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Conditioning of Biogas for Injection into the Natural Gas Grid

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1. Introduction

In the following sections, recommendations supported by schematics are given for the injection of compliant processed biogas into natural gas grids. Based on the characteristics of the natural gases distributed in Germany and taking into account the applicable

- Laws, technical rules and regulations
- Billing procedures
- and the physical and technical conditions to be taken into account solutions for each individual supply case are given.

In order to feed biogas into a natural gas grid, unwanted components need to be removed from the gas and the burning properties of the gas need to be adjusted to those of the rest of the gas in the grid. In this way, the correct operation of the gas-burning appliances and the accuracy of the billing of retail customers is assured.

The purified biogas is conditioned depending upon the properties of the base gas (Fig.1). In the case of L gas, the calorific value or Wobbe index is realised by adding air, or air and LPG. In the case of H gas characteristics, the addition of LPG is required to adjust the calorific value to that of the usually higher calorific H base gas.

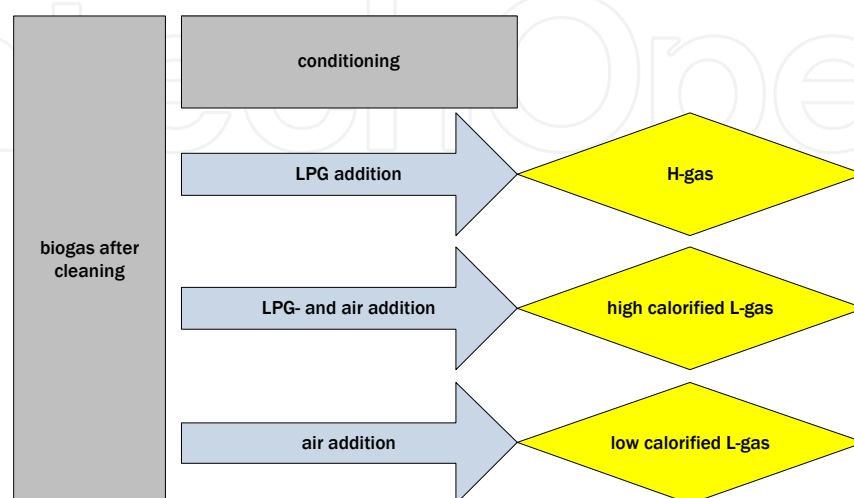


Fig. 1. gas conditioning by air and LPG addition

Schematic recommendations include the answers to the key questions listed below and allow a simple "read out" of the target properties, taking into account the current regulatory requirements. Gas utilities (GU) and operators can already in the planning phase determine the feed options and requirements with the help of the graphs. The key questions are:

1. What qualities and technical characteristics of combustion must processed biogas have at the very least so that it can be fed into grids in which the natural gases typical in Germany are present as base gases, without having to make changes to the grid?
2. What additional aspects need to be considered when feeding processed biogas into the existing natural gas grid, taking into account fairness in the billing process, properties (functionality of end-user equipment) and cost effectiveness?

The following conditions are to be observed in addition to point 1 : Engine applications, natural gas filling stations (methane, K number, condensation of higher hydrocarbons) and industrial customers.

2. Basic concepts and regulations

2.1 Characteristics of the base gas

The term base gas refers to the natural gas provided by the gas utilities (GUs) in the respective coverage areas without the addition of biogenic gas. The classification of the various natural gases distributed in Germany into H and L gases is made according to worksheet DVGW-G 260 (German Association of Gas and Water [DVGW], 2008). The Wobbe Index, which is a measure of the thermal energy released on the burner of a gas appliance or the energy transported through a pipe has a special significance here.

The Wobbe Index is an important variable to assess the interchangeability of fuel gases. When replacing one fuel gas with another, the output of the burner changes in proportion to the ratio of the Wobbe index. Its definition according G 260 is given in equation 1:

$$W_{S,n} = \frac{H_{S,n}}{\sqrt{d}} \quad d = \frac{\rho_{Gas,n}}{\rho_{Luft,n}} \quad \text{With the relative density and the calorific value } H_{S,n} \quad (1)$$

The upper value of the Wobbe index total range should not be exceeded. A shortfall in the lower value is acceptable under certain conditions and subject to a time limit. Both limits are specified in the German regulations. The nominal value listed in G 260 is used for setting the gas appliances used. Technically, the local variation range could be omitted, since the gas appliances are set to a nominal value. Currently however there are still many appliances set to differing values. The major boundary conditions are dictated by the Wobbe Index total range, the calorific range and the relative density, since conditioning with air and / or liquefied gas influences precisely these variables.

For the calorific value of a gas mixture, equation 2 states:

$$H_{s,n} = \sum_i r_i H_{s,n,i} \quad \text{or} \quad \rho_n = \sum_i r_i \rho_{n,i}^2 \quad (2)$$

¹ Indexing "S" (superior) is the formation with calorific value and "n" standard conditions

² r_i denotes the volume fraction of component i

When considering equation 2 and table 1, it is clear that even small volumes of higher hydrocarbons affect the parameters of combustion of the gas mixture, due to the greater density and calorific values. The same applies to air and carbon dioxide.

	ρ_n in kg/m ³	H _{S,n} in kWh/m ³
CH ₄ (Methane)	0,7175	11,064
C ₂ H ₆ (Ethane)	1,3551	19,537
C ₃ H ₈ (Propane)	2,010	28,095
C ₄ H ₁₀ (Butane)	2,709	37,252
CO ₂	1,9767	0
Air	1,293	0

Table 1. Standard density and calorific value of the main components

In addition to the basic requirements for the gas properties, limits for accompanying substances are specified in worksheet G 260, which may not be exceeded.

Gas Accompanying Substances	Indicative maximum	
Hydrocarbons: Condensation point	°C	Soil temperature at the respective Line pressure
Water: dew point	°C	
Fog, dust, liquid		Technically free
Percentage of oxygen - in dry distribution networks	%	3
- In humid distribution networks	%	0,5
Total sulphur		
Annual mean value (excluding odorants)	mg/m ³	30
Mercaptan	mg/m ³	6
short-term	mg/m ³	16
Hydrogen sulphide	mg/m ³	5
In exceptional cases, briefly	mg/m ³	10

Table 2. Permitted substances in the gas according to DVGW worksheet G 260 (DVGW, 2008)

Important boundary conditions are determined by the dew points, the oxygen content and the sulphur content. Information on the dew points is formulated so that condensation can be excluded. As far as the oxygen content is concerned, the grids in Germany can be regarded as dry and therefore the limit of 3 vol -% is to be applied. It should be noted at this point that at the long-range transport level significantly lower O₂ contents, usually in the low ppm range are to be observed (EASEE gas, CPB European Association for the Streamlining of Energy Exchange-gas Common Business Practice, 2005) for cross-border distribution (H gas).

The raw gas must be cleaned, processed (according to G 260) and compressed to the pressure of the grid operator. Under no circumstances should health risks arise from processed gas. For injection into the distribution network of a local GU, the gas must be

odorized according to G 280-1(DVGW, 2004). In addition, the presence of certain gas accompanying substances such as H_2S must be monitored regularly. Furthermore, for a time and heat equivalent transfer, the calorific value for billing purposes must also be known.

After processing the raw gases for the public gas supply, these can be used according to G 260 as an exchange gas (G 260 Section 4.4.2) or as additional gas (G 260 4.2, 4.3), (gas for conditioning) and be made available to the grid operator at the transfer interface. (Note: it should be noted that additional gas feeds are only possible in a single pipeline under certain circumstances.)

Put simply, it can be said that the conditions given in worksheets G 260 and G 262 (DVGW, 2007) ensure that the customers' appliances will work correctly. Sensitive industrial processes sometimes require much tighter limits on the gas properties (e.g. glass and ceramics production). The DVGW worksheet G 260 is very often a component of supply contracts and is an expression of the flexibility of the gas sector, which is necessary in the procurement of natural gas, in order to deliver natural gas from various gas fields into the transport and distribution system of the German gas industry and on to the customer. Due to its geographical location, historical and political development, in Germany natural gases from the most diverse of foreign origins as well as natural gases from its own sources are thus forwarded to the customers, with the guarantee of security of supply, functionality of the natural gas applications and fair billing.

In summary, in order to inject biogas into the natural gas grid, the above requirements must be met. In addition to excluding the gas accompanying substances by cleaning and processing the biogas, further conditioning to adjust the Wobbe Index and the calorific value to the target grid is required, depending upon the case in point.

The processed, conditioned biogas is considered to be an exchange gas, if it meets the requirements set out in G 260, G 262 and G 685. Furthermore, during conditioning with liquid gas, limits according to G 486 (DVGW, 1992) need also to be considered.

2.2 "Gas billing" according to worksheet G 685 of the DVGW regulations (DVGW, 2008)

For billing, two parameters need to be determined: The volume flow of the fuel gas under standard conditions ($T = 0^\circ C$, $p = 1.01325 \text{ bar}$) and the calorific value for billing purposes. The determination of the standard volume flow from the operational flow is done using the procedure described in G 685, taking into account the temperature and atmospheric pressure. At pressures greater than 1 bar, real gas behaviour should be taken into account (G 486). The calorific value for billing purposes is determined from the calorific values of the feed for each billing interval (such as 1 month (special contract customers) or 1 year (residential customers)) in a coverage area (the total area, which is supplied by the GU, not necessarily contiguous). If the calorific values of the feed change over time, then these are determined arithmetically or by volume-weighted methods over the month.

If gases with different calorific values are distributed, then the following, according to G 685 (DVGW, 2008), applies:

If gases are fed through geographically separate feed points into a grid or into gas supply areas which cannot be isolated, the calorific value for billing purposes is to be determined

according to the regional location of the customer. The gas delivered to customers may not deviate in calorific value by more than 2% from the calorific value for billing purposes. To check this, the mean values and the quantity-weighted average in the downstream network are to be determined.

Since worksheet G 486 is particularly applicable due to the admixing of propane and butane as considered in this report, essential aspects are explained below.

2.3 The worksheet G 486 "Gas quantity measurement, compressibility factors and gas law deviation factors of natural gases, calculation and application" from the DVGW regulations

The determination of gas quantity, or volume is carried out under operating conditions (metering conditions). The result is an operational flow $V_B (T_B, P_B)$ as a function of temperature and pressure. This operational flow needs to be converted to standard conditions ($T_N = 0^\circ \text{C}$, $p_N = 1.01325 \text{ bar}$) in order to compare volumes and so that it can be used as an input for gas billing. Since the model for an ideal gas is only approximately valid for real gases at low pressures, a compressibility factor $Z (T, p, x_i)$ is introduced into the equation of state for ideal gases. The compressibility factor is mathematically approximated by a series expansion of the molar density (virial approach). The calculation of standard volume is thus given by equation 8. 3:

$$\frac{V(T_N, p_N)}{V(T_B, p_B)} = \frac{T_N p_B Z_N}{T_B p_N Z_B} \quad (3)$$

The ratio of the compressibility factors is called the gas law deviation factor.

Two methods for calculating compressibility factors are given in G 486 including the supplementary sheets: The standard GERG-88 virial equation and the AGA8-DC92 equation of state. The former requires input parameters of p , T , H_2 , N , ρ , x_{CO_2} and X_{H_2} , the latter the mole fractions. The AGA8 equation of state requires a full analysis by means of a process gas chromatograph.

2.4 Conditioning with liquid gas (propane / butane)

The term liquid gas (Liquefied Petroleum Gas³ it refers to C3 and C4 hydrocarbons or mixtures thereof. It is generated as a by-product in petroleum refining and as an associated gas from the extraction of oil and natural gas. LPG is gaseous at room temperature under atmospheric conditions, but can be liquefied at low pressures. In liquid form, its specific volume is about 260 times smaller than in the gaseous state. Therefore, large amounts of energy can be transported and stored in relatively small containers.

The transportation of LPG is carried out worldwide by tanker ships, barges, pipelines, by rail tank cars, road tankers or in liquefied gas cylinders. LPG is stored in stationary tank facilities or in gas cylinders. Up to a tank size of 2.9 t capacity, the above-ground installation does not require a permit. From a tank capacity of 2.9 tonnes, the federal emission

³ The term LPG is not to be understood as "car gas" which has a different propane / butane mixture ratio

regulations need to be considered when granting a permit. The technical conditions for setting up tank installations are defined in TRB 801 No.25 "LPG storage tank facilities".

Commercial LPG consists of at least 95 percent by mass of propane and propene, whereby the propane content must predominate. The remainder may consist of ethane (C₂H₆), ethene (C₂H₄), butane (C₄H₁₀) and butene (C₄H₈) isomers. The classification for commercial propene, butane and butene is equivalent. Note also the degree of purity according to DIN 51 622 [DIN 1985]: Data on sulphur or sulphur compounds are listed here.

In DIN 51624 "automotive fuels - natural gas requirements and test methods" [8-15] upper limits for the propane/butane mole fractions in natural gas of 6% / 2% in the total mixture and a methane number > 70 are required. EASEE-gas CBP (EASEE, 2005) specifies a hydrocarbon dew point of -2 ° C at 1-70 bar. For the calculations shown below, a typical LPG composition of propane / butane, 95 / 5 is used.

2.5 Aspects of the energy industry act (EnWG) and the gas network access ordinance (GasNZV)

Section 19 of the Energy Industry Act stipulates that the operators of gas distribution networks are obliged, taking into account conditions set out in section 17 for the network connection of LNG facilities, de-centralised generation and storage facilities, other transmission or gas distribution systems and direct pipelines, to determine minimum technical requirements for design and operation, and to publish them on the Internet.

The minimum technical requirements set out according to these sections shall ensure the interoperability of the grids and shall be justified objectively and not be discriminatory. Interoperability includes in particular the technical connection requirements and conditions for grid-compatible gas properties, including gas generated from biomass or other types of gas, as far as they are technically able to be injected into the gas supply grid or transported through this grid without compromising security (Energy Industry Act, 2005). For ensuring technical security section 49 applies: energy facilities shall be constructed and operated so that technical security is guaranteed. Thereby, subject to other legislation, generally accepted technical rules are to be observed. Compliance with the generally recognized technical rules shall be presumed if, in the case of plants for the generation, transmission and distribution of gas, the technical rules of the German Association of the Gas and Water Industry have been complied with.

Conditions for gas grid access are described in the Gas Network Access Ordinance (GasNZV, 2005) in part 11a "special arrangements for injecting biogas into the natural gas grid". The Gas Network Access Ordinance regulates the conditions under which the gas network operators are obliged to grant transportation customers access to the gas networks.

3. Base data

After the basic principles and the definitions of terms, there follows three examples of the calorific value adaptation of biogas, before it is injected into the natural gas grid. In these selected cases, one deals with the conditioning for an H gas grid and the other two with L gas grids, where conditioning is based on the addition of air, and on LPG and air. Other

cases are described in the DVGW study "Developing a scientific basis for injecting biogas into natural gas grids."

First, the most important combustion-related characteristic data are listed for the selected base gases, in order to summarise the requirements imposed on the biogas, in particular with respect to the Wobbe index and calorific value.

Then the characteristics of the processed biogas with a methane content of 94 - 99,5 Vol.-% will be compiled in order to determine the conditioning necessary to adapt to the base gas. Processed biogases with these methane levels are generally H gases.

To attain the Wobbe index of an L gas, air must be added, which lowers the calorific value. In the case of L gases with higher calorific values, liquid gas needs to be added. When higher demands are placed on the calorific value (H gases), a liquid gas addition is necessary. A processed biogas containing 99.5 Vol.-% methane has a calorific value of 11.0 kWh / m³.

For the calculations of the compositions in the following sections, the values from the following table 3 will be used. The composition of air is taken to be 20.95 Vol.-% oxygen and 79.05 Vol.-% nitrogen. All flow rates are standard flow rates.

	$H_{S,n}$ in kWh/m ³	$\bar{v}_{m,n}$ in m ³ /kmol
CH ₄	11,064	22,36
CO ₂	0	22,261
N ₂	0	22,403
O ₂	0	22,392
C ₃ H ₈ /C ₄ H ₁₀	28,578	21,904
air	0	22,4

Table 3. Numerical values used for the calculation

3.1 Data on the base gases

For the base gas data, gas properties taken from the DVGW worksheet G 260 appendix 1 and sample values from the GASCALC computer program from e.on Ruhrgas AG have been used. The data are summarized in Table 4. Based on the technical characteristics of combustion of the base gases, the calorific ranges for the processed biogas were determined. Here, the calorific values for the calculations were assumed to be quantity-weighted averages and a + / - 2 percent band was placed around these (Tab. 5). In this way, in the following sections admixtures whose corresponding calorific values lie in this interval will be determined.

Designation	φ_{Methane} in Vol.-%	$H_{S,n}$ in kWh/m ³	$W_{S,n}$ in kWh/m ³	Density ρ in kg/m ³	Methane number (+/-2)
North Sea I	88,6	12,2	15,4	0,81	72
Holland II	82,9	10,2	12,8	0,83	86
Weser Ems L Gas	87,81	9,85	12,53	0,80	102

Table 4. Base gases

Designation	Calorific range (+/-2%) in kWh/m ³
North Sea I	11,956 - 12,444
Holland II	9,996 - 10,404
Weser Ems L Gas	9,653 - 10,047

Table 5. Calorific value ranges

3.2 Data on processed biogases

As a basis for further considerations, data for the biogas compositions as specified in Table 6 will be used. Further accompanying substances occurring in the biogas have not been taken into account, because they vary too greatly depending on the fermented substrates and type of processing.

Components	Unit	Case 1	Case 2	Case 3	Case 4
CH ₄	Vol.-%	94	96	98	99,5
CO ₂	Vol.-%	5,6	3,6	1,6	0,1
N ₂	Vol.-%	0,3	0,3	0,3	0,3
O ₂	Vol.-%	0,1	0,1	0,1	0,1
Calorific value	kWh/m ³	10,400	10,622	10,843	11,009
Wobbe - Index W _{S,n}	kWh/m ³	13,290	13,798	14,326	14,738

Table 6. Examples of the composition of processed biogases

A processing level of 99.5% vol. methane is attainable and is state of the art. The N₂ and O₂ levels are 0.3 and 0.1 vol.-% and remain constant for the calculations at these initial methane levels. The CO₂ content conforms to the relevant selected methane content within the specified range.

3.3 Requirements for compliant processed biogas

The composition, the combustion-related characteristic data and the accompanying substances in the "processed biogas" - summarized under the term "gas properties" - are crucial for injection. In particular, these are the data described in the DVGW work sheet G 260 "gas properties", G 262 "use of regeneratively produced gases" and in the DVGW Worksheet G 685 "gas billing" and G 486 and are defined within their respective limits. Table 7 shows the principal conditioning parameters for injecting into a grid.

The methane content in biogas is not subject to any defined restriction. However methane is, according to the latest technical data, the major combustible component and thus largely determines the calorific value and hence the Wobbe index, as long as no liquid gas admixture is included. According to worksheet DVGW-G 262, the maximum permissible CO₂ content is 6 Vol.-%. Since biogas consists mostly of methane and carbon dioxide,

processing to at least a minimum methane content of 94 vol -% is assumed. Together with the fractions of oxygen and nitrogen, the biogas has a maximum carbon dioxide content of 5,6 Vol.-%.

Parameter	Abbreviation	Unit	Limit	Comment
Methane volume fraction	φ_{CH_4}	Vol.-%	---	Since methane is the main combustible component of biogas, the concentration largely determines the technical combustion characteristics ($H_{S,n}$, $W_{S,n}$), (H_2 not taken into account)
Carbon dioxide volume fraction	φ_{CO_2}	Vol.-%	6.	G 262
Oxygen volume fraction	φ_{O_2}	Vol.-%	3.	This limit applies to dry networks (G 260)
LPG mole fraction	x_{LPG}	mol.-%	Propane: 3,5 (6) Butane: 1,5	According to G 486-B2 for pressures > 100 bar (<100 bar), for details see here
Nitrogen volume fraction	φ_{N_2}	Vol.-%	---	
Hydrogen volume fraction	φ_{H_2}	Vol.-%	5.	G 262 (in gases produced by fermentation usually not present)
Relative density	d		0,55-0,75	G 260
Calorific value	$H_{S,n}$	kWh/ m^3	8,4-13,1	Maximum + / - 2% variation to the distributed gas (see G 685, thermal billing)
Wobbe Index L gas H gas	$W_{S,n}$	kWh/ m^3	10,5-13,0 12,8-15,7	Total range

Table 7. Requirements for processed biogas

According G 260, the maximum permissible O₂ volume fraction is 3% in dry networks, otherwise 0.5%. German natural gas grids are considered to be dry.

It is important to note that CO₂ and O₂ in combination with moisture can lead to corrosion in pipes, fittings and equipment.

In addition to the above conditions, of course the information on sulphur compounds and other impurities and accompanying substances given in G 260 is also to be noted. The data

for the dew point temperatures lie below the requirements defined in G 260 (about 4 - 7 ° C (soil temperature at 1 m depth) at line pressure).

4. Opportunities for the production of compliant gases

In the previous sections, the conditions for injecting processed biogas into a natural gas grid were described in detail. In this chapter, appropriate mixture compositions matching the individual gas types will be determined and the possibilities for conditioning with air and / or propane / butane admixture will be discussed.

Four different methane volume fractions (processing grades) are shown, for a total of three natural gas types as a "target" properties. Depending on the application, LPG admixtures and air admixtures are applied across a large range in order to determine a suitable, practical combination.

The addition of liquid gas or air is to be understood as an additive to the processed biogas (100%). This means that the proportion of the total mixture (100% + X) is lower than the amount added. The depicted LPG addition shows the component added, the value of the Wobbe Index, calorific value and the limits of propane and butane components resulting from the total mixture.

$$x_{LPG \text{ im Gemisch}} = \frac{\dot{V}_{LPG \text{ Zugabe}}}{\dot{V}_{LPG \text{ Zugabe}} + \dot{V}_{Biogas}} \quad (4)$$

The type of conditioning selected depends upon economic and technical factors and will ensure that the broadest possible spectrum of combustion values is achieved.

For implementation in practice, it should be noted that the methane volume fractions arising from processing may be subject to fluctuations. Equally, the composition of the LPG may vary and the measuring instruments and the control and regulating equipment will have tolerances, so that error propagation through the system needs to be noted when trying to achieve the desired bandwidth of "target" properties.

4.1 Target properties: North sea I H gas

For the production of compliant H gas with technical combustion characteristics matching North Sea I specifications, conditioning by admixing LPG is examined below.

The figures 2 to 5 show the potential composition of biogas mixtures, based upon methane levels in the processed bio-gas of 94, 96, 98 and 99,5 vol.-%, to which propane/butane (in a ratio of 95 / 5) is added. The necessary LPG admixtures for the desired calorific range for a methane content of 94, 96 and 98 vol -% in the treated biogas, lie above the limits as defined in G 486-B2 and DIN 51624, at 9.4 to 12.6 Vol -%, from 8.1 to 11.3 Vol -% and 6.8 to 9.9 vol -%. For processing to a methane content of 99.5 Vol -%, the limit according to G 486-B2 for pressures <100 bar is numerically satisfied up to a propane / butane admixture of 6.5 vol -%. The applicability criteria as described in section 2 apply. On the basis of this restriction, only an admixture of 5.8 to 6.5Vol.-% of LPG for an initial methane content of 99.5Vol.-% is possible. This would then cover a calorific range of 11.971 to 12.080 kWh/m³.

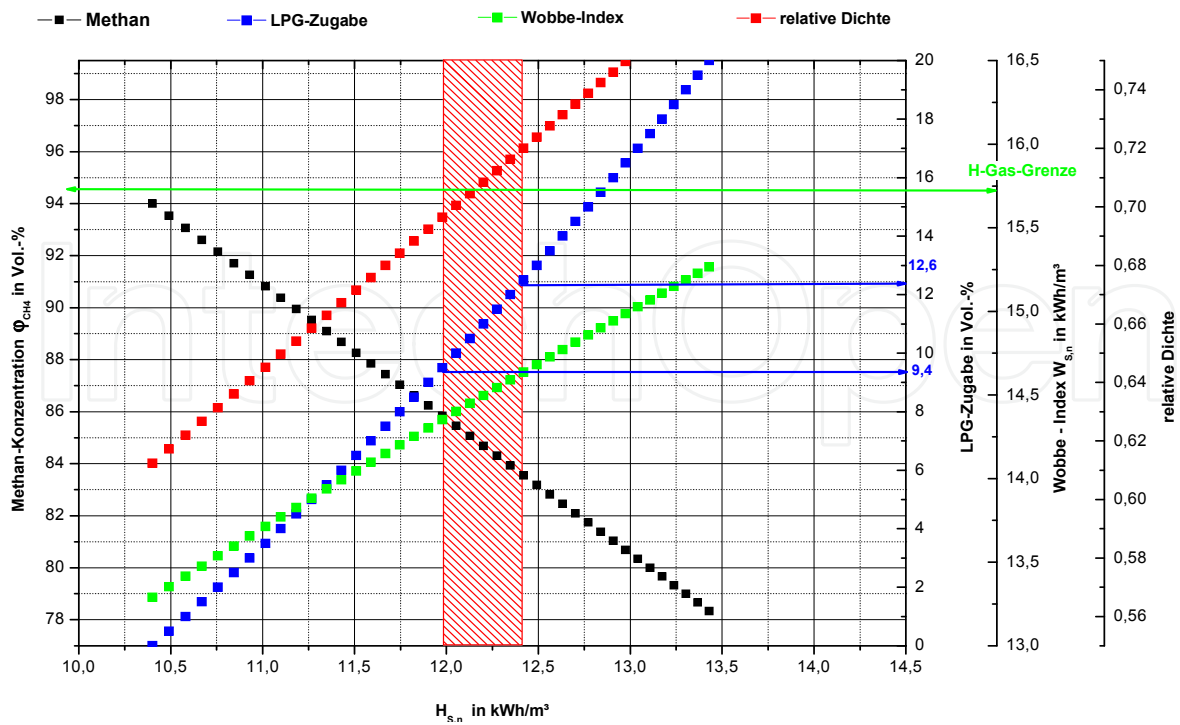


Fig. 2. Possible H gas mixtures by admixing LPG to an initial concentration of 94 Vol. -% methane

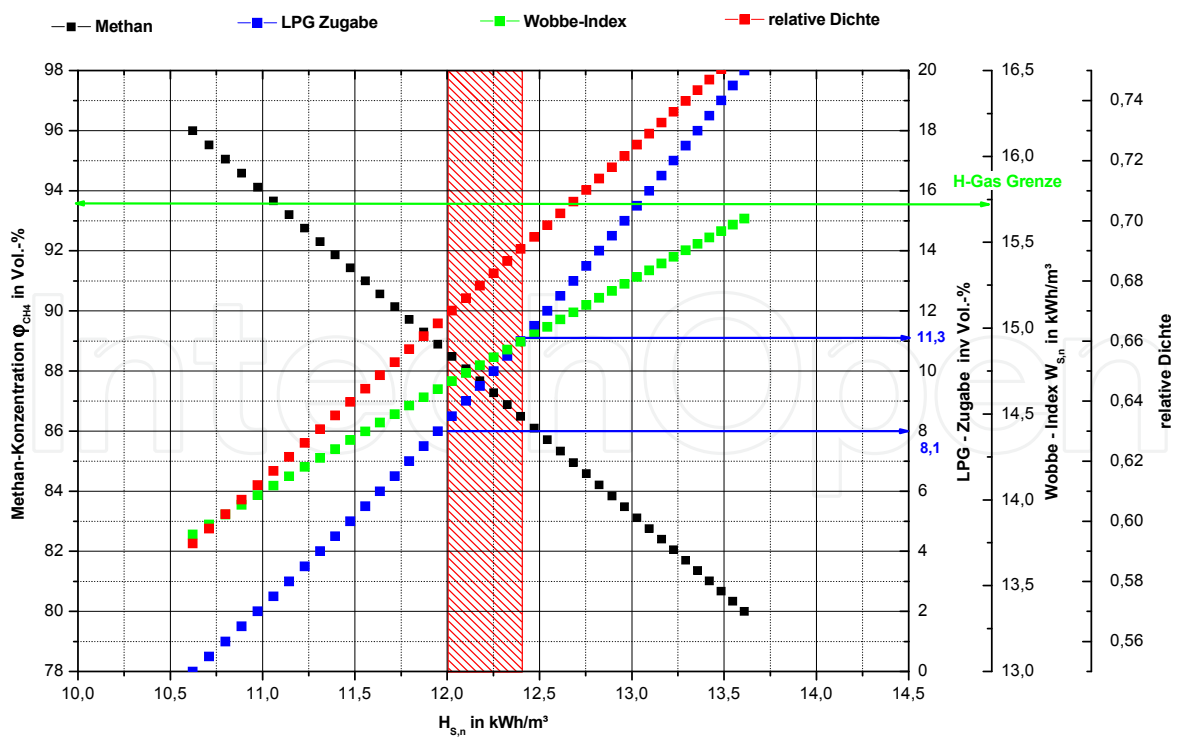


Fig. 3. Possible H gas mixtures by admixing LPG to an initial concentration of 96 Vol. -% methane

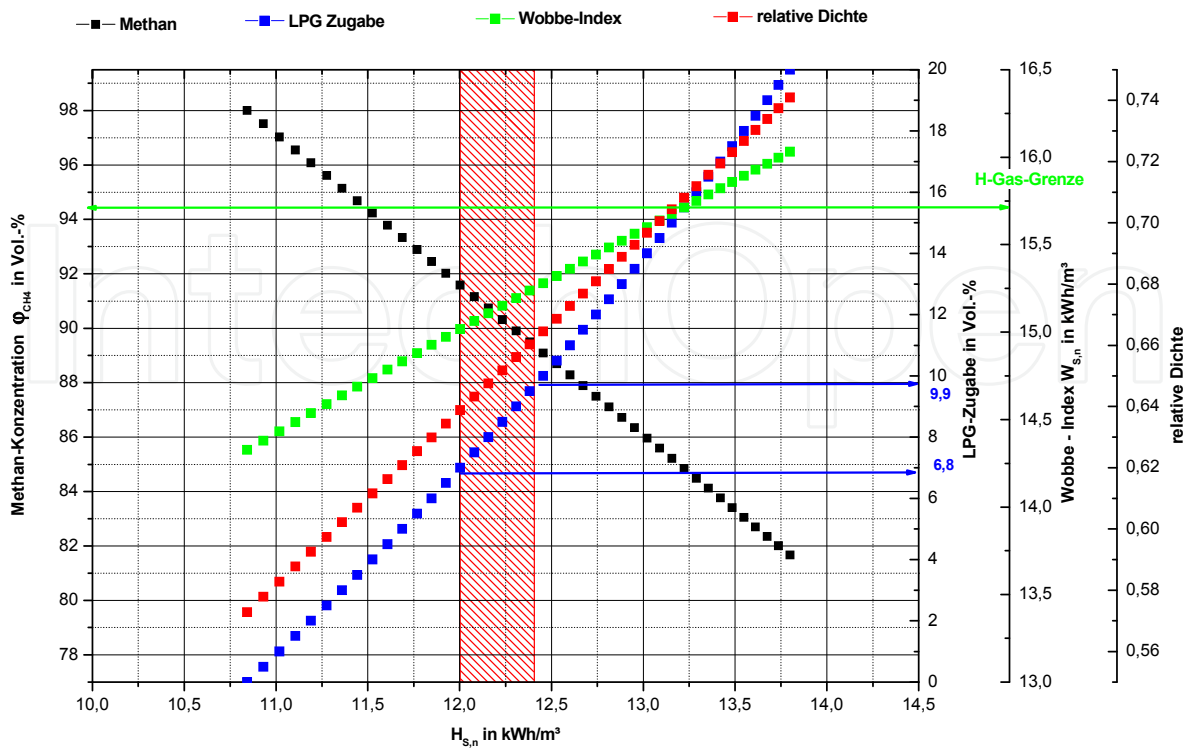


Fig. 4. Possible H gas mixtures by admixing LPG to an initial concentration of 98 Vol. -% methane

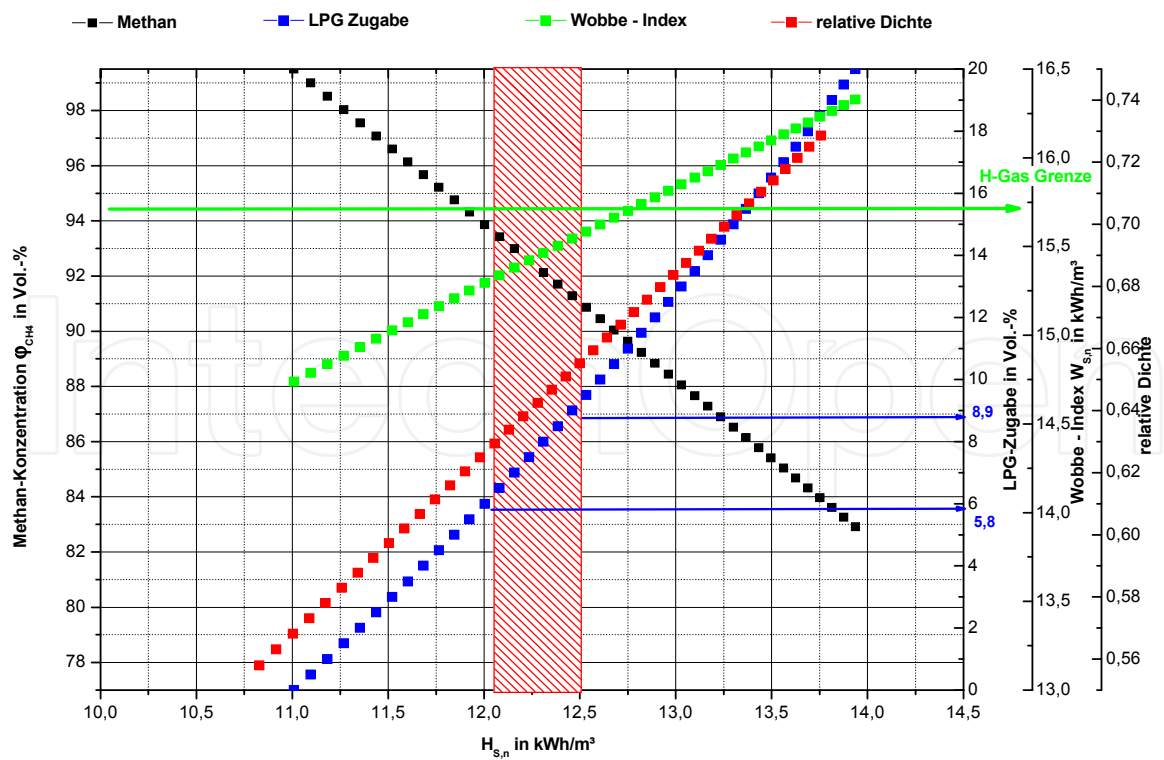


Fig. 5. Possible H gas mixtures by admixing LPG to an initial concentration of 99,5 Vol. -% methane

Table 8 shows a summary of LPG additions necessary to achieve an average target calorific value of approx. 12.2 kWh/m³.

Methane After processing	North Sea I $H_{S,n} = 12,2 \text{ kWh/m}^3$
Vol.-%	Vol.-%
94	11,1 ²
96	9,7 ²
98	8,3 ²
99,5	7,3 ⁴

Table 8. LPG quantities necessary to achieve the average target calorific value

4.2 Target properties: Weser ems L gas

For the production of compliant, low calorific L gas, conditioning by the addition of air is described in the following sections.

Figures 6 to 9 inclusive show possible fuel gas mixtures with a calorific value range of 9.653 to 10.047 kWh / m³, which can be achieved by the addition of air.

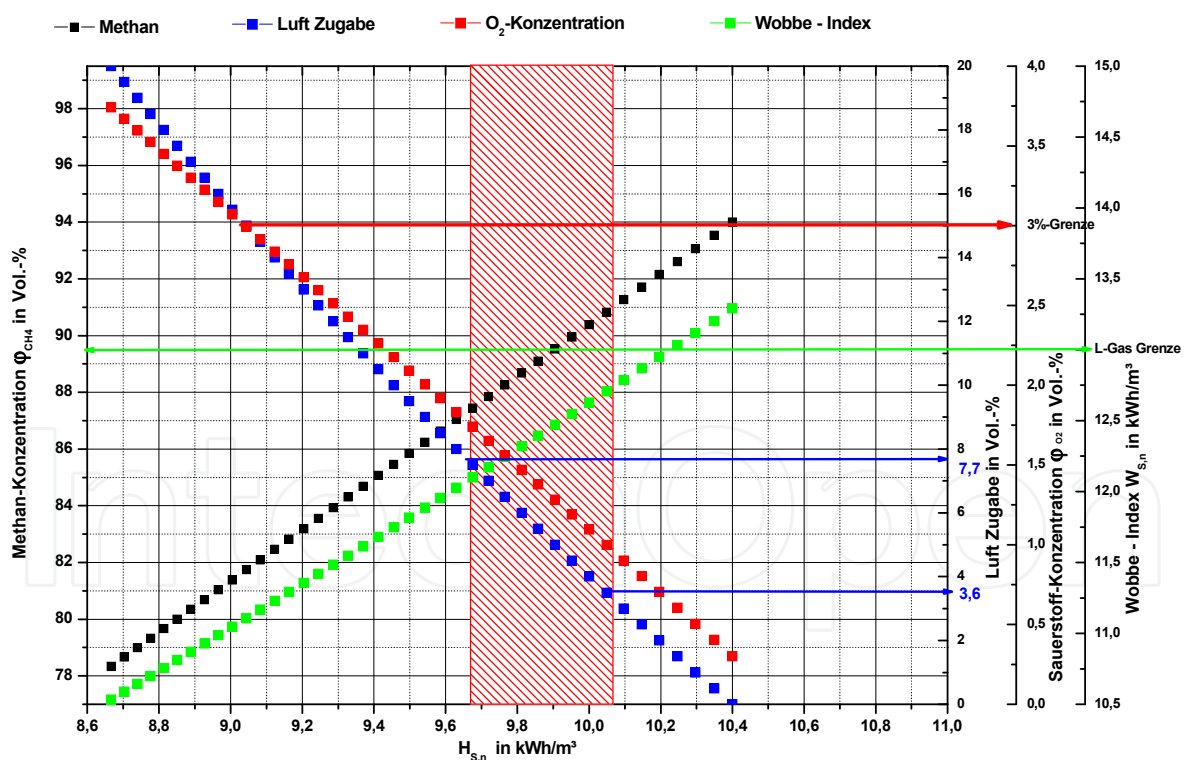


Fig. 6. Possible low calorific L gas mixtures achieved by admixing air to an initial concentration of 94 Vol. -% methane

⁴ Exceeds the maximum concentration of propane for $p < 100$ bar according to G 486-B2

Figure 6 shows the possible mixture compositions, when air is added to an initial methane content of 94 vol -% . When interpreting this, please note that the data points for the Wobbe index, the methane content and the air belong together along the line of constant calorific value. A +/- 2% range has been set for the calorific value limits, based on the calorific value defined in DVGW worksheet G 260. All values with a Wobbe index of less than 13 kWh / m³ and an O₂ content of less than 3 vol -% meet requirements. All other boundary conditions are shown in the table above.

Figure 7 show the possible mixture compositions, when air is added to initial methane content of 99,5 Vol.-%.

The two cases presented with initial methane contents of 94 and 99.5 Vol -% in the biogas, clearly show that increases in methane content also make necessary increased amounts of air, in order to achieve the desired calorific value and Wobbe index.

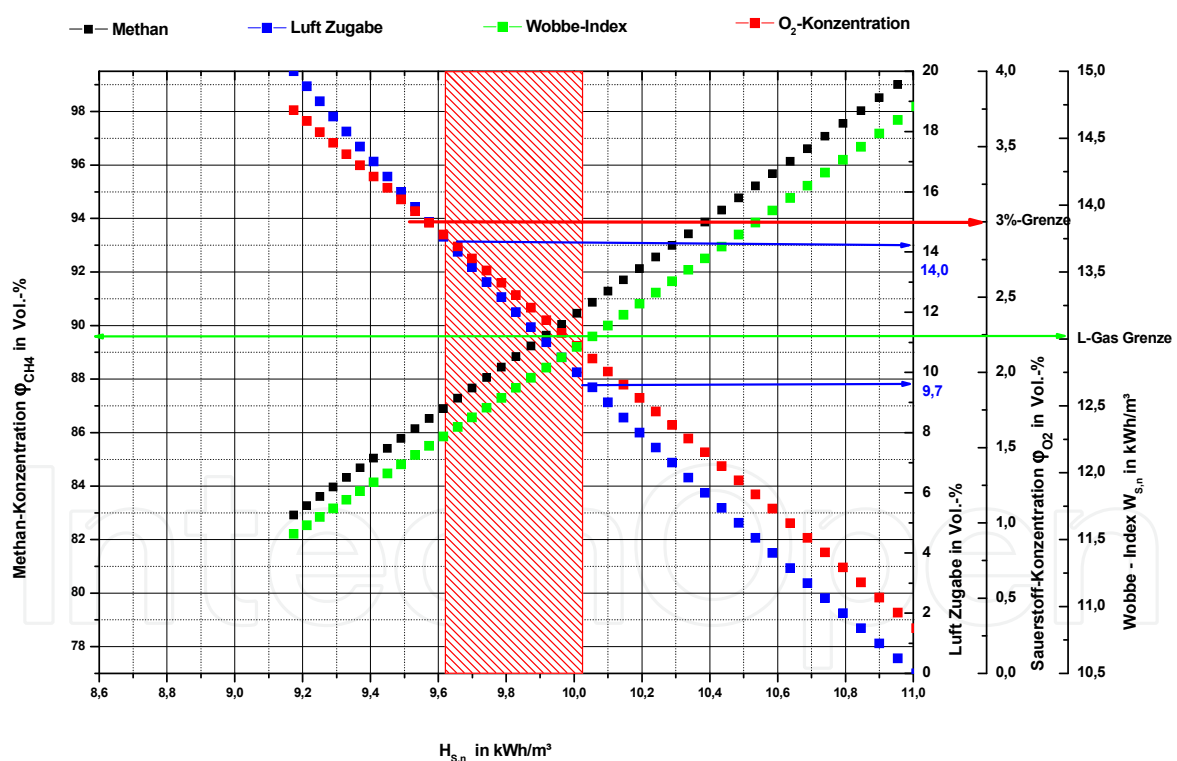


Fig. 7. Possible low calorific L gas mixtures achieved by admixing air to an initial concentration of 99,5 Vol. -% methane

Table 9 shows the respective admixtures.

Methane concentration after processing in vol.-%	Weser Ems L Gas $H_{s,n} = 9,85 \text{ kWh/m}^3$	
	Air added to the biogas in Vol.-%	Wobbe Index in kWh/m ³
94,0	5,6	12,379
96,0	7,8	12,492
98,0	10,1	12,589
99,5	11,8	12,664

Table 9. Air admixture to Weser Ems L-Gas and corresponding Wobbe-Index

The higher the initial content of methane in the biogas is, the greater is the approximation to the maximum compliant O₂ content of 3 vol.-% from conditioning.

Thus the O₂ levels upon reaching the lower calorific value band are:

- at 94 % vol. methane 1,776% vol. O₂
- at 96 % vol. methane 2,177% vol. O₂
- at 98 % vol. methane 2,562% vol. O₂
- at 99,5 % vol. methane 2,836% vol. O₂

Reaching of the required calorific value band (9.653 to 10.047 kWh / m³) is possible from all four initial methane contents.

Figure 8 shows a summary of the air admixture ranges of the four initial methane levels. The red line indicates the maximum permissible volume fraction of 3% of O₂ in the mixture.

Niedrigkalorisches L-Gas: Zusammensetzungen für einen Brenwertbereich von $H_{s,n} = 9,653-10,047 \text{ kWh/m}^3$

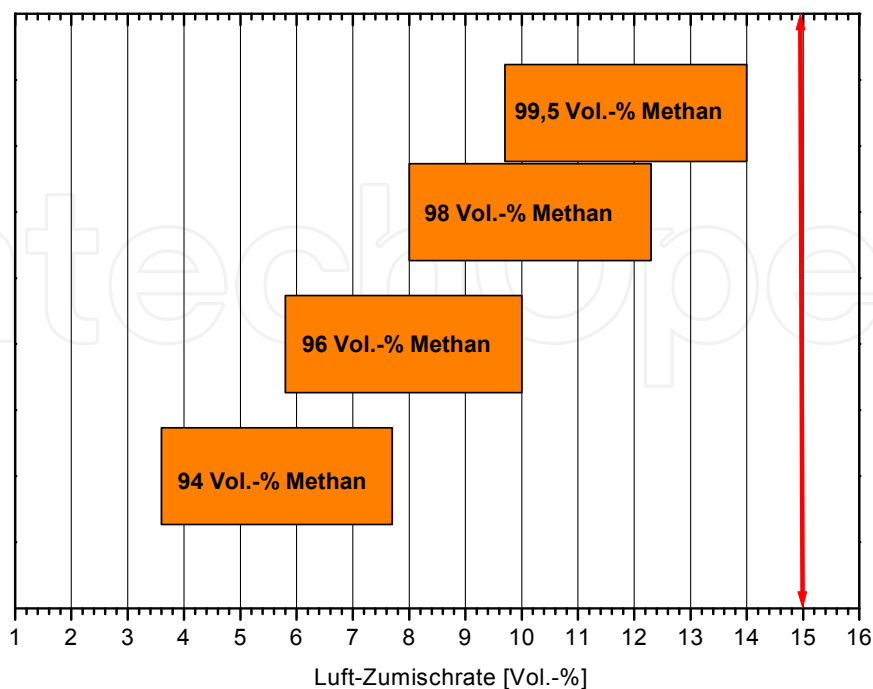


Fig. 8. Rates of air admixture at different initial concentrations of methane

4.3 Target properties: Holland II L gas

For the production of compliant, high calorific L gas, conditioning by the addition of air and LPG is described in the following section.

Please note the following when interpreting the diagrams below: The field of admixtures includes a range of 0 - 20 Vol -% for presentational purposes. In practice, for technical and economic reasons, it is desirable to make the least possible admixtures with a "target" Wobbe Index of 12.4 kWh / m³ for example (setting of the gas appliances). In this context it should be noted that according to G 486 appendix B, the mole fractions of propane are not to exceed 3.5 mol% (6 mol% at p <100 bar) and butane max.1.5 mol% in natural gas, in order make a conversion of standard and operating conditions using the AGA8-DC92 equation of state.

The "field" of the possible mixtures is bounded by the Wobbe Index of 13 kWh / m³, the given calorific value limits, the max. oxygen volume fraction of 3%, and the maximum propane/butane or air admixture. For each value of air addition, there is always a value for the propane / butane addition.

The following figures apply only to the four initial properties of the biogas used.

Figures 9 and 10 show the calorific values and the Wobbe index for an air and LPG admixture of 0 to 20 vol -% to a biogas with an initial methane content of 94 vol -% and 96 vol -%.

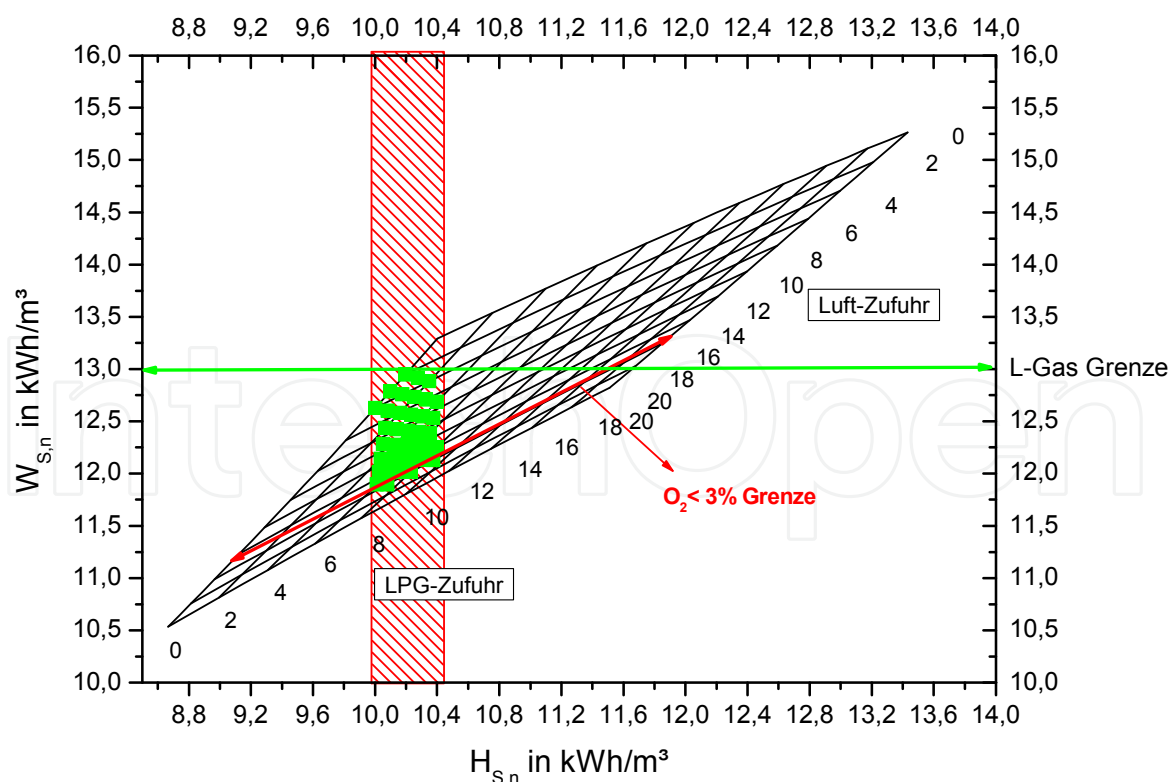


Fig. 9. Possible highly calorific L gas mixtures by admixing air and LPG to an initial concentration of 94 Vol. -% methane.

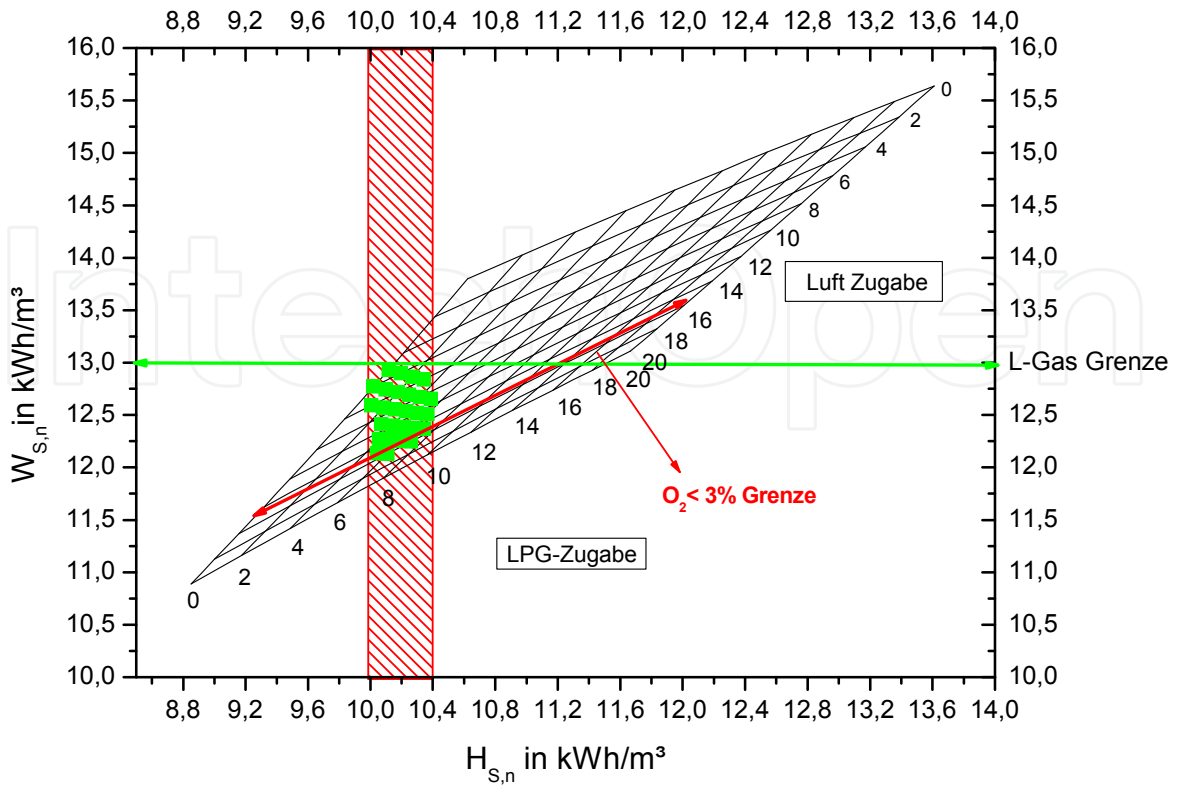


Fig. 10. Possible highly calorific L gas mixtures by admixing air and LPG to an initial concentration of 96 Vol. -% methane.

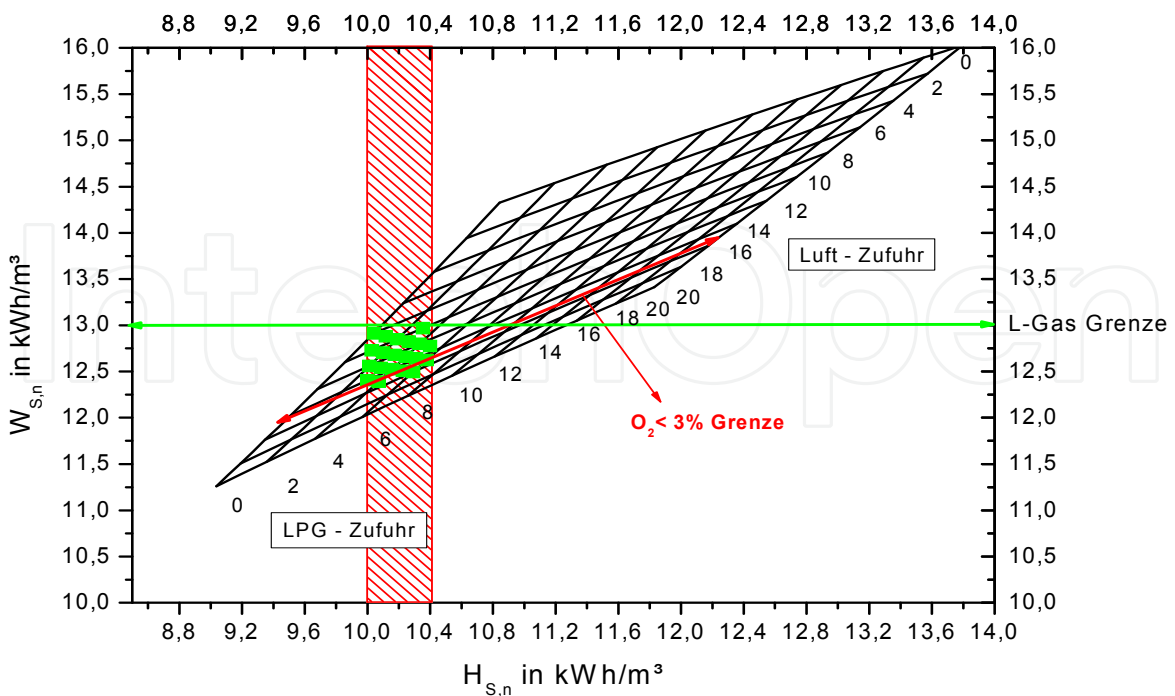


Fig. 11. Possible highly calorific L gas mixtures by admixing air and LPG to an initial concentration of 98 Vol. -% methane

Figures 11 and 12 show the calorific values and the Wobbe index for an air and LPG admixture of 0 to 20 vol -% with an initial methane content of 98 vol -% and 99,5 vol -%.

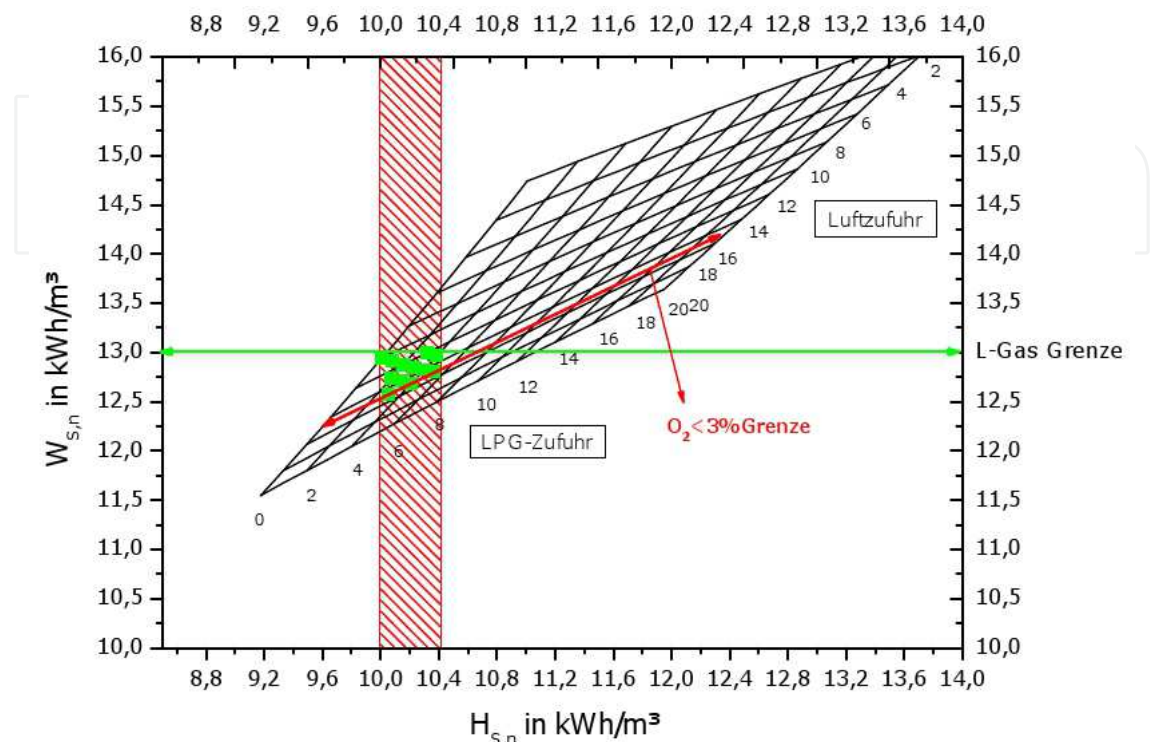


Fig. 12. Possible highly calorific L gas mixtures by admixing air and LPG to an initial concentration of 99,5 Vol. -% methane

The red area represents the required calorific value range from 9.97 to 10.4 kWh / m³. The green dots show the possible, compliant mixtures that lie within all the conditions to be fulfilled.

5. Condensation curves and methane numbers

The conditioning with air and / or liquid gas to adjust the technical combustion characteristics may influence both the methane number and the condensation of higher hydrocarbons in the combustion gas mixture.

The methane number - equivalent to the octane number of petrol - is a statement of the anti-knock properties of fuel combustion in a engine, where the term anti-knock refers to the tendency to uncontrolled and undesirable self-ignition. Methane has by definition a methane number of 100, hydrogen a methane number of 0. A methane number of 80 for example means that the gas mixture associated with this methane number has the same anti-knock properties as a mixture of 80% vol. methane and 20 vol. -% hydrogen. Some inert mixture components such as CO₂ increase the methane number, higher hydrocarbons, reduce it. The calculated methane numbers (Gascalc, E.on Ruhrgas) of L gases are generally greater than those of H gases (nitrogen not factored out). As a lower limit for the smooth

operation of modern engines, a methane number of $MZ > 70$ is considered necessary (DIN 51624, 2008).

For multi-component mixtures such as natural gases, the condensation and boiling curves do not lie together, but span a conditional area, where different gas-liquid compositions are possible. Between the critical pressure and the cricondenbar point with increasing temperature, and between the critical temperature and the criconden therm point with falling pressure, condensate (retrograde condensation) can form when the throttle curve touches the dew line, intersects or the final state lies in the two-phase region (Höner zu Siederdisen & Wundram, 1986).

An admixture of propane / butane to natural gas and processed biogas generally manifests itself in a shift of the dew curve to higher temperatures. According to (Oellrich et al., 1996), in the case of Russian H gas, condensation is only to be expected at temperatures of $-35\text{ }^{\circ}\text{C}$, while it will occur with Dutch L gas already at $-5\text{ }^{\circ}\text{C}$. If liquid gas/air is admixed within the limits described in DVGW worksheet G 260, the criconden therm point moves toward $+15\text{ }^{\circ}\text{C}$ or $+45\text{ }^{\circ}\text{C}$, but at higher pressures. For mixtures of natural gas and processed conditioned biogas, this is to be expected to a lesser degree, since the concentrations of propane / butane are correspondingly smaller.

It should be noted that the calculation of the condensation curves of natural gases requires an analysis that takes into account the higher hydrocarbons, since even small amounts in the ppm range result in a significant shift. Furthermore, the process of condensation is not in itself critical, but the quantity of condensate is the decisive criterion. For large flow rates, a seemingly low volume of condensate can therefore lead to problems (Oellrich et al., 1996).

The following Table 10 and Figure 13 show cases of condensation in conditioning by the addition of LPG, in order to meet the North Sea I specification. The lowest and the highest admixtures were selected for the diagrams. It should be noted that at the highest level of admixing, the restrictions imposed by G 486 were not observed.

Initial concentration of CH_4 in the biogas in Vol.-%	LPG addition to biogas in Vol.-%	Calorific value in kWh/m^3	Wobbe Index in kWh/m^3	rel. Density	Methane number
94,000	9,400	11,960	14,339	0,696	71
94,000	12,600	12,432	14,642	0,721	67
96,000	8,100	11,965	14,654	0,667	72
96,000	11,300	12,442	14,946	0,693	67
98,000	6,800	11,970	14,998	0,637	73
98,000	9,900	12,438	15,268	0,664	67
99,500	5,800	11,971	15,276	0,614	74
99,500	8,900	12,443	15,534	0,642	67

Table 10. Cases of condensation for mixtures of the North Sea I H gas specification

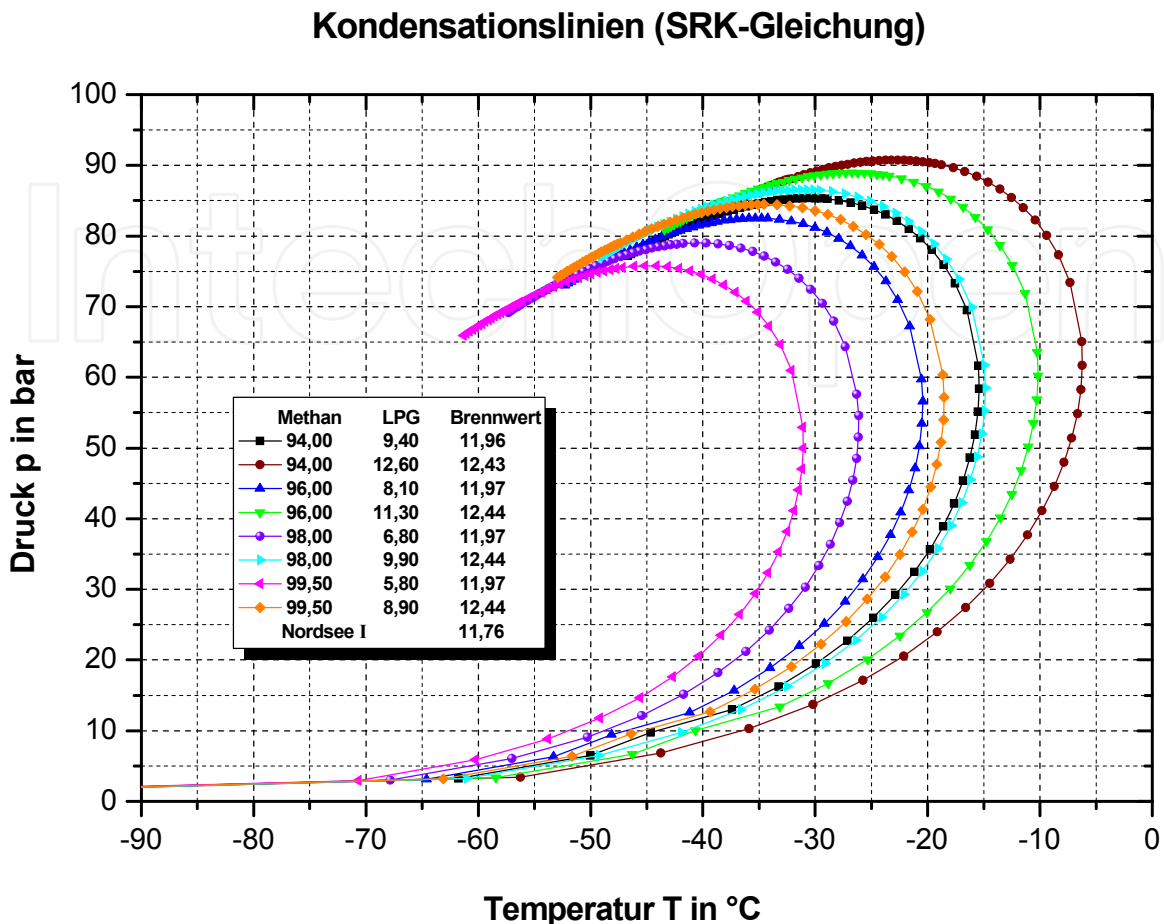


Fig. 13. Condensation curves for mixtures of the North See I H gas specification

In summary, it can be said that the cricondena points of the H gases in Germany lie below temperatures of -20°C . An exception to this are the higher calorific mixtures of the North Sea quality - here, 0°C is also possible. However, the mixtures were ignored in the calculation of the limits in G 486 and DIN 51 624, so that it applies mainly to the higher LPG quantities added. Generally, this means that process procedures, in which pressure and temperature lie in the two-phase region, should be avoided.

6. Conclusion

This section shows a summary of all the mixing rates of LPG and / or air to attain the base gas properties under consideration.

6.1 Conditioning: Target H gas

The table 11 shows the determined rates of admixture for LPG to attain the appropriate target calorific value range. With the LPG quantities shown, the respective initial concentrations of methane, the entire calorific value range of the respective base gas quality is covered, with some restrictions.

LPG mixing rates to achieve the target calorific value + / - 2%	
Methane concentration after processing in vol -%	North Sea I H gas $H_{S,n} =$ 11,956 - 12,444 kWh/m ³
	LPG in Vol.-%
94,0	9,4 - 12,6
96,0	8,1 - 11,3
98,0	6,8 - 9,9
99,5	5,8 - 8,9
Restriction of the lower calorific value range by high processing levels	

Table 11. Air and LPG additions of the investigated H gas properties

For the practical implementation of the listed quantities of the LPG admixtures, limits as given in Table 12 are to be observed, in accordance with the requirements presented on the need for the use and applicability of SGERG88 and AGA8 procedures and the resulting maximum admixture quantities according to Table 12. Due to these limits, defined in DVGW G 486-B2, it will not be possible in every case to reach the upper calorific value range at higher pressures. In addition, the availability of appropriate measuring technology for higher liquid gas fractions is limited. At the very high degrees of methane processing, there are limitations on attaining the lower calorific value range, since when processing to 99.5 Vol -% methane, an H gas with a calorific value of 11.009 kWh / m³ results.

	Descriptor	Unit	Limit according to G 486 supplementary sheet 2 Appendix B p> 100 bar	Limit according to G 486 supplementary sheet 2 Appendix B p> 100 bar
Propane	$\times C_3H_8$	mol.-%	3,5	6.
Butane	$\times C_4H_{10}$	mol.-%	1,5	1,5

Table 12. Limits according to DVGW G 486 supplementary sheet 2 appendix B

Table 13 shows the maximum possible , compliant LPG admixture, a propane / butane mixture of 95 / 5 Mass .-%. As a result, it is clear that processing to a maximum methane content of 99.5% vol. with the maximum permissible LPG admixtures, a calorific value of maximum 11,361 kWh/m³ (NTP) is possible at pressures above 100 bar, and a maximum of 12,075 kWh/m³ (NTP) at pressures below 100 bar.

Methane content in biogas	LPG as admixture	Propane content in admixture	Butane content in admixture	Calorific value	Wobbe Index	Relative Density
in Vol.-%	in Vol.-%	in mol .-%	in mol .-%	in kWh/m ³	in kWh/m ³	
94,000	3,7	3,497	0,141	11,044	13,733	0,647
95,000		3,497	0,141	11,151	13,969	0,637
96,000		3,497	0,141	11,257	14,210	0,628
97,000		3,497	0,141	11,364	14,454	0,618
98,000		3,497	0,141	11,471	14,704	0,609
99,000		3,497	0,141	11,577	14,959	0,599
99,500		3,497	0,141	11,631	15,088	0,594
94,000	6,5	5,978	0,241	11,501	14,039	0,671
95,000		5,978	0,241	11,605	14,265	0,662
96,000		5,979	0,241	11,709	14,495	0,653
97,000		5,979	0,241	11,813	14,729	0,643
98,000		5,979	0,241	11,917	14,967	0,634
99,000		5,979	0,241	12,021	15,209	0,625
99,500		5,980	0,241	12,073	15,332	0,620

Table 13. Gas properties with maximum compliant LPG additions

Figure 14 shows the admixture required to achieve the corresponding H gas properties. The limits on the maximum concentration of propane are also shown according to DVGW regulations G 486 supplementary sheet 2 a ppendix B. Admixtures to achieve the properties of North Sea I / North Sea II H gas are, based upon all levels of methane processing, above the limits. A compliant mixture is not possible in this case, or needs to be tested on an individual basis.

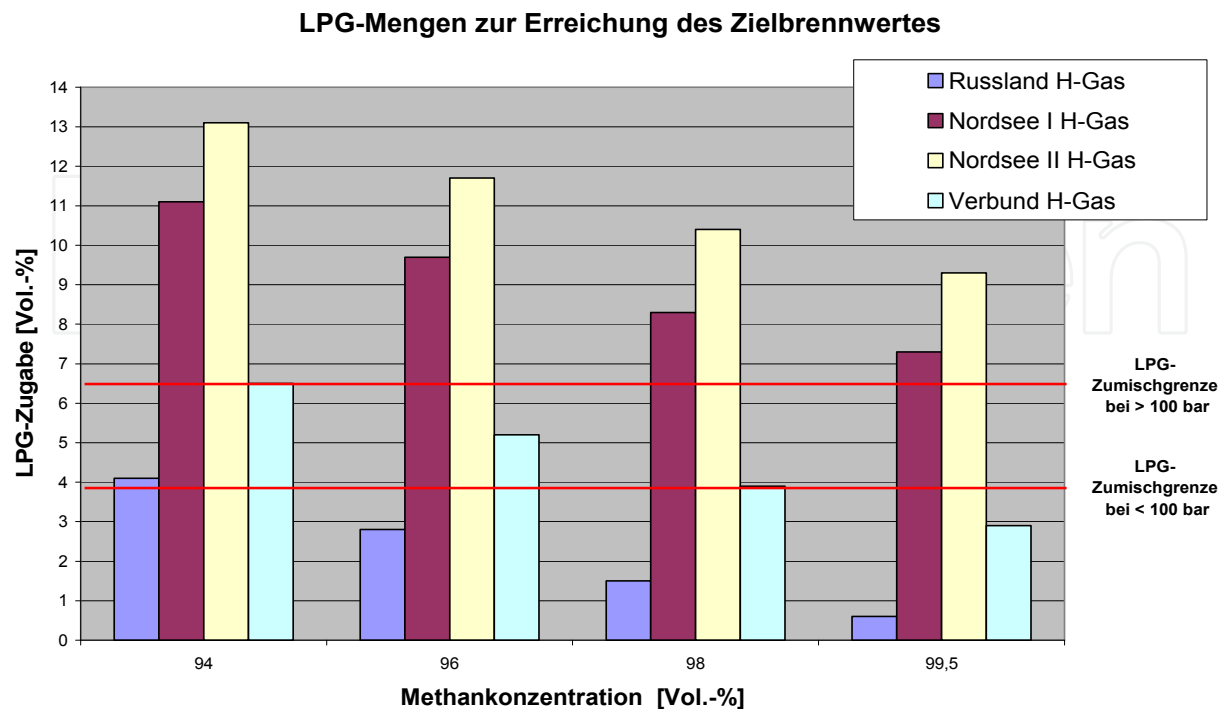


Fig. 14. LPG quantities necessary to achieve the target calorific value

In order to achieve higher calorific values, alternative conditioning measures can be employed. For example, ready-made mixtures with customized propane / butane ratios can be used for conditioning. This can increase the calorific value, but technical and physical effects, such as condensation behaviour, methane number and k-number deviations need to be considered.

6.2 Conditioning: Target L gas

Two different L gas target properties have been described. Because of their basic constitutions, one bio-methane mixture is conditioned with air and the other is conditioned with a combination of air and LPG.

Table 14 shows a summary of the admixtures with which a target calorific value-oriented mixture for the low calorific base gas property can be achieved.

In the case of simple air addition, particular attention should be paid to compliance with the maximum O₂ volume fraction. This should not exceed 3 % vol. in dry networks according to DVGW worksheet G 260. This quantity is reached when adding pure air to the processed biogas, at an admixture of 15 vol -% of air. In the low caloric L gases (e.g. Weser Ems gas), this limit is never reached.

Furthermore, a minimum air addition may also be necessary, in order to achieve the required Wobbe Index according to DVGW worksheet G 260.

Table 15 shows the minimum air addition for the individual processing grades of methane to achieve an L gas compliant Wobbe Index of under 13.0 kWh/m³ (NTP).

Air admixtures to attain the target calorific value +/- 2%	
Methane concentration after processing in vol -%	Weser Ems L Gas
	H _{S,n} = 9,653 - 10,047 kWh/m ³
	Air admixture in Vol.-%
94,0	3,6 - 7,7
96,0	5,8 - 10,0
98,0	8,0 - 12,3
99,5	9,7 - 14,0

Table 14. Air additions to the H gas properties under investigation

Methane in Biogas	Methane in admixture	CO ₂ in admixture	Air to the Biogas	O ₂ in admixture	Calorific value	Wobbe Index	rel. Density
in Vol.-%	in Vol.-%	in Vol.-%	in Vol.-%	in Vol.-%	in kWh/m ³	in kWh/m ³	
94,000	92,429	5,506	1,700	0,645	10,226	12,999	0,619
96,000	91,778	3,442	4,600	1,208	10,154	12,996	0,611
98,000	91,163	1,488	7,500	1,741	10,086	12,993	0,603
99,500	90,702	0,091	9,700	2,126	10,035	12,988	0,597

Table 15. Minimum quantity of air to attain L gas specification

For the high-caloric L gas mixtures (target properties according to Holland II L gas) the processed biogas is conditioned with air and LPG. Table 16 shows the correlating LPG-air additions, to reach the calorific value range (+ / -2%).

The gray-shaded areas show where a compliant combination of air and LPG additions is impossible. With increasing LPG additions, the necessary addition of air is limited by the maximum O₂ volume fraction of 3 %. If too little LPG is added, only the lower calorific value range can be covered. The broadest coverage of the calorific value range lies in between and is marked by the wider bandwidth of air additions.

Methane concentration in the Vol -%		LPG - addition [Vol -%]														
		0			2.			4			6			8		
Holland II H _{s,n} = 9,996 - 10,404 kWh/m ³	94	2	-	4	4	-	7	7	-	10	10	-	14	14	-	16
	96	5	-	5	7	-	9	9	-	12	12	-	16	16	-	16
	98		-		10	-	11	11	-	15	14	-	16		-	
	99,5		-		12	-	13	13	-	15	16	-	16		-	

Table 16. Air addition, depending on the addition of LPG and methane concentration

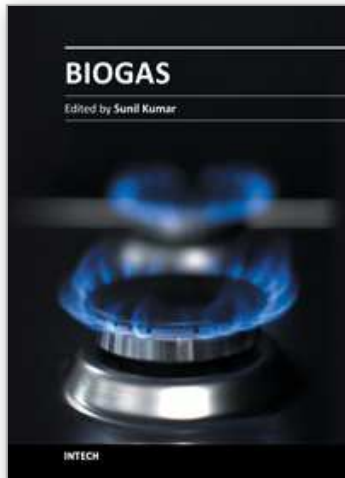
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This book contains research on the chemistry of each step of biogas generation, along with engineering principles and practices, feasibility of biogas production in processing technologies, especially anaerobic digestion of waste and gas production system, its modeling, kinetics along with other associated aspects, utilization and purification of biogas, economy and energy issues, pipe design for biogas energy, microbiological aspects, phyto-fermentation, biogas plant constructions, assessment of ecological potential, biogas generation from sludge, rheological characterization, etc.

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