Article

Impact of Liquefied Natural Gas Composition Changes on Methane Number as a Fuel Quality Requirement

Szymon Kuczyński[iD]**, Mariusz Łaciak**[iD]**, Adam Szurlej and Tomasz Włodek ***[iD]

Drilling, Oil and Gas Faculty, AGH University of Science and Technology, PL30059 Krakow, Poland; skuczyns@agh.edu.pl (S.K.); laciak@agh.edu.pl (M.Ł.); szua@agh.edu.pl (A.S.)
* Correspondence: twlodek@agh.edu.pl; Tel.: +48-12-617-3668

check for updates

Abstract: The one of main quality requirements of natural gas as an engine fuel is the methane number (MN). This parameter indicates the fuel's capability to avoid knocking in the engine. A higher MN value indicates a better natural gas quality for gas engines. Natural gas with higher methane content tends to have higher MN value. This study presents analysis of deviation of liquefied natural gas (LNG) composition and its impact on LNG quality as an engine fuel. The analysis of higher hydrocarbons and nitrogen content impact on LNG parameters was considered for several samples of LNG compositions. Most engine manufacturers want to set a new, lower limit value for methane number at 80. This fact causes significant restrictions on the range of variability in the composition of liquefied natural gas. The goal of this study was to determine the combination of the limit content of individual components in liquefied natural gas to achieve the strict methane number criterion (MN > 80). To fulfill this criterion, the methane content in LNG would have to exceed 93.7%mol, and a significant part of the LNG available on the market does not meet these requirements. The analysis also indicated that the methane number cannot be the only qualitative criterion, as its variability depends strongly on the LNG composition. To determine the applicability of LNG as an engine fuel, the simultaneous application of the methane number and Wobbe index criteria was proposed.

Keywords: LNG; liquefied natural gas; methane number; fuel; alternative fuel; LNG composition

1. Introduction

Liquefied natural gas (LNG) is commonly used in power industry as a fuel for gas engines to produce electricity or as a fuel for natural gas vehicle (NGV) engines. Natural gas utilization in the power or automotive industry require quality standards in accordance with the effective design of the engine to obtain maximum power [1–5]. For reciprocating gas engines the methane number (MN) is one of the natural gas quality parameters. Methane number is a measure of the resistance of fuel gases to engine knock. It is assigned to a tested fuel based on operation in a knock testing unit at the same standard knock intensity [1–3]. The knocking phenomenon results from the spontaneous ignition of a portion of the gas mixture in the combustion chamber ahead of the propagating flame [4,5]. The required minimum MN value depends on the engine manufacturer or automotive associations. A higher MN value indicates a better gas fuel quality and allows one to avoid knocking which is one of the reasons for engine power decreases [6]. The methane number of pure methane (CH_4) is 100. It means that during fuel combustion knocking phenomena does not occur. Pure hydrogen (H_2) has a value of MN 0 (zero) which means it very easily causes knocking in the engine [5–7]. More and more engine manufacturers or automotive associations require fuel with a minimum methane number of 80. Some engine manufacturers still maintain methane number limits below 80 (most often 70) [8–19].

The heavier natural gas components content range can be extended with lower methane number values. In the LNG regasification process, high methane number of natural gas can be obtained only from light LNG, in which the methane mole content usually exceeds 95%. Increasing the mole fraction of CH4 can be achieved by reducing the content of heavier components by substituting them i.e., from C_2H_{6+} to CH4. This study determines the combination of LNG individual component limit contents in terms of maintaining the assumed criteria of methane number values. Knowledge of the features of burning fuels based on LNG is crucial for suppliers and traders in providing reliable and efficient products. Analysis of liquefied natural gas composition variability impact on the possibility of its utilization as an engine fuel in terms of the methane number criterion is not a widely recognized research area. While in case of classical fuels such as gasoline or diesel, the basic properties of the fuel, including the qualitative ones, are described in great detail and standardized, for liquefied natural gas, the most important aspect is the variability of its composition, which results in fuel quality changes. For LNG, different compositions, which depend on the export sources causes significant changes in fuel quality. Variability of LNG quality parameters does not have to adversely affect the basic methods of using natural gas after regasification, and in the case of maintain restrictive quality conditions, it is always possible to apply additional gas treatment methods. Fuel quality is very important for proper operation of precisely designed car engines. Development of the LNG market causes that deliveries of this fuel take place from new different sources, causing significant fluctuations in the values of LNG physical and quality parameters. The aim of this study is to define, systematize and standardize universal limit values of individual LNG components for which the assumed quality of defined methane number value can be achieved.

2. Basics of Liquefied Natural Gas

Liquefied natural gas (LNG) plays an important role in the global natural gas market. Global demand for natural gas will grow over the coming years [20,21]. Diversification of supplies of this eco-friendly fuel is the key element of the energy security of each country [22–24]. Liquefied natural gas is transported by ships and stored in suitable storage tanks. The main component of LNG is methane and remaining components are primarily ethane, propane, butane and nitrogen. LNG composition may vary significantly depending on its origin. Generally liquefied natural gases from different sources can be divided into three groups, depending on the content of individual components. The first group is 'Light LNG', in which the methane content is usually above 90%mol or even above 95%mol. LNG with a methane content below 90% is usually considered as 'Heavy LNG'. It has a high ethane content (usually up to 10%), propane (usually up to about 3–4%), butanes (usually up to 1.5%) and trace amounts of pentanes and heavier components. In addition to hydrocarbons, liquefied natural gas contains small amounts of nitrogen.

In general, the content of nitrogen in LNG does not exceed 0.5%, and the requirements for LNG indicate that its content should not exceed 1%. Due to its strong influence on the LNG evaporation process, LNG which contains more than 1% of nitrogen should be qualified to a separate LNG group ('LNG with nitrogen'). Table 1 presents the assumed approximate limits for the content of individual components in liquefied natural gas.

Table 1. Typical content limits of liquefied natural gas components.

Component	Minimum Molar Content	Maximum Molar Content
Methane	87%	>99%
Ethane	<1%	10%
Propane	<1%	5%
Butanes	<1%	1.5%
Nitrogen	<0.1%	1%

Quality Criteria for Liquefied Natural Gas

Liquefied natural gas parameters and composition are governed by strict quality requirements, which are generally determined by domestic regulations and specifications for regasified natural gas and by strict requirements for the natural gas liquefaction installations at the LNG producer side. A separate group of requirements is indicated by carriers who receives LNG directly in the liquid phase (e.g., LNG carriers or bunkering ships). Generally, typical elements of the quality specification of liquefied natural gas are:

(1) Molar content of methane in LNG (see Table 1);
(2) LNG higher heating value and Wobbe Index (usually min - max range) (Table 2);
(3) Boiling temperature range (Table 2);
(4) Relative density (the ratio of the average molecular weight of gas to that of air), (Table 2);
(5) Maximum permitted levels of impurities (H_2S, H_2O, CO_2, S) (Table 3);
(6) Molar content of heavier hydrocarbons, in particular C_{4+} (Table 3);

Table 2. Typical quality parameters limits of liquefied natural gas based on various sources and calculated from various available LNG compositions (own calculations).

Component	Min	Max
Higher (Gross) Heating Value, MJ/m_n^3	39.4	46.0
Wobbe Index, MJ/m_n^3	52.7	56.9
Relative density, -	0.55	0.66
Boiling temperature (p = 1 atm), K	108.7	115.5

Commonly the most important quality criterion used by the LNG recipient is the so-called Wobbe index [25,26]. In many countries, the maximum limit of the Wobbe index of natural gas is assumed around 56–57 MJ/m_n^3.

Table 3. Maximum impurities limits for liquefied natural gas [27,28].

Impurity/Component	Maximum Content	
Vapor water H_2O	0.1 ppmv	0.8 mg/m_n^3
Hydrogen Sulphide H_2S	4 ppmv	6.07 mg/m_n^3
Sulphur S	28 ppmv	40 mg/m_n^3
Carbon dioxide CO_2	50 ppmv	98.21 mg/m_n^3
Mercury Hg	0.01 $\mu g/m_n^3$	
Butanes and heavier hydrocarbons C_{4+}	2%	
Pentanes and heavier hydrocarbons C_{5+}	0.1%	
Nitrogen N_2	1%	

Most liquefaction processes begin with some form of gas pre-treatment. During this process natural gas should be cleaned by removing impurities like carbon dioxide, hydrogen sulfide, mercury and water vapor. Next, the natural gas without non-hydrocarbon impurities is passed to a fractionation process where the heavy hydrocarbons content (C2+) is reduced. This process includes also make-up unit which adds heavy hydrocarbons to adjust the composition if necessary. The natural gas treatment process at the LNG liquefaction plant has a key role in the preparation of gas to achieve the quality requirements for natural gas before liquefaction process. Required permitted maximum limits of impurities in liquefied natural gas are presented in Table 3.

3. Methane Number Criteria

3.1. Methane Number

LNG is produced in various locations around the world. The composition of LNG depends on its geographical origin due to differences in natural gas sources, production technologies and target markets for LNG. Table 4 presents approximate compositions of liquefied natural gas from various export sources. In addition, the 'evaporation' of volatile components during LNG transport and storage leads to a change in composition, also known as 'LNG aging'. Methane number is not a gas thermodynamic property, so it cannot be calculated using the equation of state (EOS). This means that the methane number determination methods are based on empirical experiments. The results obtained with individual methods may vary significantly. It should also be noted that some of these calculation methods do not include components heavier than butane. Usually the content of components heavier than butane should be small, so they are usually added to the butane content as an approximation, but in order to determine the methane number it may be necessary to additionally modify these basic calculation methods.

Table 4. LNG compositions from various export sources [20].

Composition / Source	Methane C_1	Ethane C_2	Propane C_3	C_{4+}	Nitrogen N_2
Australia NWS	87.33	8.33	3.33	0.97	0.04
Australia Darwin	87.64	9.97	1.96	0.33	0.1
Algieria–Skikda	91.4	7.35	0.57	0.05	0.63
Algieria–Bethioua	89.55	8.2	1.3	0.31	0.64
Algieria–Arzew	88.92	8.42	1.58	0.37	0.71
Brunei	90.12	5.34	3.02	1.48	0.04
Egypt–Idku	95.31	3.58	0.74	0.35	0.02
Egypt–Damietta	97.25	2.49	0.12	0.12	0.02
Indonesia–Badak	90.14	5.46	2.98	1.41	0.01
Libya	81.39	12.44	3.51	0.64	2.02
Malaysia–Bintulu	91.69	4.64	2.6	0.93	0.14
Nigeria	91.7	5.52	2.17	0.58	0.03
Norway	92.03	5.75	1.31	0.45	0.46
Oman	90.68	5.75	2.12	1.25	0.2
Peru	89.06	10.26	0.1	0.01	0.57
Qatar	90.91	6.43	1.66	0.73	0.27
Russia–Sakhalin	92.54	4.47	1.97	0.95	0.07
Trynidad	96.78	2.78	0.37	0.06	0.01
USA–Alaska	99.7	0.09	0.03	0.01	0.17
Yemen	93.17	5.92	0.77	0.12	0.02

The description of methane number is simple if the gas mixture consists of only two methane and hydrogen components. However, in the case of natural gas, where in its composition, in addition to methane, there are heavier components like ethane, propane, etc., determination of methane number is much more. There are various methods to determine the methane number based on natural gas composition. Some of them are proposed by standardization associations and some are proprietary methods proposed by engine manufacturers. The results of these methods can vary significantly [29–31].

3.2. Methane Number Calculation Methods

Among developed methods for methane number determination, some have been proposed by standardization associations. The most common standard for methane number determination is ISO-TR-22302: 2014 "Natural gas–Calculation of methane number". This standard describes two methods for methane number determination. The first simple method is based on the linear dependence of the motor octane number (MON) on the mole content of natural gas components. This method has

some disadvantages which limit the motor octane number determination only to hydrocarbons up to butanes. In addition, it includes linear factors for carbon dioxide and nitrogen content. The hydrogen to carbon ratio (H/C) is the second method for motor octane number calculation and then the methane number. Formula for determination of motor octane number contained in ISO-TR-22304:2014 standard is given by Equation (1) [30–32]:

$$MON = 406.14 + 508.04R\text{-}173.55R^2 + 20.17R^3 \tag{1}$$

where *R*–ratio of hydrogen atoms to carbon atoms in molecule (H/C).

In addition to the methods for MN calculation mentioned above, several semi-empirical methods commonly used in the automotive industry were developed. These methods are based on experimental measurements for various natural gas compositions and include: AVL method, improved AVL methods and methods developed by engine manufacturers (Cummins (Columbus, IN, USA); Wartsilla (Helsinki, Finland), Caterpillar (Deerfield, IL, USA)). Methods developed by engine manufacturers usually operate best for the criteria specified for the engines produced by a given company. Most of these methods have disadvantages such as limited accuracy for heavier than butane hydrocarbons due to the fact empirical studies for hydrocarbon mixtures do not consider hydrocarbons heavier than butanes. Generally, the differences in obtained results (methane number determined by various methods) do not exceed 5 between minimum and maximum value [30–33].
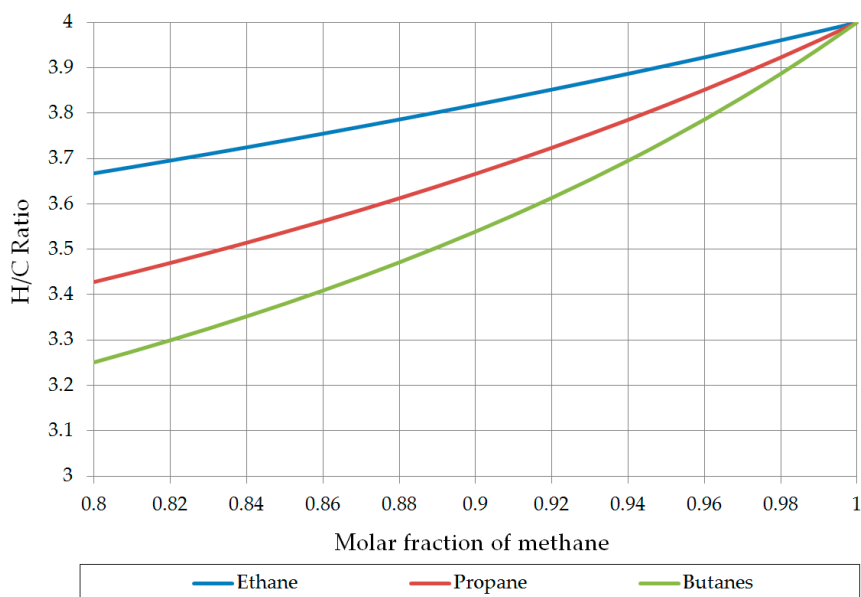
3.3. Hydrogen to Carbon (H/C) Ratio

H/C ratio is defined by the ratio of the hydrogen atoms number to carbon atoms number in a given molecule. For example, for methane it is H/C = 4, for ethane it is H/C = 3, etc. The situation becomes more complicated when a mixture of hydrocarbons has more components. Figure 1 shows the dependence of the H/C ratio on the molar fraction of methane in a binary mixture with ethane, propane or butanes. The relationship to determine the H/C ratio for multi-component hydrocarbon mixtures is presented in Equation (2):

$$R = \frac{H}{C} = \frac{\sum\limits_{i=1}^{k} x_i \cdot N_{iH}}{\sum\limits_{i=1}^{k} x_i \cdot N_{iC}} \tag{2}$$

where x_i–mole content of each component, N_i–number of atoms of hydrogen or carbon in each component molecule and *k*–number of components.

Figure 1 shows the dependence of the H/C ratio on the molar fraction of methane in a binary mixture with ethane, propane or butanes. H/C ratio was calculated with use Equation (2). Hydrogen and carbon atoms are separately summed taking into consideration the molar content of each component, next obtained sum of hydrogen atoms is divided by sum of carbon atoms in assumed mixture. High H/C ratio determines higher hydrogen molecules in the fuel. Hydrogen has the highest burning velocity among fuels weather gases or liquids. Increasing hydrogen content in the fuel combination causes that the fuel burning velocity will be higher and cleaner as burning hydrogen only produces water.

Figure 1. Hydrogen to carbon ratio (for ethane, propane and butanes) vs. methane molar fraction for binary mixtures.

3.4. Methane Number Criteria for Motor Engines

Highly developed engines are designed for MN ≥ 80 so that they can achieve high power, low emissions and excellent fuel economy. Lower methane number values can reduce the economics of gas engine applications but increase greenhouse gas emissions or decrease engine efficiency [25,29]. Considering the above issues, changes in standardization which describes the acceptable limits of methane number for internal combustion engines should be expected in near future. The current standard for natural gas combustion engines is a minimum methane number of 70 (DIN 51,624 standard). This requirement is fulfilled by liquefied natural gases from most of the world's sources (except Australia, Libya–similarly to the Wobbe index criterion).

The current world trends related to maximizing the engine energy efficiency and limiting emissions into the natural environment increase the probability of tightening the methane number criteria for internal combustion engines. The first proposals to tighten these requirements appeared already in 2011 and were submitted by the European Commission and the European association of engine manufacturers Euromot [34]. After considering methane number as a gas quality parameter, the proposal (Euromot) specified that the value of methane number should be as high as possible in order to avoid incorrect operation of internal combustion engines and increase their efficiency. Euromot recommends in its proposal that the methane number of natural gas as engine fuel should not be lower than 80.

4. Methane Number Determination for Different LNG Compositions

4.1. Assumptions

The main purpose of this work is to present the dependence of changes in the value of methane number on the content of individual components in liquefied natural gas.

Fifteen sets of exemplary LNG compositions were selected for analysis, in which the content of individual components is described by a linear relationship (Table 5). In these sets of compositions, binary systems methane-ethane, methane-propane, methane-butanes were also presented for comparison purposes. Linear relationships describing the variability of natural gas compositions are presented in Table 4. In addition to the three comparative binary systems, the relationships for the C_1-C_2-C_3, C_1-C_2-C_3-C_4, C_1-C_2-C_3-C_4-C_5 systems are presented as main subject of prepared analysis.

LNG composition containing nitrogen was also presented - for comparative purposes to determine the differences in obtained quality parameters of the Wobbe index and the methane number.

Table 5. Assumed sets of liquefied natural gas compositions (molar composition).

Set No.	Methane C_1	Ethane C_2	Propane C_3	Butanes C_4	Pentanes C_5	Nitrogen N_2
1	$(100 - n)\%$	$0.75\,n\%$	$0.25\,n\%$	-	-	-
2	$(100 - n)\%$	$0.6\,n\%$	$0.4\,n\%$	-	-	-
3	$(100 - n)\%$	$0.8\,n\%$	$0.15\,n\%$	$0.05\,n\%$	-	-
4	$(100 - n)\%$	$0.65\,n\%$	$0.25\,n\%$	$0.1\,n\%$	-	-
5	$(100 - n)\%$	$0.55\,n\%$	$0.35\,n\%$	$0.1\,n\%$	-	-
6	$(100 - n)\%$	$0.6\,n\%$	$0.25\,n\%$	$0.15\,n\%$	-	-
7	$(100 - n)\%$	$0.45\,n\%$	$0.35\,n\%$	$0.2\,n\%$	-	-
8	$(100 - n)\%$	$0.7\,n\%$	$0.2\,n\%$	$0.07\,n\%$	$0.03\,n\%$	-
9	$(100 - n)\%$	$0.6\,n\%$	$0.25\,n\%$	$0.1\,n\%$	$0.05\,n\%$	-
10	$(100 - n)\%$	$0.6\,n\%$	$0.2\,n\%$	$0.12\,n\%$	$0.08\,n\%$	-
11	$(100 - n)\%$	$0.5\,n\%$	$0.25\,n\%$	$0.15\,n\%$	$0.1\,n\%$	-
12	$(100 - n)\%$	$n\%$	-	-	-	-
13	$(100 - n)\%$	-	$n\%$	-	-	-
14	$(100 - n)\%$	-	-	$n\%$	-	-
15	$(99 - n)\%$	$0.8\,n\%$	$0.15\,n\%$	$0.05\,n\%$	-	1%

4.2. Methane Number and Component Content

The assumed sets of liquefied natural gas (LNG) compositions were analyzed to determine the most significant aim of this paper, i.e., to determine the dependence of the methane number value on the content of individual components. Figures 2–5 show the dependence of the methane number (calculated using the H/C ratio method) on the methane, ethane, propane and butanes content in liquefied natural gas. For methane, the methane number criterion above 80 was achieved for selected composition sets for methane content above 92–95%mol excluding methane-ethane binary systems (above 90.5%mol C_1) and methane-butanes binary systems (above 97%mol C_1). For ethane, the methane number is higher than 80 for its maximum content of 2.5–6 mol%, and especially for the binary system C_1-C_2 maximum 9.5%mol. In liquefied natural gas, the propane content should not exceed 1.2–2.8%mol, and the butane content should not exceed 0.4–1.2%mol, so that the methane number is higher than 80. If the methane number criterion is lowered to 70, the methane content may be reduced to a minimum 86.3%mol and in the case of a binary system with ethane up to 83 mol%. In such cases the ethane content can be increased to 4.3–10.8%mol and for a binary system with methane up to 17 mol%. The propane content for the methane number criterion 70 should not exceed 2–5%mol, and the butane content 0.7–1.9%mol. Specification of the methane number values criteria allows to approximately determine the maximum content of heavier hydrocarbons and the minimum content of methane for various LNG compositions. Unfortunately, on basis of different LNG compositions, it is only possible to approximate the maximum content of individual components and the minimum content of methane for a given criterion of methane number. The obtained value ranges for various combinations of composition should be confronted with other LNG quality parameters.
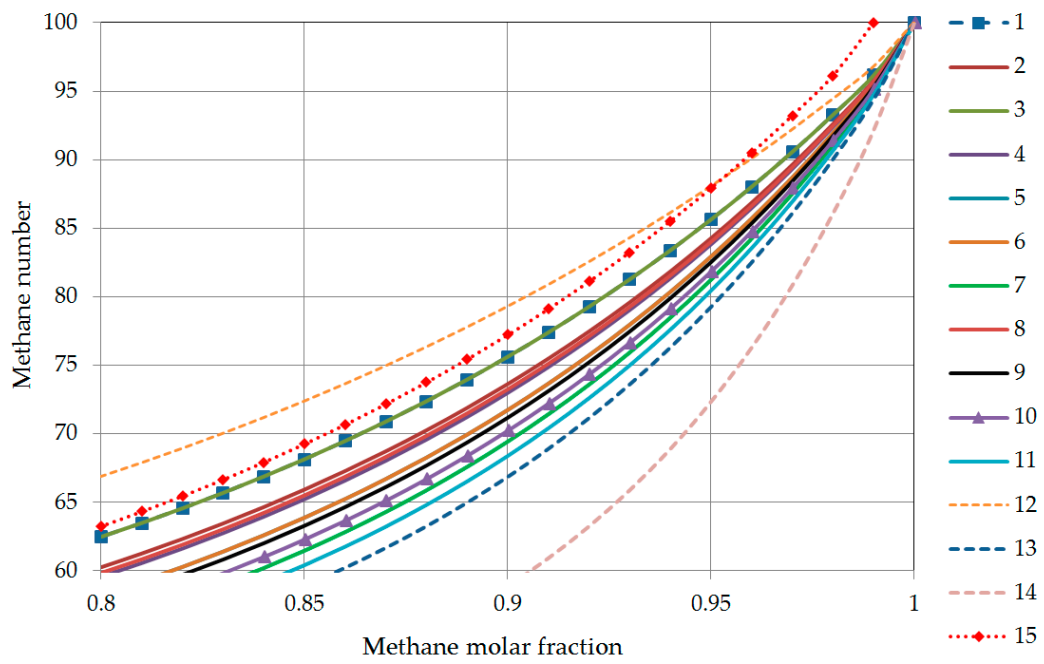
Figure 2. Methane number as function of methane molar fraction in analyzed LNG composition sets.
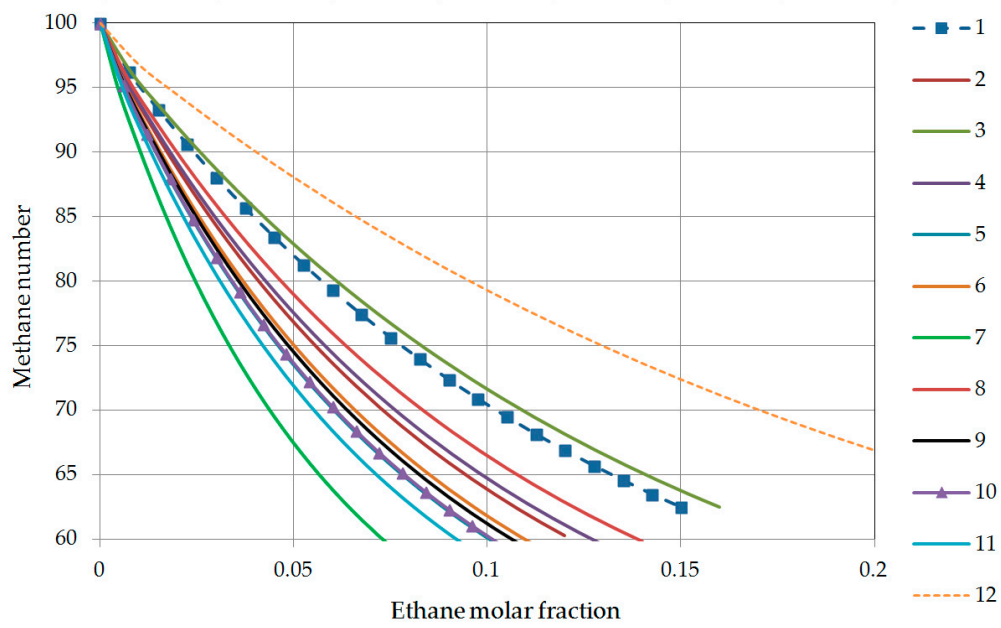

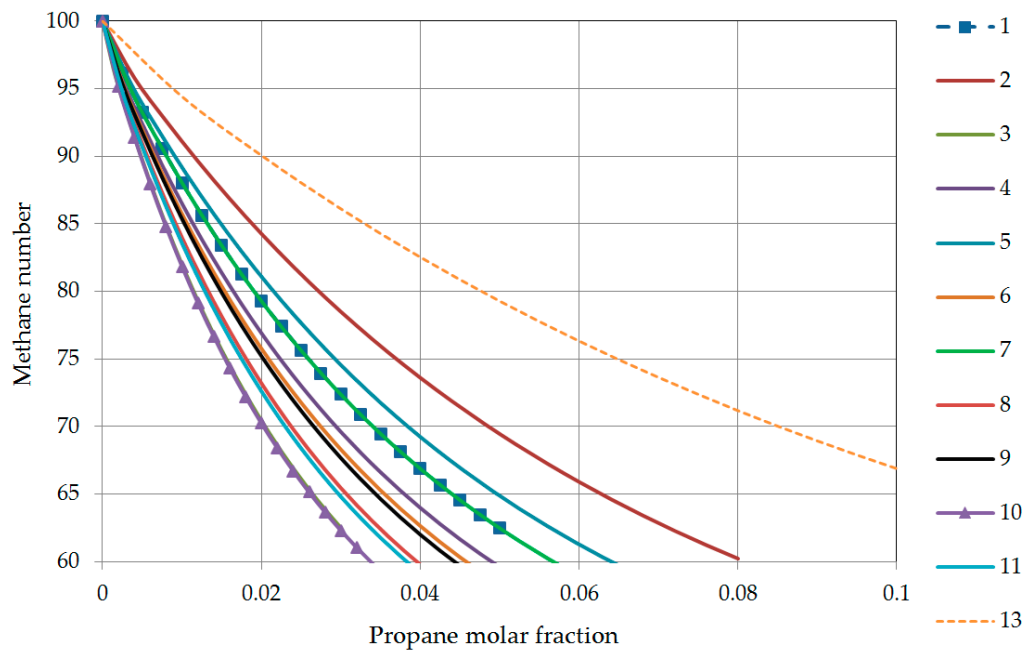**Figure 3.** Methane number as function of ethane molar fraction in analyzed LNG composition sets.

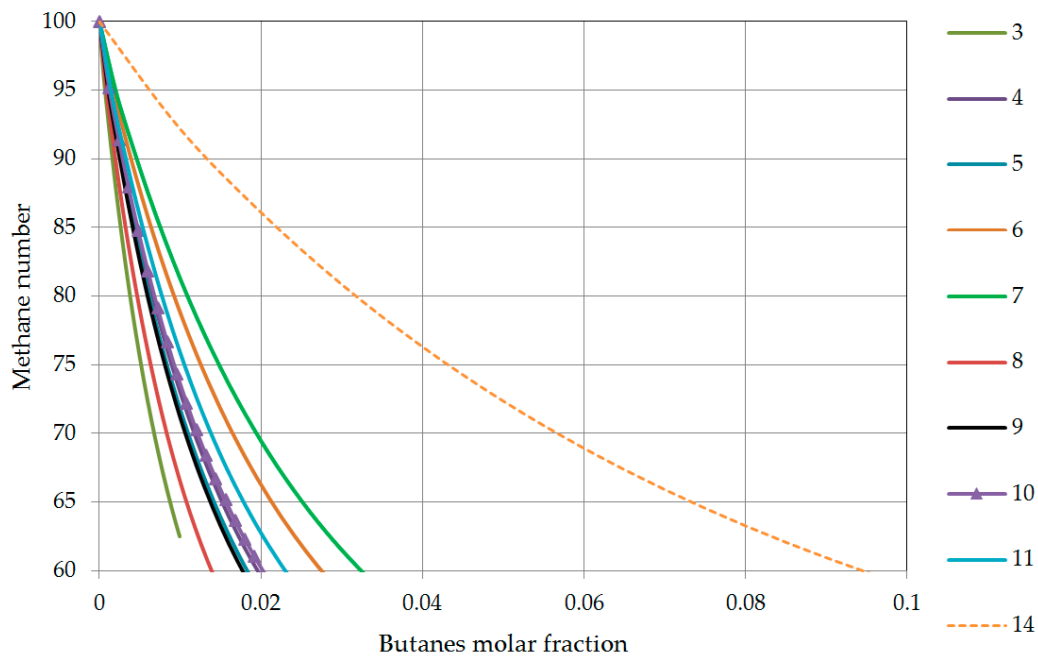**Figure 4.** Methane number as function of propane molar fraction in analyzed LNG composition sets.

Figure 5. Methane number as function of butanes molar fraction in analyzed LNG composition sets.

Figure 6 presents the relation between the ratio of hydrogen to carbon atoms in molecule and methane content for given sets of liquefied natural gas compositions. Due to the fact that the methane number is determined in one of the methods based on the value of H/C ratio, the dependence of this coefficient on the molar content of methane is similar to the dependence of the methane number on the content of methane in the LNG composition. The H/C ratio for a methane number above 80 should be a minimum of 3.83 and for a methane number above 70 - 3.71.
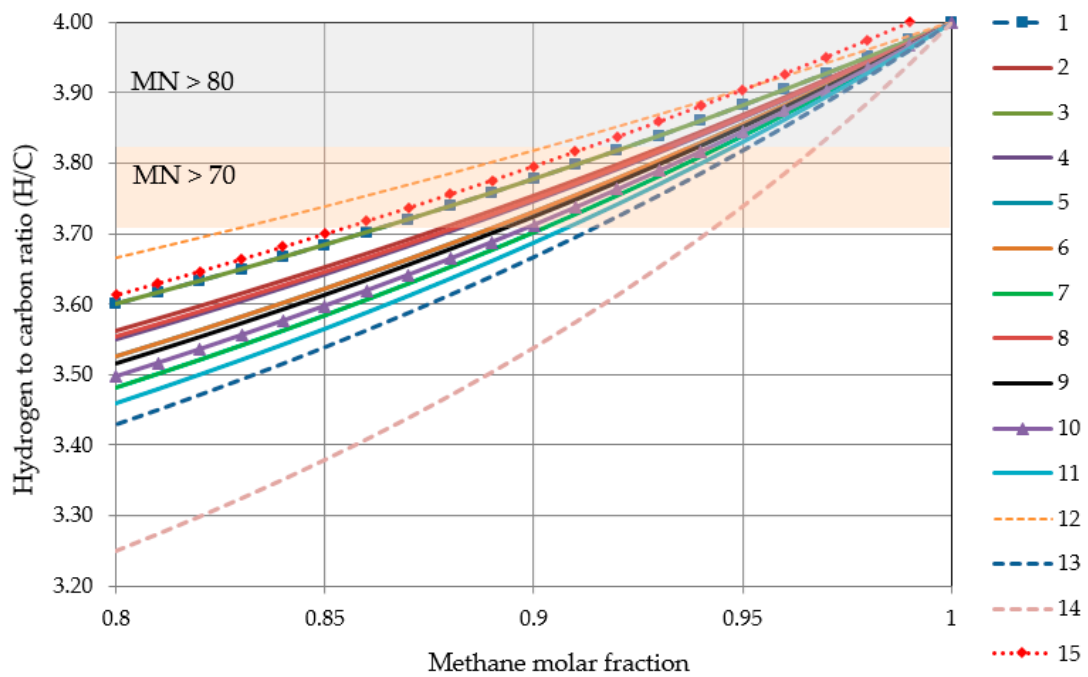
Figure 6. Hydrogen to carbon ratio vs. molar fraction of methane for assumed LNG compositions sets.

Figures 7 and 8 show the detailed dependence of the methane number on the molar fraction of individual components of LNG for selected sets of liquefied natural gas compositions (sets 2 and 7) with areas marked for the methane number values criteria >80 and >70. For set 2, the limits of contents of individual components for the methane number 70 criterion are: C_1–minimum 87.8%mol, C_2–maximum 7.4%mol, C_3–4.8% mol, and for MN > 80: minimum C_1–93.2%mol, maximum C_2 4.1% mol, max C_3 2.7%mol. Detailed component limit contents for individual sets of compositions are presented in the Tables 6 and 7.
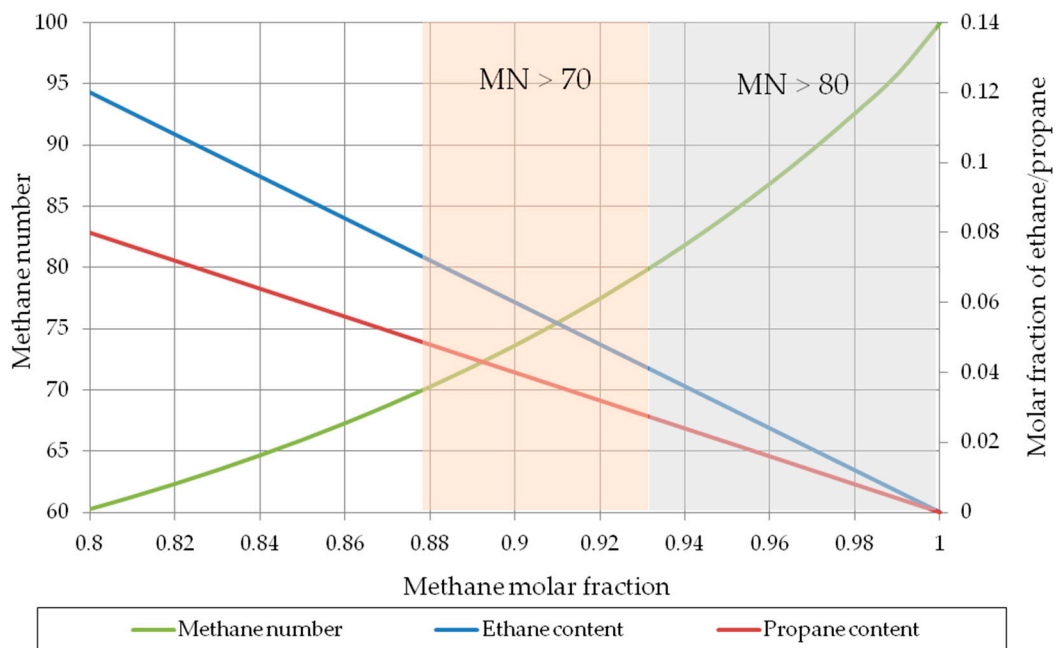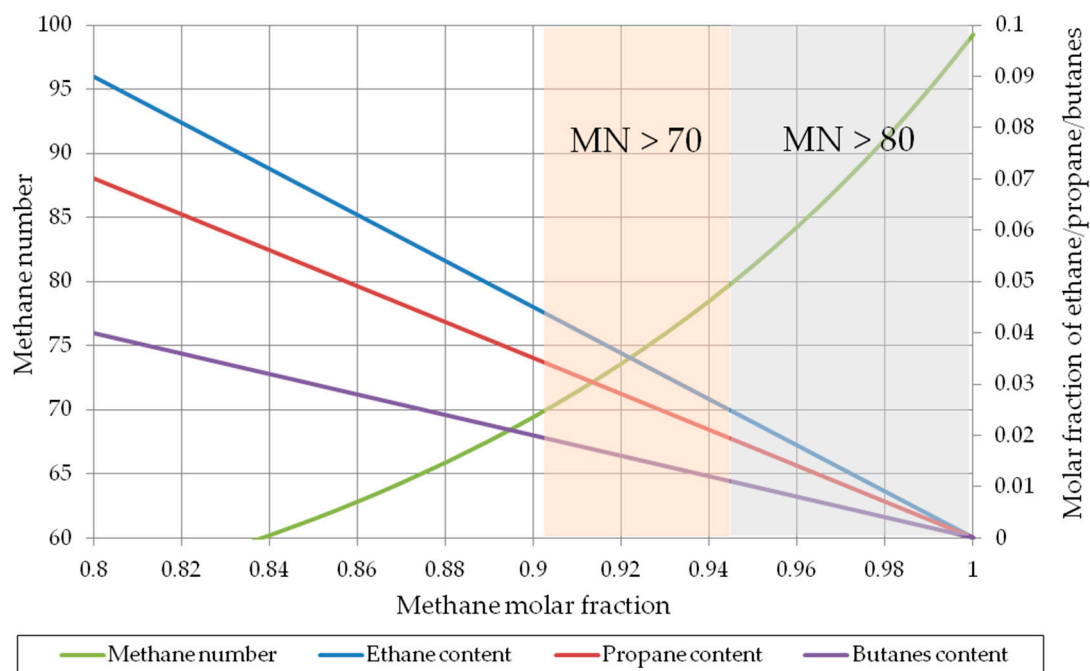

Figure 7. Methane number as function of methane and other components molar fraction for LNG composition set 2.

Figure 8. Methane number as function of methane and other components molar fraction for LNG composition set 7.

Table 6. Limit contents of methane and other components for methane number equal to 80.

Set No.	Methane C_1	Ethane C_2	Propane C_3	Butanes C_4	Pentanes C_5	Nitrogen N_2
	Min %mol	Max %mol	Max %mol	Max %mol	Max %mol	%mol
1	92.5	5.6	1.9	-	-	-
2	93.2	4.1	2.7	-	-	-
3	92.3	6.2	1.2	0.3	-	-
4	93.5	4.2	1.7	0.6	-	-
5	94.0	3.3	2.1	0.6	-	-
6	94.0	3.6	1.5	0.9	-	-
7	94.5	2.5	1.9	1.1	-	-
8	93.3	4.7	1.3	0.5	0.2	-
9	94.0	3.6	1.5	0.6	0.3	-
10	94.3	3.4	1.1	0.7	0.5	-
11	95.0	2.5	1.3	0.7	0.5	-
12	90.5	9.5	-	-	-	-
13	95.2	-	4.8	-	-	-
14	96.8	-	-	3.2	-	-
15	91.5	6.1	1.1	0.3	-	1.0

The performed analysis showed that an increase in heavier hydrocarbons content causes an increase in the minimum methane content limit for the assumed methane number criterion. Also, appearance of a new heavier component in the LNG composition causes a significant reduction in methane number. Therefore, in order to maintain the assumed criteria for the value of methane number, it is necessary to increase the minimum limit of methane content in the LNG composition. For instance, if the LNG composition contains hydrocarbons not heavier than propane, the minimum required methane content oscillates near 92–93%mol for the criterion of methane number equal to 80. If the LNG contains butanes, the minimum required methane content for this criterion usually increases to 93–94%mol, although combinations are possible in which the minimum methane limit decreases below 93%mol in particular for a high ratio of ethane to heavier components contents. The appearance of trace amounts of pentanes in the LNG composition means that the criterion of the

minimum methane number equal to 80 can be maintained usually for minimum methane content in the range of 94–95 mol%, with special combinations up to minimum 93.5%mol.

Table 7. Limit contents of methane and other components for methane number equal to 70.

Set No.	Methane C_1	Ethane C_2	Propane C_3	Butanes C_4	Pentanes C_5	Nitrogen N_2
	Min %mol	Max %mol	Max %mol	Max %mol	Max %mol	%mol
1	86.5	10.2	3.3	-	-	-
2	87.8	7.4	4.8	-	-	-
3	86.4	10.8	2.0	0.8	-	-
4	88.2	7.7	3.0	1.1	-	-
5	89.0	6.1	3.8	1.1	-	-
6	89.0	6.6	2.8	1.6	-	-
7	90.5	4.3	3.3	1.9	-	-
8	88.0	8.4	2.4	0.8	0.4	-
9	89.5	6.3	2.6	1.1	0.5	-
10	90.0	6.0	2.0	1.2	0.8	-
11	91.0	4.5	2.3	1.3	0.9	-
12	83.0	17.0	-	-	-	-
13	91.5	-	8.5	-	-	-
14	94.3	-	-	5.7	-	-
15	85.5	10.8	2.0	0.7	-	1.0

Similar results were obtained for the criterion of methane number equal to 70. The minimum methane content oscillates from 86%mol (for the LNG composition including only methane, ethane and propane) to 91%mol (with trace amounts of pentanes). These results do not apply to binary systems and nitrogen containing compositions.

4.3. Wobbe Index and Methane Number

The basic quality criterion used in the natural gas industry is the Wobbe Index, which is the ratio of the calorific value determined for one cubic meter of natural gas to square root of its relative density, under the same reference conditions. The Wobbe Index exists in two forms related to the heat of combustion (gross/higher heating value) and calorific value (lower heating value) and they are described by the Equations (3) and (4) respectively:

$$WI_U = \frac{HHV}{\sqrt{d}} \tag{3}$$

$$WI_L = \frac{LHV}{\sqrt{d}} \tag{4}$$

where WI_U–upper Wobbe Index, MJ/m_n^3, WI_U–lower Wobbe Index, MJ/m_n^3, *HHV*–gross heating value, MJ/m_n^3, *LHV* –lower heating value, MJ/m_n^3 and *d*–specific density.

The higher heating value (HHV) is determined by bringing all the products of combustion back to the original pre-combustion temperature, and in particular condensing any vapor produced. Lower heating value (LHV) is determined by subtracting the heat of vaporization of the water from the higher heating value. The energy required to vaporize the water therefore is not released as heat.

In the performed analysis, the relation of the methane number was referred to the upper Wobbe Index as the main quality parameter of natural gas. Figure 9 shows the dependence of the Wobbe Index on the molar fraction of methane for fifteen tested sets of natural gas compositions. The Wobbe Index increases with a decrease in the molar fraction of methane and with an increase in the molar fraction of heavier hydrocarbons. For composition sets containing pentane and butanes, the increase in Wobbe Index is higher. It is clearly presented for the binary mixture methane-butanes (Set 14), where the butanes content increase more rapidly.
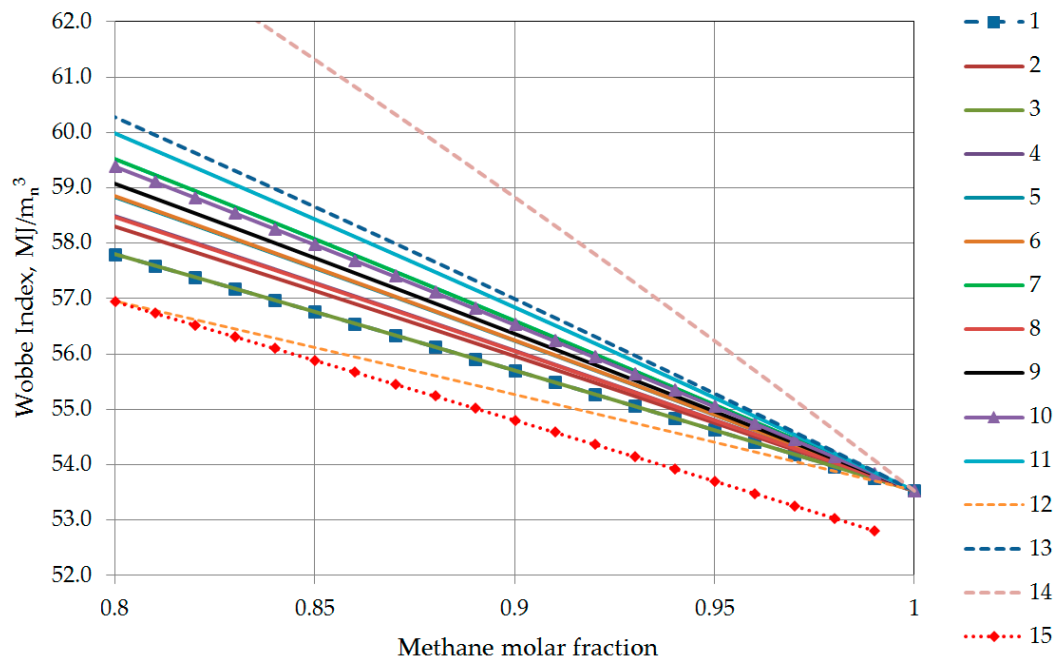
Figure 9. Wobbe Index as a function of methane molar fraction for tested sets of LNG compositions.

When linking the Wobbe Index to the methane number, a convergent relationship can be seen for all LNG composition sets containing only hydrocarbons, so for LNG with a composition that contains only hydrocarbons, you can link approximately a value of the methane number for a specific Wobbe Index value. For the methane number equal to 80 the maximum value of the Wobbe Index is approximately 55.2 MJ/m_n^3 and for the minimum methane number 70 56.6 MJ/m_n^3. This relationship does not apply to LNG compositions containing components other than hydrocarbons, e.g., nitrogen, which reduces the Wobbe Index, but does not cause changes in the methane number value for most correlations (Figure 10).

Analysis of compositions of liquefied natural gas available from world exporters, showed that LNG from most sources achieved the criterion of methane number higher than 70 (among the analyzed sources, only LNG from Libya and Australia NWS had methane numbers lower than 70) [20]. In the case of tightening the methane number criterion to 80, the number of LNG sources for which the composition achieves this criterion decreases significantly (Figure 11).

The theoretical results obtained during the analysis were superimposed on the operational conditions of the LNG unloading and storage terminal. The changes direction in content of components of liquefied natural gas in storage tank as a function of time was examined. During the analyzed period, LNG was delivered to the terminal from a source other than before. The new delivery was characterized by a higher methane content (approx. 96 mol%) compared to the 93%mol in previously stored LNG. The change in methane content resulted in a characteristic increase in methane number (Figure 12).

Figure 10. Wobbe Index as a function of methane number.
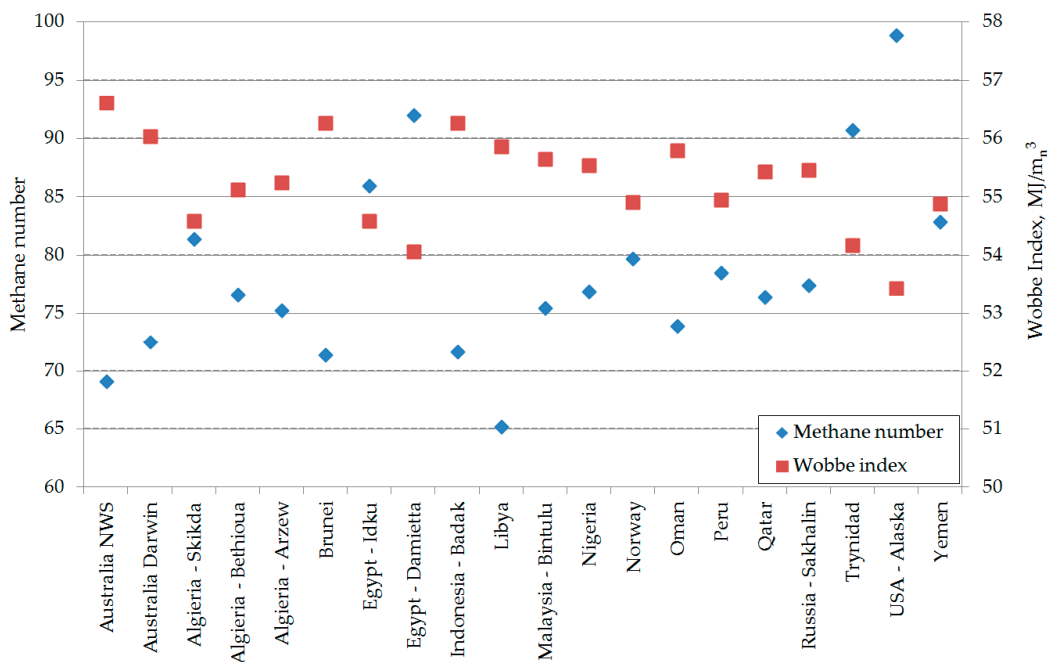
Figure 11. Methane number and Wobbe Index of LNG from different sources. Own calculations based on compositions from [20].

In analyzed operational data from the LNG storage terminal, a decrease in the methane value was also observed, which was caused by the increased content of ethane in the LNG composition. The increased molar fraction of ethane is reflected in the higher Wobbe Index value. Observing the curves describing the the methane number and Wobbe Index values it should be noted that they are approximately a mirror reflection of each other (Figure 13). The increase in methane content observed during LNG delivery from other source reduces the Wobbe Index.
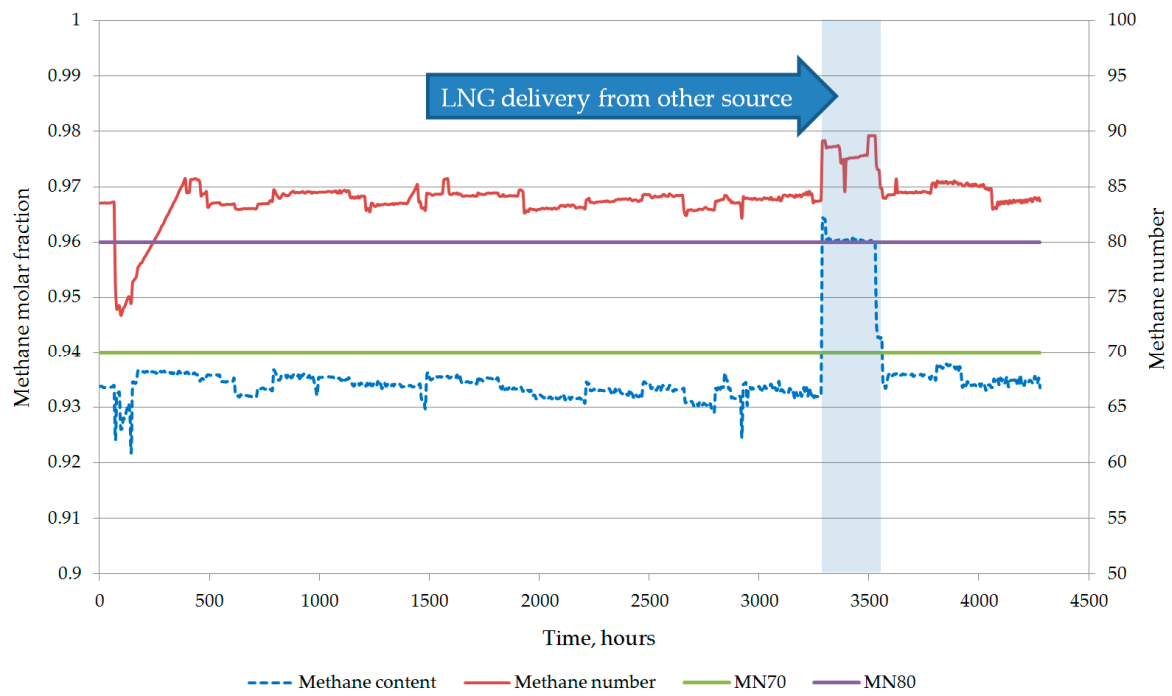
Figure 12. Methane number and methane content changes in exemplary operational conditions at LNG Terminal.
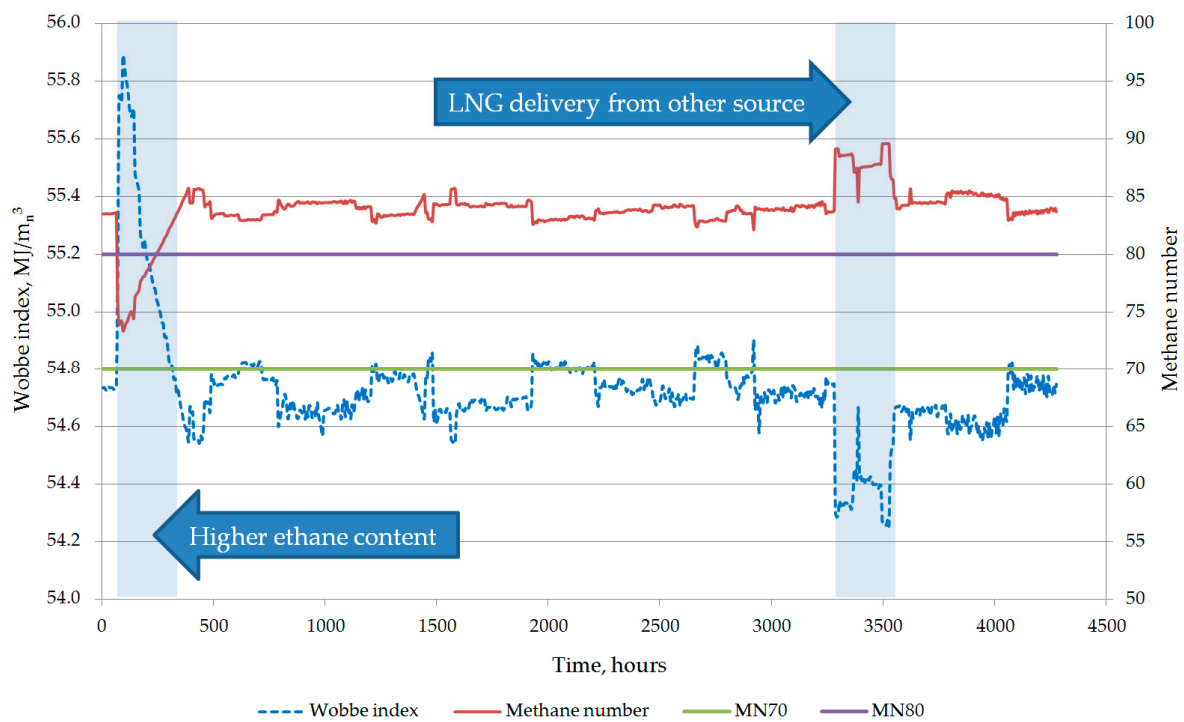
Figure 13. Methane number and Wobbe Index changes in exemplary. Operational conditions at LNG Terminal.

4.4. Nitrogen Content Impact on Methane Number

Nitrogen as a component of natural gas is only a ballast without energy value. Similarly, the presence of nitrogen in liquefied natural gas is undesirable because of its characteristic properties. Nitrogen evaporates from LNG as first due to lower boiling point temperature than methane. For the moment, the content of methane in the liquid phase increases, while in the gas phase at the beginning of evaporation process nitrogen can reach up to 50% of the evaporated gas.

The increased content of nitrogen can lead to instability of the LNG storage process and in some range contribute to the phenomenon referred to the stratification of stored liquefied natural gas into two layers of different densities, which might lead to a dangerous roll-over phenomenon. Roll-over should be understood as a very rapid evaporation of methane from the LNG storage tank. It is caused by rapid mixing of the stored LNG which occurs after density equalization of both previously stable layers inside the tank. For this reason, it is recommended that the nitrogen content should not exceed 1% in liquefied natural gas.

Impact of nitrogen on the natural gas quality parameters was analyzed for selected compositions (set 3–0% nitrogen and set 15–1% nitrogen) and intermediate variants with the molar fraction of nitrogen 0.3% and 0.6%, the contents of other hydrocarbons change analogously as for sets 3 and 15. Nitrogen content increase in the LNG composition to 1% causes an increase in the methane number value as a function of methane molar fraction (Figure 14). This change occurs due to the fact that nitrogen as a part of the system does not reduce the ratio of hydrogen atoms to carbon atoms (H/C). The Wobbe Index for the assumed value of methane number decreases by about 0.7 MJ/m$_n^3$ due to nitrogen content increase to 1 mol% (Figure 15).

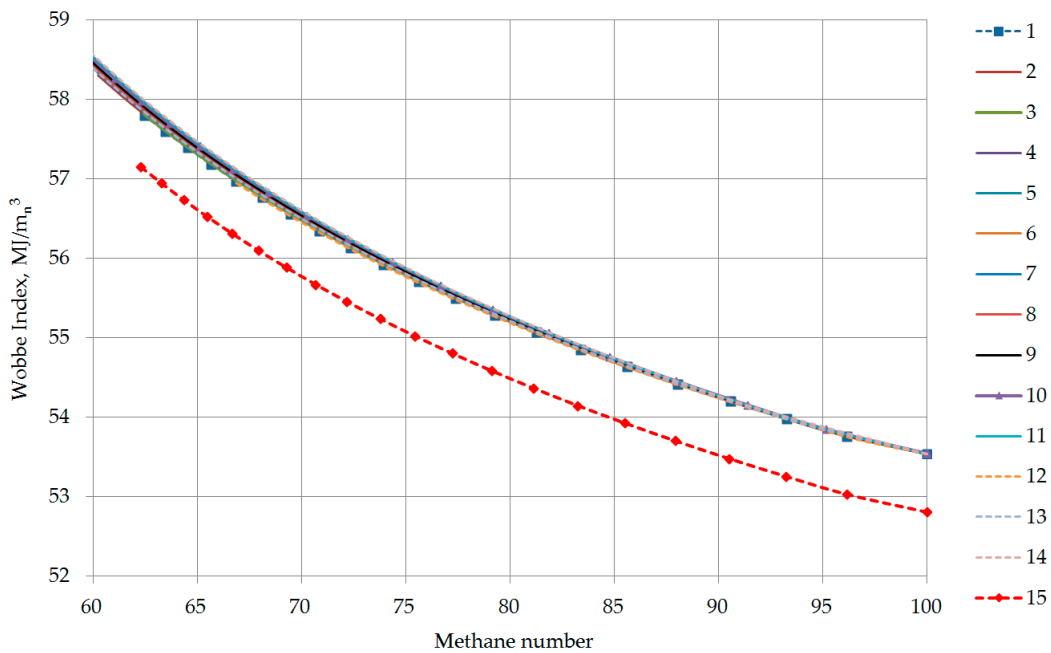**Figure 14.** Methane number as function of methane molar fraction for composition sets which contains nitrogen.
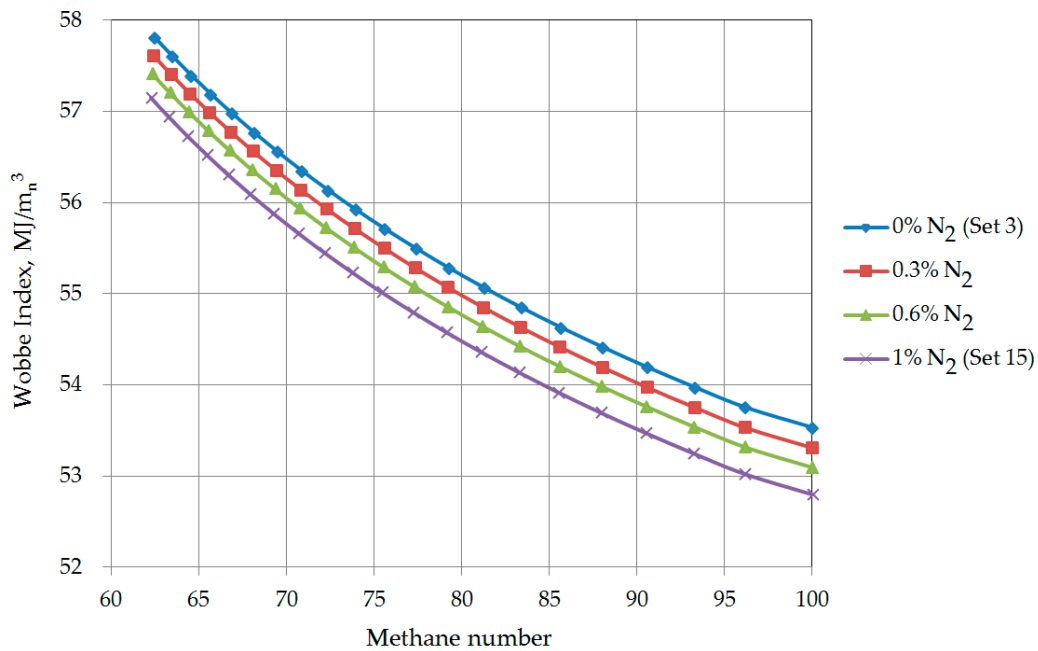
Figure 15. Wobbe Index as function of methane number for composition sets, which contains nitrogen.
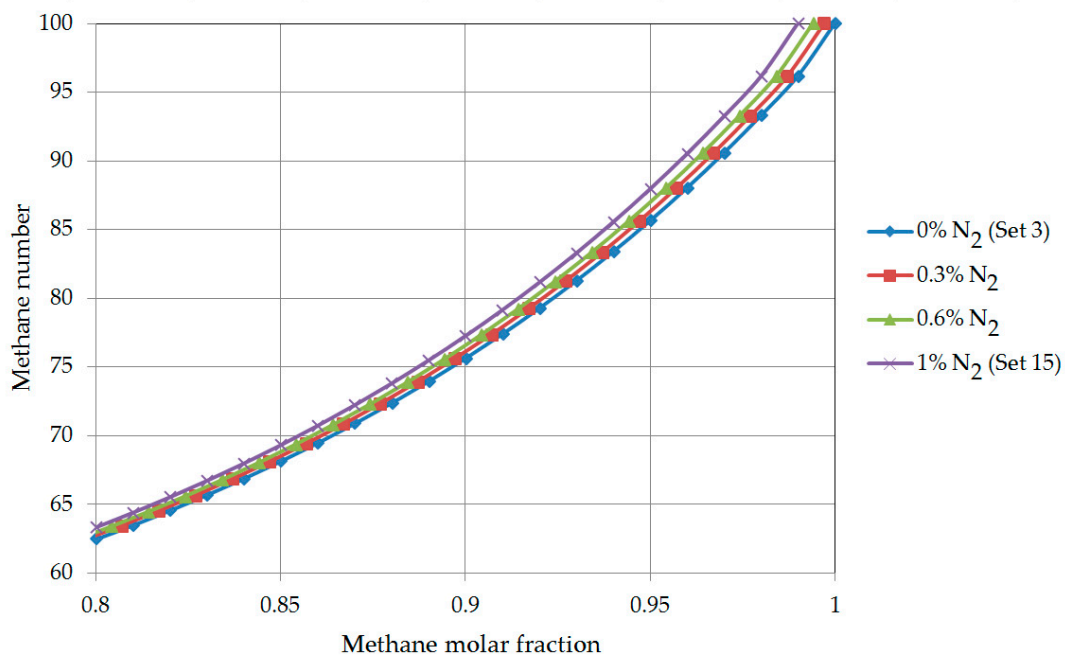
4.5. Composition Measurement Uncertainty Impact

Previous studies on LNG has indicated the uncertainty which results from the sampling methodology (to be able to determine composition of LNG, sample need to be regasified and tested in the laboratory), and the methodology to determine the content of individual components (most often by gas chromatography), which are 0.3% and 0.2% respectively [35]. Considering the processes at the LNG terminal and the methodology of the measurement (calibration gases in gas chromatography), the total uncertainty for the methane content in LNG which contains approx. 90%mol of methane is approx. 0.5–0.6 %mol. Using the same procedures and methodologies for other hydrocarbons uncertainties are lower [35]. A possible uncertainty in the measurement of the LNG composition may affect the value of the methane number, especially if the content of heavier components is lower than the actual one. In the presented analysis, the methane number and Wobbe index were determined for the assumed composition which did not include measurement uncertainties. The change of LNG component content results from measurement uncertainties and automatically changes the value of the methane number or the Wobbe index. Therefore, the measurement uncertainties do not burden the method of methane number calculation with an error, but only the input data for the calculations, so the methane number uncertainty results directly from the assumed uncertainties related to the LNG composition.

5. Discussion

The results show that to determine the composition of liquefied natural gas for the assumed methane number criteria require additional criteria to describe the exact limit content. The criterion of methane number equal to 80 means that for various combinations of LNG compositions, the minimum methane content may vary from 92.3% to 95.0%mol. The maximum content of other hydrocarbons are in the following ranges: ethane 2.5–6.2%mol, propane 1.1–2.7% mol, butanes up to 0.7% mol, pentanes up to 0.5% mol. The obtained ranges, despite their precise determination, are still quite wide, therefore it is necessary to introduce the simultaneous application of the most popular quality criterion for natural gas, which is the Wobbe Index. For a methane number equal to 80, the Wobbe Index should not exceed 55.2 MJ/m_n^3. A significant share of the liquefied natural gas available on the global market does not meet this requirement (MN > 80). The obtained results from the analyzed exemplary and real

compositions indicate that methane number criterion (MN > 80) may eliminate LNG supplies from some regions. It should also be noted that a large part of the LNG available on the global gas market has a methane number slightly lower than the proposed criterion MN > 80. In this case, three solutions are possible: increasing the methane number of a given gas by removing heavier hydrocarbons from its composition before liquefaction, changing operational characteristics of the liquefaction plant or consider methane number lower value for this criterion.

For the criterion of methane number equal to 70, it is possible to specify wider ranges of the maximum content of individual components and the minimum content of methane which may vary from 86.4% to 91.0% mol. Maximum hydrocarbon contents are accepted in following ranges: ethane 4.3–10.8% mol, propane up to 2.0–4.8% mol, butanes up to 1.6% mol, pentanes up to 0.9% mol. Obtained ranges are wider than for criterion of MN > 80. Therefore, it is necessary to describe a supplementary criterion of the Wobbe Index, which in this case should have a maximum value of 56.6 MJ/m_n^3. LNG from most world exporters achieve the milder methane number criterion (MN > 70), however it should be noted that engines designed for this criterion will not work with maximum efficiency and will generate higher emissions. The discussion with the results presented in other publications is difficult because the scope of the literature regarding the methane number as a quality parameter of LNG is very limited.

6. Conclusions

Engines can use natural gas with wide range of quality as a fuel The methane number of liquefied natural gas is a very important parameter in the power production process in gas engine which describes the knocking characteristic of fuel. Generally, engines which use natural gas as a fuel to produce maximum power need a minimum MN value of 80. Lower methane numbers should be improved by reducing the molar contents of heavier hydrocarbons, especially butanes and pentanes. Fluctuation of the fuel quality may have a significant impact on engine performance and produced greenhouse gases emissions. Highly developed presently produced engines are designed for methane number values above 80 (a criterion about to be introduced in the European Union) to achieve a high power density, low greenhouse gases emission levels and excellent fuel efficiency. To ensure normal operation conditions for gas engines the knocking characteristic (methane number value range) should be given for natural gas. Specific criteria for the quality of natural gas as motor fuel should guarantee the safe, reliable and cost-effective operation of the engine, which should also be environmentally friendly through low greenhouse gas emissions.

A higher natural gas methane number means higher engine efficiency and lower emissions. Unfortunately, for a significant part of the liquefied natural gas available on the global market, the methane number criterion of 80 is impossible or difficult to achieve. The rules and methods for calculating the methane number should be defined and they should be standardized for the entire global natural gas market. Due to different combinations of individual natural gas components content, it is impossible to indicate specific limit contents for each component for the criterion of methane number of a given value. There are two possible solutions to this situation. Firstly, average limit contents (Table 8) for all components can be accepted as a compromise. There is a possibility for some combinations of LNG compositions for which accepted content limits may be imprecise. A second solution involves the introduction of a complementary criterion. The most reasonable supplementary criterion probably will be the Wobbe Index. The simultaneous application the Wobbe Index criterion in addition to methane number allows to define specific limit values of individual LNG components for a given case.

Table 8. Proposed compromise limit contents of LNG components for various methane number criteria.

Component	MN > 70	MN > 80
	%mol	%mol
Methane	>88.7	>93.65
Ethane	<7.55	<4.35
Propane	<3.4	<1.9
Butanes	<0.8	<0.4
Pentanes	<0.45	<0.2

Nomenclature

AVL	Anstalt für Verbrennungskraftmaschinen List, the world's largest independent company for the development, simulation and testing of engine systems
HHV	gross heating value, MJ/m$_n^3$,
LHV	lower heating value, MJ/m$_n^3$,
LNG	liquefied natural gas
MON	motor octane number
MN	methane number
WI	Wobbe Index
WI$_U$	upper Wobbe Index, MJ/m$_n^3$,
WI$_U$	lower Wobbe Index, MJ/m$_n^3$,
R	ratio of hydrogen atoms to carbon atoms in molecule (H/C)
d	specific density,
k	number of components
N$_i$	number of atoms of hydrogen or carbon in each component molecule,
x$_i$	mole content of each component

References

1. Tjojudo, D.H.; Kartohardjono, S. Methane number improvement of gas from LNG regasification unit. *E3s Web Conf.* **2018**, 67. [CrossRef]
2. Palmer, G. Methane number. *J. Nat. Gas Eng.* **2019**, *2*, 134. [CrossRef]
3. Gieseking, B.; Brown, A.S. Novel algorithm for calculating the methane number of liquefied natural gas with defined uncertainty. *Fuel* **2016**, *185*, 932–940. [CrossRef]
4. Gupta, S.K.; Mittal, M. Predicting the methane number of gaseous fuels using an artificial neural network. *Biofuels* **2019**. [CrossRef]
5. Melenshek, M.; Olsen, D.B. Methane number testing of alternative gaseous fuels. *Fuel* **2009**, *88*, 650–656. [CrossRef]
6. Ryan, T.W., III; Callahan, T.J.; King, S.R. Engine knock rating of natural gases—Methane number. *J. Eng. Gas Turbines Power.* **1993**, *115*, 769–776. [CrossRef]
7. Heather, T.; James, J.C.; James, J.W. Natural gas as a marine fuel. *Energy Policy* **2015**, *87*, 153–167.
8. Flynn, P.C. Commercializing an alternate vehicle fuel: Lessons learned from natural gas for vehicles. *Energy Policy* **2002**, *30*, 613–619. [CrossRef]
9. Nijboer, M. *The Contribution of Natural Gas Vehicles to Sustainable Transport*; International Energy Agency: Paris, France, 2010.

10. De Carvalho, A.V., Jr. Natural gas and other alternative fuels for transportation purposes. *Energy* **1985**, *10*, 187–215. [CrossRef]

11. Pfoser, S.; Schauer, O.; Costa, Y. Acceptance of LNG as an alternative fuel: Determinants and policy implications. *Energy Policy* **2018**, *120*, 259–267. [CrossRef]

12. Keith, D.R.; Struben, J.; Naumov, S. The diffusion of alternative fuel vehicles: A generalized model and future research agenda. *J. Simul.* **2020**. [CrossRef]

13. Khan, M.I. Policy options for the sustainable development of natural gas as transportation fuel. *Energy Policy* **2017**, *110*, 126–136. [CrossRef]

14. Lopez Alvarez, J.A.; Buijs, P.; Kilic, O.A.; Vis, I.F.A. An inventory control policy for liquefied natural gas as a transportation fuel. *Omega* **2020**, *90*, 101985. [CrossRef]

15. Chen, Z.; Zhang, F.; Xu, B.; Zhang, Q.; Liu, J. Influence of methane content on a LNG heavy-duty engine with high compression ratio. *Energy* **2017**, *128*, 329–336. [CrossRef]

16. Karavalakis, G.; Hajbabaei, A.; Jiang, Y.; Yang, J.; Johnson, K.C.; Cocker, D.R.; Durbin, T.D. Regulated, greenhouse gas, and particulate emissions from lean-burn and stoichiometric natural gas heavy-duty vehicles on different fuel compositions. *Fuel* **2016**, *175*, 146–156. [CrossRef]

17. Kakaee, A.-H.; Paykani, A.; Ghajar, M. The influence of fuel composition on the combustion and emission characteristics of natural gas fueled. *Renew. Sustain. Energy Rev.* **2014**, *38*, 64–78. [CrossRef]

18. Vallabhunia, S.K.; Leleb, A.D.; Patela, V.; Lucassena, A.; Moshammera, K.; AlAbbadc, M.; Farooqc, A.; Fernandesa, R.X. Autoignition studies of liquefied natural gas (LNG) in a shock tube and a rapid compression machine. *Fuel* **2018**, *232*, 423–430. [CrossRef]

19. Hwang, S.-K. Methane number control of fuel gas supply system using combined cascade/feed-forward control. *J. Mar. Sci. Eng.* **2020**, *8*, 307. [CrossRef]

20. International Group of LNG Exporters (GIIGNL), Annual Report 2018, International Group of LNG Exporters. 2018. Available online: https://giignl.org/sites/default/files/PUBLIC_AREA/Publications/rapportannuel-2018 pdf.pdf (accessed on 28 May 2020).

21. U.S. Energy Information Administration, EIA Report, Annual Energy Outlook 2020, U.S. Energy Information Administration. 2020. Available online: https://www.eia.gov/outlooks/aeo/pdf/AEO2020%20Full%20Report .pdf (accessed on 29 May 2020).

22. International Energy Agency. *World Energy Outlook: Are We Entering a Golden Age of Gas?* International Energy Agency: Paris, France, 2011.

23. BP. *Statistical Review of World Energy*; BP: London, UK, 2016.

24. International Gas Union: World LNG Report-2019 Edition, International Gas Union. 2019. Available online: https://www.igu.org/app/uploads-wp/2019/06/IGU-Annual-Report-2019_23.pdf (accessed on 3 June 2020).

25. Liu, J.; Dumitresu, C.E. Numerical investigation of methane number and Wobbe index effects in lean-burn natural gas spark-ignition combustion energy. *Fuels* **2019**, *33*, 4564–4574. [CrossRef]

26. Mozgovoy, A.; Burmeister, F.; Albus, R. Contribution of LNG use for the low calorific natural gas network's safe and sustainable operation. *Energy Procedia* **2015**, *64*, 83–90. [CrossRef]

27. Klinkenbijl, J.; Grootjans, H.; Rajani, J. Best practice for deep treating sour natural gases (to LNG and GTL). In Proceedings of the GasTech 2005 Conference & Exhibition, Bilbao, Spain, 14–17 March 2005.

28. Mokhatab, S.; Mak, J.Y.; Valappil, J.V.; Wood, D.A. *Handbook of Liquefied Natural Gas*; Gulf Professional Publishing (Elsevier Inc.): Houston, TX, USA, 2014.

29. GIE Position Paper on Impact of Including Methane Number in the European Standard for Natural Gas, November 2012, Gas Infrastructure Europe. Available online: https://giignl.org/system/files/mn-position-p aper-giignl.pdf (accessed on 3 June 2020).

30. ISO-TR-22302: 2014 Natural Gas-Calculation of Methane Number. Available online: https://www.iso.org/st andard/63772.html (accessed on 24 April 2020).

31. Kubesh, J.; King, S.R.; Liss, W.E. *Effect of Gas Composition on Octane Number of Natural Gas Fuels*; 922359; SAE: Troy, MI, USA, 1992.

32. Partho, S.R.; Christopher, R.; Sang Keun, D.; Chan Seung, P. Development of a natural gas methane number prediction model. *Fuel* **2019**, *246*, 204–211.

33. *Algorithm for Methane Number Determination for Natural Gasses*; Dansk Gasteknisk Center: Hørsholm, Denmark, 1999.

34. Euromot, Position Paper: Methane number as a Parameter for Gas Quality Specifications. 2012. Available online: https://www.euromot.eu/wp-content/uploads/2017/03/GAS_QUALITY_methane_number_calcula tion_2012-04-04.pdf (accessed on 8 May 2020).

35. Graham, E.; Kenbar, A. LNG energy transfer uncertainty-sensitivity to composition and temperature changes. *Flow Meas. Instrum.* **2015**, *44*, 79–88. [CrossRef]