not transparent, then the water limit and test method as given in the Section 6.12 of the ISO 8217 shall apply.

Appendix C

Table A3. Measured Flash Point and Initial Boiling Point Temperatures.

Lubricating Oil Grade	Lubricating Oil Contamination with Diesel Oil (% m/m)	0	1	2	5
SAE 30 -	Measured flash point [°C]	180	166	160	134
5AE 30 -	Measured initial boiling point [°C]	275	271	267	264
SAE 40 -	Measured flash point [°C]	178	160	150	132
5AE 40 —	Measured initial boiling point [°C]	263	260	259	254
Lubricating Oil Grade	Lubricating Oil Contamination with Diesel Oil (% m/m)	10	20	50	100
CAE 20	Measured flash point [°C]	110	96	78	65
SAE 30 —	Measured initial boiling point [°C]	256	237	228	181
SAE 40 -	Measured flash point [°C]	100	93	74	65
5AE 40 -	Measured initial boiling point [°C]	250	231	224	181

References

- 1. Wiaterek, D.; Chybowski, L. Assessing the topicality of the problem related to the explosion of crankcases in marine main propulsion engines (1972–2018). *Sci. J. Marit. Univ. Szczecin, Zesz. Nauk. Akad. Mor. W Szczec.* **2022**, 71. Available online: http://repository.scientific-journals.eu/handle/123456789/2720 (accessed on 8 June 2022).
- 2. Bejger, A.; Chybowski, L.; Gawdzińska, K. Utilising elastic waves of acoustic emission to assess the condition of spray nozzles in a marine diesel engine. *J. Mar. Eng. Technol.* **2018**, *17*, 153–159. https://doi.org/10.1080/20464177.2018.1492361.
- Graddage, M. Crankcase Explosions Detection or Prevention? In Crankcase Explosions; IMAREST: London, UK, 2002; pp. 126– 147.
- 4. Bowen, P.J. Current Understanding of Oil-Mist Explosions. In Crankcase Explosions; IMAREST: London, UK, 2002; pp. 149–164.

Energies **2022**, 15, 7927 14 of 15

5. Chybowski, L. *Eksplozje w Skrzyniach Korbowych Silników Okrętowych—Przyczyny, Zapobieganie i Minimalizacja Skutków;* Akademia Morska w Szczecinie: Szczecin, Poland, 2022.

- 6. Technomics International Case Study—Fuel Dilution of Engine Oil in Locomotives. Available online: https://www.techenomics.net/case-studies/fuel-dilution-engine-oil/ (accessed on 8 June 2022).
- 7. Total Energies Fuel Dilution of Engine Oil: Causes and Effects. Available online: https://lubricants.totalenergies.com/fuel-dilution-engine-oil-causes-and-effects (accessed on 14 June 2022).
- 8. AMETEK Spectro Scientific Measuring Fuel Dilution in Lubricating Oil. Available online: https://www.azom.com/article.aspx?ArticleID=12880 (accessed on 14 June 2022).
- 9. Zhong, Y.; Bao, Q.; Yuan, L.; Liu, J.; Cai, Y.; Chen, X. Analysis of Microplastics in Aquatic Shellfish by Pyrolysis–Gas Chromatography/Mass Spectrometry after Alkali Digestion and Solvent Extraction. *Polymers* **2022**, *14*, 3888. https://doi.org/10.3390/polym14183888.
- 10. Kretzschmar, N.; Seifert, M.; Busse, O.; Weigand, J.J. Prediction of Retention Indices and Response Factors of Oxygenates for GC-FID by Multilinear Regression. *Data* **2022**, *7*, 133. https://doi.org/10.3390/data7090133.
- Akram, N.; Usman, M.; Haider, S.; Akhtar, M.S.; Gul, K. Impact of Diisocyanates on Morphological and In Vitro Biological Efficacy of Eco-Friendly Castor-Oil-Based Water-Borne Polyurethane Dispersions. *Polymers* 2022, 14, 3701. https://doi.org/10.3390/polym14173701.
- Kadota, T.; Yamasaki, H. Recent advances in the combustion of water fuel emulsion. *Prog. Energy Combust. Sci.* 2002, 28, 385–404. https://doi.org/10.1016/S0360-1285(02)00005-9.
- 13. Wattrus, M. Fuel Property Effects on Oil Dilution in Diesel Engines. *SAE Int. J. Fuels Lubr.* **2013**, *6*, 2013–01–2680. https://doi.org/10.4271/2013-01-2680.
- Kaminski, P. Experimental Investigation into the Effects of Fuel Dilution on the Change in Chemical Properties of Lubricating Oil Used in Fuel Injection Pump of Pielstick PA4 V185 Marine Diesel Engine. *Lubricants* 2022, 10, 162. https://doi.org/10.3390/lubricants10070162.
- CNBOP-PIB-BW03P:2016 Standard; CNBOP-PIB Metody Badania Temperatury Zapłonu Substancji Ciekłych Niebezpiecznych Pożarowo – Wytyczne. Centrum Naukowo-Badawcze Ochrony Przeciwpożarowej im. Józefa Tuliszkowskiego – PIB: Józefów, Poland, 2016.
- 16. Babrauskas, V. Ignition Handbook; Society of Fire Protection Engineers: Gaithersburg, MD, USA, 2003.
- 17. ISO 2719:2016; Determination of Flash Point—Pensky-Martens Closed Cup method; 4th ed. International Organization for Standardization (ISO): Geneva, Switzerland, 2016.
- 18. ISO 13736:2021; Determination of Flash Point—Abel Closed-Cup Method. 4th ed.; International Organization for Standardization (ISO): Geneva, Switzerland, 2021.
- 19. ISO 1516:2002; Determination of Flash/no Flash—Closed Cup Equilibrium Method; 3rd ed. International Organization for Standardization (ISO): Geneva, Switzerland, 2002.
- 20. ISO 1523:2002; Determination of Flash Point—Closed Cup Equilibrium Method; 3rd ed. International Organization for Standardization (ISO): Geneva, Switzerland, 2002.
- 21. TSE TSE—TS 1080; Method of Test For Flash Point With Tagliabue Open Cup. TSE: Ankara, Turkey, 1993.
- 22. ISO 2592:2017; Petroleum and Related Products—Determination of Flash and Fire Points—Cleveland Open Cup Method; 3rd ed. International Organization for Standardization (ISO): Geneva, Switzerland, 2017.
- 23. *ISO* 3679:2015; Determination of Flash No-Flash and Flash Point—Rapid Equilibrium Closed Cup Method; 5th ed. International Organization for Standardization (ISO): Geneva, Switzerland, 2015.
- 24. CIMAC. Guideline on the Relevance of Lubricationt Flash Point in Connection with Crankcase Explosions; CIMAC Working Group 8 "Marine Lubricants": Frankfurt, Germany, 2013.
- 25. Ferguson, G.W. Diesel Engine Crankcase Explosion Investigation. SAE Tech. Pap. 1951, 510104, 1–28 https://doi.org/10.4271/510104.
- 26. Bureau of Ships. Diesel Engine Maintenance Training Manual; Maritime Press: Bremen, Germany, 2015.
- 27. Krupowies, J. Badania i Ocena Zmian Właściwości Użytkowych Olejów Urządzeń Okrętowych; Maritime University of Szczecin: Szczecin, Poland, 2009.
- 28. Shayler, P.J.; Winborn, L.D.; Scarisbrick, A. The Build-Up of Oil Dilution by Gasoline and the Influence of Vehicle Usage Pattern. *SAE Tech. Pap.* **2000**. https://doi.org/10.4271/2000-01-2838.
- 29. Hu, T.; Teng, H.; Luo, X.; Lu, C.; Luo, J. Influence of Fuel Dilution of Crankcase Oil on Ignitability of Oil Particles in a Highly Boosted Gasoline Direct Injection Engine. *SAE Tech. Pap.* **2015**. https://doi.org/10.4271/2015-01-2811.
- 30. Stradling, R. Gasoline Volatility and Vehicle Performance; Concawe: Brussels, Belgium, 2012; ISBN 978-2-87567-003-8.
- 31. Yanowitz, J.; McCormick, R.L. Review: Fuel Volatility Standards and Spark-Ignition Vehicle Driveability. *SAE Int. J. Fuels Lubr.* **2016**, *9*, 408–429. https://doi.org/10.4271/2016-01-9072.
- 32. Sokal, W. Wskaźniki Charakterystyczne Paliw Ciekłych. Available online: https://slideplayer.pl/slide/59984/ (accessed on 28 August 2022).
- 33. Chybowski, L. Diagnozowanie Silników Okrętowych z Zapłonem Samoczynnym w Oparciu o Analizę Procesów Wtrysku i Spalania Paliwa; Maritime University of Szczecin Press: Szczecin, Poland, 2019.

Energies **2022**, 15, 7927 15 of 15

34. Ramadan, O.; Menard, L.; Gardiner, D.; Wilcox, A.; Webster, G. Performance Evaluation of the Ignition Quality Testers Equipped with TALM Precision Package (TALM-IQT™) Participating in the ASTM NEG Cetane Number Fuel Exchange Program. SAE Tech. Pap. 2017. https://doi.org/10.4271/2017-01-0720.

- 35. Chybowski, L. *Lube Oil—Diesel Oil Mixes—Dataset*; 2022; Volume Ver. 2. Mendeley Data, V2, 10/20/2022. Available online: https://data.mendeley.com/datasets/scbx3h2bmf/2 (accessed on 12 July 2022). doi: 10.17632/scbx3h2bmf.2.
- 36. PAC L.P. Herzog Cetane ID 510; PAC L.P.: Houston, TX, USA, 2019.
- 37. Akdağ, A.; Ozturk, E. Distillation Methods of Essential Oils. S. Ü. Fakültesi Derg. 2019, 45, 22–31.
- 38. Dutton, J. Distillation Methods. Available online: https://www.e-education.psu.edu/fsc432/content/distillation-methods (accessed on 12 October 2022).
- 39. Riazi, M.R.; Eser, S. Properties, Specifications, and Quality of Crude Oil and Petroleum Products. In *Petroleum Refining and Natural Gas Processing*; ASTM International: Conshohocken, PA, USA, 2013; p. 80.
- 40. PKN Orlen S.A. Olej Napędowy. Ecodiesel Ultra B,D,F, Olej napędowy Arktyczny Klasy 2, Efecta Diesel B,D,F, Verva ON B,D,F; PKN Orlen: Płock, Poland, 2021.
- 41. Oleje-Smary AGIP Cladium 120 SAE 30 CD. Available online: https://oleje-smary.pl/pl/p/AGIP-Cladium-120-SAE-30-CD-20-litrow/186 (accessed on 12 July 2022).
- 42. Oleje-Smary AGIP Cladium 120 SAE 40 CD. Available online: https://oleje-smary.pl/pl/p/AGIP-Cladium-120-SAE-40-CD-20-litrow/188 (accessed on 12 July 2022).
- 43. ITALCO (Far East) Pte Ltd. Product Data Sheet Eni Cladium 120 (Series); ITALCO: Singapore, 2017.
- 44. Bartuś, T. Analiza Regresji i Korelacji Dwóch Zmiennych. Available online: http://home.agh.edu.pl/~bartus/index.php?action=dydaktyka&subaction=statystyka&item=regresja_i_korelacja (accessed on 28 Auguat 2022).
- Society of Automotive Engineers. SAE J300-2021. Engine Oil Viscosity Classification; SAE International: Warrendale, PA, USA, 2021.
- 46. Hasan-Zadeh, A.; Poshtiban, M. Car Engine Oil: Investigation of Function and Related Challenges, and Provision of Environmental Solutions. *Asian J. Appl. Sciences.* **2021**, *9*, 35-44. https://doi.org/10.24203/ajas.v9i1.6486.
- 47. ISO 8217:2017; Petroleum Products—Fuels (class F)—Specifications of Marine Fuels; 6th ed.; Organization for Standardization (ISO): Geneva, Switzerland, 2017