Secrétariat

**Comité d'experts du transport des marchandises dangereuses
et du Système général harmonisé de classification
et d'étiquetage des produits chimiques**

Sous-Comité d'experts du transport des marchandises dangereuses

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Produits actuels et futurs dans le secteur du gaz de pétrole liquéfié (GPL) − Ajout d'une nouvelle disposition spéciale pour les Nos ONU 1075 et ONU 1965 − Informations complémentaires, travaux de recherche et essais

Communication de la World Liquid Gas Association (WLGA, anciennement WLPGA)*

I. Introduction

1.   Dans le présent document, la WLGA demande que soit adoptée une nouvelle disposition spéciale pour les Nos ONU 1075 et 1965 afin d'autoriser l'ajout d'éther diméthylique (No ONU 1033), jusqu'à une teneur de 12 % en masse, au GPL qui relève de l'un ou l'autre de ces numéros ONU.

2.   On trouvera en annexe des informations complémentaires, ainsi que des précisions sur les travaux de recherche et les essais menés par la WLGA et validés par Risktec TUV et KIWA Technology B.V.

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*   A/78/6 (Sect. 20), tableau 20.5.

Annexe

[*Anglais seulement*]

"Drop-in" Dimethyl Ether Blend (DME) ratio determination considerations

A.   Executive Summary

Renewable and Recycled Carbon Dimethyl Ether (rDME) is a promising fuel for the Liquid Gas industry as it shares similar properties to LPG, Propane and Butane. As such, it can be blended with LPG or used as a fuel on its own, using LPG infrastructure and equipment which require varying degrees of modification.

When blended with LPG up to a defined limit, no modifications are required. The World Liquid Gas Association (WLGA) have established a working group focused on the technical and safety assessment of blending rDME with LPG. This working group has established a "drop-in" blend ratio (rDME-LPG) which can be safely used with the existing transport and storage infrastructure without modifications and continues to develop knowledge and standards for the full range of rDME/LPG blends.

This document presents the case, based upon evidence gathered from research and testing undertaken by the WLGA working group, for the inclusion of blends of DME up to **12 %** mass in LPG within the regulatory definitions which currently exist for LPG storage and transportation.

The process followed for establishing the "drop-in" blend ratio described in this document and the resulting conclusions, have been endorsed by the external independent reputable bodies, RiskTec TÜV Rheinland and KIWA Technology B.V.

B.   Introduction

Dimethyl Ether (DME) is an attractive blending fuel for the LPG industry as it can be efficiently produced from sustainable feedstocks (resulting in renewable DME - rDME) and can lower the carbon intensity of existing product streams. Through blending with fossil LPG, immediate carbon reduction is achievable. In the longer term a further significant reduction may be achievable through blending with renewable LPG. The World Liquid Gas Association (WLGA), in association with regional LPG associations and equipment manufacturers have undertaken full assessments of the related technical and safety implications relevant to the addition of DME up to a set "Drop-in" limit.

DME (UN1033) like LPG, is a flammable, non-toxic gas and, not harmful to the environment and it has the same UN classification of 2.1 and Hazard Identification Number (23).

Both the World Health Organisation and the EU classify both DME and LPG as being non-toxic and not harmful to the environment. As no chemical reaction occurs when they are blended this classification remains correct and will not require change.

For the purposes of this document, DME and rDME are considered interchangeable as they have identical chemical make-up, and for consistency the term DME is used throughout this document.

This document summarises the findings of WLGA's investigations into the compatibility of the existing transport and storage infrastructure with DME in a blended form with LPG. Blending DME with LPG will address the industry's need for immediate decarbonisation and initial testing and research will support the safe adoption of DME and high ratio DME/LPG blends in the future. The 12wt % blend proposed considers operational conditions, existing safety factors and normative controls. To do this, there was a need to establish a maximum DME % limit that can be blended with LPG, which does not require any changes to the existing transport and storage infrastructure.

Research and testing are currently in progress for consumer equipment, and the current findings are that for many counties/regions (including, Australia, Europe, Japan, North America), a 12 % DME blend by mass is fully compatible and does not have any negative effects or safety issues. It has also been identified however that in some countries, elastomers have been used for domestic consumer equipment that are only suitable for lower DME to LPG ratio blends. Existing controls, such as those preventing the use of butane in propane devices (or vice-a-versa), will enable markets which use unsuitable elastomeric materials in consumer equipment to ensure that the DME content is appropriately managed. Examples of such controls are regional quality specifications; whilst the UN numbers used to transport and store LPGs may be identical, regional quality specifications may dictate different limits on non-LPG and specific LPG components to ensure the safety and operability of the appliance or end use.

All references to blend ratio in this document refer to mass blend ratio, this prevents any errors occurring due to temperature/expansion ratio differences of the DME and LPG.

This document, written by the WLGA and its members, aims to provide a summary of the current knowledge, data, and evidence available to the association at the time of writing.

This document recommends a conservative maximum blend-ratio based on the testing and research that has been undertaken, relating to the safe transport and storage of DME/LPG blends.

C. WLGA Approach and Background

C.1 Approach

The WLGA has undertaken a full supply chain assessment of the proposed introduction of DME as a blend component. The assessment process was undertaken in 4 phases.

> Phase 1 – Literature review and collection of evidence
>
> Phase 2 – Top-Down HAZID-based risk identification exercise and GAP analysis
>
> Phase 3 - Empirical testing and trials
>
> Phase 4 – Creation of guidance to support adoption.

The literature review was conducted to establish available public and private domain sources of information relevant to the LPG industry. This information was assessed for limitations or areas when information was missing or incomplete within the discipline/field in question. A full supply chain Hazard Identification assessment, facilitated by Risktec TUV, was conducted in over 40 hours of workshops involving subject matter experts. For ease of administration, the scope was divided into four disciplines, Materials compatibility, Storage and Operations, Transportation and Applications and equipment. During these workshops, the risks identified were risk-scored and any further applicable gaps in knowledge identified were documented. These risks were prioritised according to their risk score and the credibility, and availability of supporting evidence, as well as their relevance to the storage and transportation of LPG. These risks were then analysed through testing and/or developing appropriate controls, and then the risk scores were reviewed for closure. Findings from the testing and research have been used in the determination of the safe drop-in level of DME in LPG.

The WLGA has now been working for over 18 months to address the identified gaps in knowledge and understanding that were highlighted through the workshops and resulting work. The results have enabled the determination of the safe drop-in blend ratio (DME to LPG) for the Transportation and Storage elements.

<div align="center">WLGA – 4 stage assessment process</div>
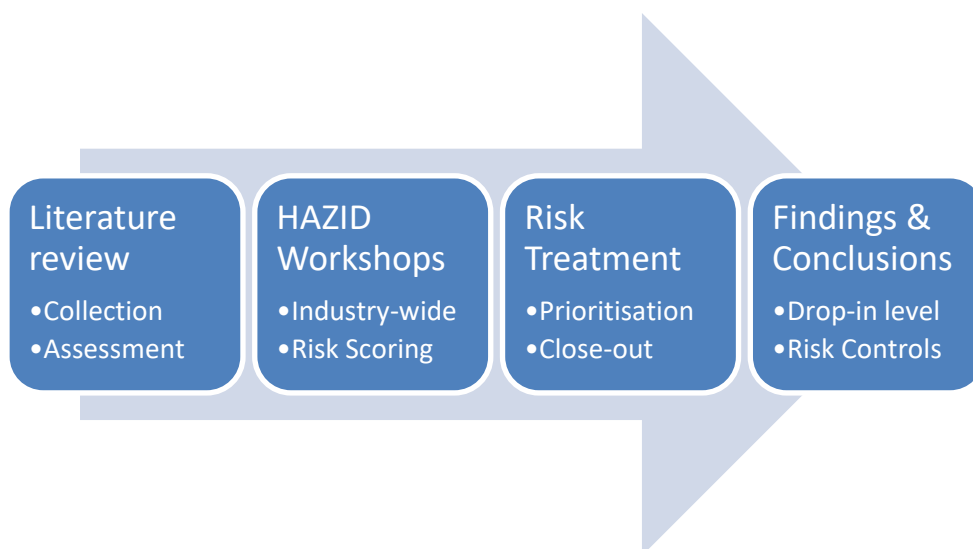
All work undertaken employed the UK's HSE hierarchy of risk control theorem (which is generally accepted worldwide) where possible risks should be eliminated. If this is not possible, substitution of that risk with lower-risk approaches should be considered. If further risk reduction is required, engineering controls and/or administrative measures (procedures or working practices) should be applied. Thus, recommendations from the working group should not be made based upon solely the application of operational measures, but rather through the proposal of a full suite of measures to directly address the risks.

WLGA has now completed phase 3 of the project for transport and storage. The next phase of work, specific to construction and use standards, is dependent on whether DME blended with LPG to the 'drop-in' level can be assigned by the application of a Special Provision to the current LPG UN numbers (UN 1075 and UN 1965).

The Phase 2 risk identification exercise developed a comprehensive Risk Register to capture risks highlighted by the working group subject matter experts. This paper focuses on medium and high priority risks identified with respect to the transport and storage aspects of the supply chain which have been fully evaluated through testing and the application of controls in subsequent project phases (3 and 4).

C.2 Background

DME/LPG blends are not uncommon and have been used widely in the aerosol industry for many decades. It is recognised, however, that the approach taken within the aerosol industry is quite different to the approach taken by the LPG industry, and as such, scrutiny of the specific effects of DME was undertaken.

Evidence with various degrees of credibility is available from the IDA (the International DME Association), Japanese LPG and DME Associations, Total, WLGA, KIWA and other noteworthy organisations; much of this evidence is available within the WLGA rDME technical library. From consideration of the documentation within the library, a volume of evidence exists in support of the use of DME blends of between 20 % and 25 %. WLGAs' aim was to establish a conservative risk-based conclusion on 'drop-in' blend ratio, taking into account other factors such as evaporation behaviour and cyclic accumulation that can occur during use through natural vaporisation. Effects on combustion in appliances are considered secondary given that further downstream controls remain in place and that preliminary testing supports use of much higher blends.

All evidence reviewed within the various phases of the project was verified for applicability to international LPG practices; particular attention was paid to test conditions, assumptions or model variables/parameters and their effect on limiting the scope of the findings to specific regions or practices. Where necessary, testing was repeated to ensure applicability of results to the global LPG industry.

D. Transport and Storage

Risks identified for transport and storage as high and medium priority risks are detailed further in 3.1 to 3.7:

Material compatibility – Not all materials, particularly some non-metallic materials are compatible with DME and DME/LPG blends (above a specific DME content).

Increase in DME concentration within the liquid and vapour phases due to the evaporation behaviour and cyclic refilling of DME/LPG containers.

Controlling the blend to ensure consistency throughout the supply chain.

Equipment compatibility; particularly relating to valves and hoses.

Odorant compatibility – Odour fade and potency.

Increase in net weight of full storage and transport infrastructure (increased static loading from the higher liquid density of DME and potential to overload transport).

Effects on storage practices – Separation distances, Pressure relief sizing, Deluge/Sprinkler systems and Hazardous areas.

The following sections review these risks with respect to the evidence made available or testing conducted by the WLGA. Where possible, approaches defined within accepted normative references have been used to conclude a conservative blend ratio. Where relevant, alternative approaches or risk controls have been proposed to manage the residual risk.

D.1. Discussion

LPGs ('Liquefied Petroleum Gases') are a broad spectrum of short-chain saturated and unsaturated hydrocarbons in the range C2-C5. Predominantly made up of C3 and C4 components (as C2 and C5 are valuable for petroleum and plastics industries and as such their yield from production tends to be maximised), product specification is standardised at a regional level, with few globally recognised standards. Table 1 (next page) provides a comparison of properties of Propane, Butane, DME, 20 % DME/Propane blend and a 20 % DME/Butane blend.

Table 1 – Comparison of different properties

Property	Unit	Propane	Butane	Dimethyl Ether	20 % DME in Propane	20 % DME in Butane
Chemical Formula	-	C_3H_8	C_4H_{10}	CH_3OCH_3	NA	NA
Gas Density	Kg/m^3	1.899	2.544	1.993	1.916	2.431
Relative Density	-	1.550	2.075	1.627	1.564	1.984
CO_2 Max	%	13.7	14.02	14.97	13.85	14.21
Net Calorific Value	MJ/m^3	88.00	116.09	57.26	82.09	104.34
Gross Calorific Value	MJ/m^3	95.65	125.81	63.03	89.38	113.26
Wobbe Index (Net)	MJ/m^3	70.69	80.58	45.16	64.04	73.42
Wobbe Index (gross)	MJ/m^3	76.74	87.33	49.53	71.47	79.57
Burning Velocity	Cm/s	43	41	50	44	42
Auto-Ignition Temperature (ASTM E659)	˚C	450	405	350	444	384
Maximum Experimental Safe Gap (MESG)	mm	0.92*	0.94/0.95 *	0.84*	0.902	0.926
Lower Explosion Limit	Vol %	2.37	1.86	3.4	2.2 % (Gexcon)[1]	TBC
Upper Explosion Limit	Vol %	9.5	8.41	27.0	10.84 % (Gexcon)[1]	TBC

*Taken from IEC 80079-20 Annex B

Commercial grades of LPG range from relatively pure Propane or Butane through to an array of mixtures of both, include high levels of unsaturated hydrocarbons (Propene, Butene etc) and/or including some heavier and lighter hydrocarbon components alongside trace levels of other contaminants. Due to the chemical similarity of propane and butane, most of the storage and transportation equipment which is suitable for propane is also suitable for butane. However, unsaturated hydrocarbons, due to their higher reactivity, have been known to cause deterioration to elastomer materials and in some instances (e.g. Vaporisers) oligomerise to form longer-chain hydrocarbons (oils and waxes, often termed 'heavy ends' which may also be present from production sources). This is often not directly considered during the testing used for the certification of LPG suitable equipment and has not yet been identified as a safety concern. LPG quality can have a significant impact on the supply chain and appliances, and as such, for purposes of this report, assumptions as to the quality of the LPG used when creating the blend have been made.

The only internationally accepted LPG quality standard relating to commercial grade propane and butane is ISO 9162[2], however many countries have regional standards. A brief review of the more common standards; (ISO 9162[2], BS 4250[3], EN 589[4], ASTM D1835-22[5]) demonstrates that 'Trace' contaminants such as sulphur, mercaptans, ammonia etc are generally minimised. Permitted in significant quantities, unsaturated components (Dienes, Propene, Butene etc) are controlled in two ways: through limiting the maximum vapour pressure of the gas within the relevant standard, or through stated maximum concentration. In standardisation regimes where there is no stated maximum concentration, and which impose a maximum vapour-pressure, it is possible to include high levels of propene (not permitted by some LPG standards) by blending butane to the stated limit to counteract the relative higher vapour pressure of propene. Fig 1 shows the vapour pressure curve of different common mixtures of LPGs, and DME.

Figure 1 - Equilibrium vapour pressure of different LPGs, and DME
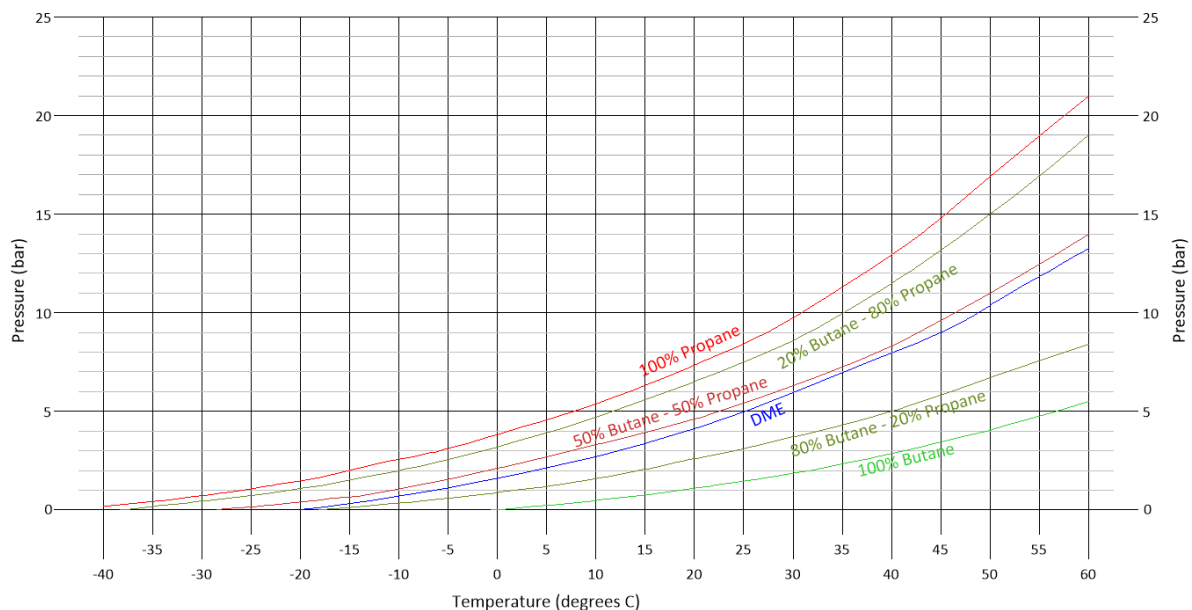
DME's equilibrium vapour pressure sits between butane and propane for typical operating temperatures (-40 degrees C - + 60 degrees C). As such, per Dalton's law of partial pressures, when DME is added to butane it has the effect of increasing the vapour pressure and when mixed with propane, it has the effect of reducing it. Like the addition of butane to reduce the equilibrium vapour pressure of propene, the addition of DME to propene could permit even higher levels whilst remaining within vapour pressure limit of the relevant product standards, where this is the relevant normative approach (as opposed to specific non-propane maximum limits).

The addition of the drop-in blend of DME into the existing LPG market does not justify deviation from the known and understood LPG quality requirements in existence today. Consequently, the creation of a blend of high propene balanced with limit levels of butane and high levels of DME to achieve the relevant vapour pressure specification must be

discounted from scope. LPG must meet the current required specifications prior to blending with DME, and DME should meet either ASTM 7901-20[6] or ISO 16861[7]; both of which are broadly aligned (technically).

The following sections assume no change to existing infrastructure or equipment is required to facilitate the blend; however, it should be noted that changes will be required to incorporate blending facilities or facilities to handle the mixture prior to being fully mixed. Operators choosing to introduce DME into their facilities are duty-bound to ensure compliance will existing regional regulations, and consider the implications from a health, safety and environment perspective.

D.2   Risks

D.2.1   Material Compatibility

Research and testing have been undertaken on the compatibility, with the DME/LPG blend, of materials used for the transport and storage of LPG. The blend used for the testing (unless otherwise indicated) was 20 % DME and 80 % propane, and control samples were tested (unless otherwise indicated) using 100 % propane.

Metallic materials

ISO 11114-1[8] does not indicate if bronze (a large LPG pump and compressor manufacturer supplies these for DME and DME/LPG applications; both versions safely use bronze components) or Zamak are compatible with DME. Bronze is used for the impellers in some pumps, parts of gas compressors, certain valve packings and also in older appliances. Zamak is an alloy of Zinc, Aluminium and Copper and is used for parts of level gauges and in the bodies of pressure reduction regulators. All alloying components of ZAMAK are considered compatible with DME per ISO 11114-1[8], however the alloy has not been previously tested for compatibility. WLGA has undertaken exposure testing, in an accredited laboratory (Kiwa 2023[9]) on both bronze and Zamak, the results show that these materials are suitable with no/negligible changes to hardness, bending or tensile strength properties.

Non-metallic materials

For composite materials, ISO 11114-2[10] lists various plastics that are suitable for unblended (pure) DME but does not refer to their use as a cylinder liner. Manufactures of composite cylinders with non-metallic liners have undertaken testing on the suitability of the materials they are using with DME/LPG blends (this testing was undertaken on a blend of 35 % DME/65 % propane). The verified and witnessed results (Hexagon Regasco/TUV 2023[11]) show that both the liner and the outer composite material are suitable for the blends up to this composition.

The compatibility of elastomeric materials in contact with LPG is predominantly controlled through standards. Many of these standards refer to ISO 1817 "Rubber, vulcanized or thermoplastics. Determination of the effect of liquids" for the testing of compatibility of elastomers, for instance, EN 549 "Rubber materials for seals and diaphragms for gas appliances and gas equipment", and EN 1762 "Rubber hoses and hose assemblies for liquefied petroleum gas, LPG (liquid or gaseous phase), and natural gas up to 25 bar (2,5 MPa) - Specification". The UL[12] series of standards for LPG equipment all follow similar methodologies, utilising an analogous test liquid for immersion of materials for a duration of 72 hours. The effects of the liquid are measured immediately after immersion and following subsequent kiln-drying to determine if extraction has occurred. The use of analogous test media (pentane in EN 549[4] and hexane in the UL[12] series of standards for LPG equipment) simplifies these tests as they can be conducted at ambient conditions and minimise measurement difficulties caused through volatility of the evaporating test medium.

Testing in accordance with ISO 1817[13] may simulate service conditions, although no direct correlation with service behaviour can be assumed. For example, the drying of materials following immersion is unlikely to happen in practice, but this test is designed to accelerate aging of elastomers through extraction of components within the material. The rubber giving the lowest change in volume is not necessarily the best one in service. The thickness of the

rubber needs to be considered, since the rate of penetration of liquid or gas is time-dependent and many thick rubber products may remain unaffected for the whole of their' projected service life. A gasket, for instance, is only exposed to the liquid/gas on its inner edges. Additionally, the action of a liquid/gas on rubber, especially at high temperatures, can be affected by the presence of atmospheric oxygen. The effect of a liquid or gas on a material also depends on the nature and magnitude of any stress within the rubber. A diaphragm for instance, under tension and in some case point-loading, has different mechanical requirements to a supported static seal where swell is unlikely to cause leakage. Swell may actually reduce leakage when the elastomer is used for sealing applications. The testing that has been undertaken by WLGA (2023)[48] approaches this variability by making direct comparisons between the material behaviour in DME/LPG blends with its behaviour in LPG. Thus, if there are no significant effects, it is unlikely that the in-service behaviour or performance will be affected significantly. Where effects are more significant, limits as defined within relevant normative references are applied alongside practical evidence of the specific applications for the materials in question.

Material performance is predominantly affected in two ways.

(a)   Firstly, materials which swell through absorption of the vapour/liquid may suffer from reduced sealing performance or failure as their mechanical properties (Tensile strength, elasticity etc) are reduced. This first phenomenon in isolation would result in the material returning to its original state after drying if damage has not occurred. Swell is measured immediately after immersion, and prior to any drying, and involves either weight change (increase) or volumetric change.

(b)   Secondly, where the material is chemically affected by the vapour/liquid, the material can become brittle or lose shape/become porous. This is caused by the removal of components within the elastomer that aid elasticity or are used to fill pores within the elastomer. The purpose of drying materials after immersion is to quantify the degree of extraction suffered by the elastomer.

UL (2023)[14], DCC (2021)[15], IDA (2017)[16], Kiwa (2022)[17], Rochester (2023)[18], and Clesse (2022)[19] have performed testing of common materials with liquid and vapour-phase DME/LPG blends. To summarise the conclusions of these works:

(a)   Elastomer material composition and performance is highly manufacturer specific and as such a wide range of materials from different manufacturers have been tested to improve statistical confidence.

(b)   Silicone and EPDM are most significantly affected by DME but are also the poorest materials for sealing in LPG applications. These are limited within the standards to low-pressure vapour phase applications only and are rarely used within the LPG industry due to their poor performance. They are not relevant for transportation and storage operations.

(c)   Most materials transition from normal levels of volume/mass addition (Swell) to higher-than normal levels of swell above a 20 % DME/LPG blend ratio. UL (2023)[14] state compatibility with 20 % DME for all materials tested, including NBRs, FKM, FVMQ and CR (Neoprene) using Diethyl Ether as an analogous test medium.

(d)   FKM and low ACN content NBR most consistently swell excessively when subject to liquid DME/LPG blends with a DME content above 20 % but perform adequately in vapour service.

(e)   Kiwa (2022)[17] found that all materials when exposed to 100 % DME vapour performed adequately, with effects at least an order of magnitude lower than the effects of liquid.

(f)   Clesse (2022)[19] found that in general all materials tested were compatible in the vapour phase with 20 % DME in Propane. Viton (FKM) did swell (when subject to liquid phase) by approximately 11 % (mass, not volume; the limit in EN 549[4] is 10 %) however this could be due to higher liquid density of DME/LPG. Importantly FKM had little mass extracted after drying, and across all materials, hardness and glass transition temperature did not vary significantly.

(g)   Rochester (2023)[18] performed compatibility tests with pure DME on a range of metallic and non-metallic components. Visual inspection showed little change to all materials other than some which experienced minor discolouring, expected to be related to the dyes used in their manufacture.

(h)   The relative low reactivity of DME does not cause dangerous chemical interactions with elastomers (confirmed by ISO 11114-2[9]) but may cause deterioration or high material swelling.

(i)   Kiwa, DCC and The Japanese DME forum showed that when using a 20 % DME/LPG blend, extraction of material from seals was shown to be within the normal range of that found in LPG service.

(j)   The testing exposes both sides of the sample to the medium, however for most in service applications only one; side or edge will be exposed to the medium, which has the effect of reducing any material changes.

WLGA have undertaken materials testing using an DIS ISO 1817[20] compliant pressurised test method. The standard, which previously did not effectively address post-immersion sample measurement methods for volatile test media, has had proposed amendments to standardise on photographic methods for volume swell, and is currently at the fDIS approval stage. The testing was conducted in liquid phase, using a 20 % DME 80 % propane (by mass) blend and with 100 % propane used as the control. The proposed drop-in blend has then been calculated by including allowances for potential preferential evaporation and accumulation.

The findings of the testing are that all materials tested have remained within tolerable swell and mass-extraction limits; the limits applied depending upon the use of the actual material e.g., diaphragm, seal, hose etc and relevant standard e.g., EN 549[4], UL 157[21] etc.

WLGA have also undertaken accelerated aging testing (WLGA 2023[22]) on 10 representative materials, previously tested on a single cycle. Propene can be more aggressive in both swell and the extraction of plasticisers/fillers than propane but is permitted at various levels (according to local regulations/standards) within commercial propane. Materials were exposed to liquid which alternated between liquid blends of propane and propene (80/20), and DME and propane (20/80). Control samples alternated between liquid blends of propane and propene (80/20), and 100 % propane. The intention behind this testing was to ascertain if the effects of DME/LPG blends and propane/propene are additive. Four cycles were applied, using the standard test times in accordance with ISO 1817[20]. Results taken immediately after immersion correlate well with results from a single cycle of immersion for both propane exposed and DME/propane exposed materials. This shows that existing elastomers, having been exposed to propane and propene in prior service, are not expected to swell significantly more upon first exposure to DME/LPG blends. Extraction: that is the removal of material from the elastomer was marginally higher after cyclic exposure than the single cycle results. This applied to comparisons of both control samples and DME/LPG blend samples (single-cycle and cycled). This provides a high degree of confidence in the performance of existing elastomers in service, and in the longevity of elastomers used with DME/LPG blends.

Hoses represent one of the most challenging elastomeric systems when considering compatibility. Hoses are dynamic systems incorporating a liner, a reinforcement layer, and an outer sleeve. In use, hoses require flexibility, and the liner cannot allow gases/liquids to permeate at a higher rate than permitted by the standard to which they are manufactured. Swell is a less significant concern, with most of the hoses' pressure-holding capability being undertaken by the reinforcement. This said, loss of flexibility through extraction of materials from the liner can lead to material deterioration and leaks. Manufacturer-specific elastomers are generally selected with good flexibility/low hardness and resistance in mind, and testing has been undertaken by WLGA to assess real-world performance. Testing included basic material testing alongside durability tests to determine any significant effects to adhesion (inner/outer layers) and connection to couplings. Given general material results and a low-ratio blend, long-term durability of hoses can be managed through enhanced, regular condition-based inspection and repair/replacement, best practice in LPG operations.

Work, to simplify the material test method (through determination of a suitable analogue liquid to enable testing to be undertaken at ambient temperatures and pressures) is also underway. Establishing a suitable analogue must be based upon volumetric measurements of different materials in the proposed LPG/DME mixtures given the difficulty in obtaining stable mass measurements from materials immediately after exposure to volatile media. These volumetric measurements can then be compared directly with measurements of the same materials in propane (Not using the pentane/hexane analogue). As EN 549[4] predominantly measures mass, this requires a change in understanding of swell limits, from a mass-base to volume-based determination of performance. KIWA (2022)[23] and UL (2023)[14] have both made attempts to standardise on different liquid analogues, opting to utilise n-Butyl Acetate and Diethyl Ether respectively. Real-world performance of these analogues has been compared by calculation, however the number of variables involved in the production of elastomers presents a challenge as each of these variables can interact differently with the analogue liquid. Selection of a suitable analogue will be based upon those which are found to behave most similarly to DME or DME/LPG blends tested using the pressurised methodology and based upon robust academic logic. Once determined, the analogue may be used to aid future certification of materials to be used in service with blends; however, this doesn't affect our ability to draw conclusions today on the compatibility of previously (LPG) certified elastomers.

It should be noted that very few references could be found which relate to operation at very low or elevated temperatures (e.g., in vaporisers). Operators must therefore consider the effects of operation below – 40 °C and above 60 °C.

Floats, often used in gauges or as stop-valves to prevent overfilling, have been tested and found to be suitable. Included in the testing were separate floats, float gauges and float-operated stop-valves. Testing was also undertaken to ascertain if the float to operating arm resistance to pull-off had been reduced, which could result in failure. All floats and float mechanisms continued to operate correctly, no loss of weight, change in hardness, swelling or reduced pull-off value was recorded (WLGA 2023[22])

Where materials of construction of float gauges and float operated stop-valves are predominantly metallic or utilise polyethylene terephthalate (PET), polypropylene (PP), polyether ether ketone (PEEK), or Nylon (PA), these are considered compatible (Kiwa 2020[25]), and ISO 11114-2[9] provides a full list of plastics compatible with 100 % DME).

Jointing, sealing and gasket materials that are in common use with the LPG industry, have been tested according to the EN 751[26] series of standards, which requires testing of completed joints, and have all been found satisfactory for the proposed blend.

Hazards from incompatibility with leak-detection fluids have been investigated. DME safety data sheets show reactivity and compatibility hazards, with hydrogen fluoride, oxygen and strong oxidising agents. Leak detection sprays are highly unlikely to contain any of these reactants due to their acidity or more general risks in contact with flammable gases. Compatibility with leak detection fluids is not considered to be a risk however operators should always ensure compatibility at an operational level.

The Safety Data sheets (SDS) for typical DME composition do not highlight any compatibility concerns from a reactivity perspective. Common additives are not expected to cause concern.

From a review of the material compatibility data as described above, it can be concluded that a 20 % blend ratio of DME/LPG is feasible and safe for all parts of the transport and storage and transport infrastructure. However, the effects of cyclic accumulation and preferential evaporation (see 3.2.2) have also been considered when defining the 12wt % drop-in blend ratio.

D.2.2   Storage and Evaporation Behaviour

Simulations and testing in various countries have identified concerns relating to change in composition of DME/LPG blends due to the differences in volatility of components within the mixture. For the purposes of this report, this is termed 'preferential evaporation'.

Preferential evaporation occurs when vapour is drawn from a mixture of liquified gases with different equilibrium vapour pressures. Vapour drawn from the storage vessel will generally contain higher concentrations of the more volatile components until these have a reduced concentration within the liquid phase; allowing the less volatile components to vaporise and make up larger components within the vapour. The composition of the vapour and liquid phase components therefore vary during cylinder and tank depletion cycles during natural vaporisation/vapour withdrawal.

The secondary impact of this phenomenon occurs when the correct blend ratio is used to refill a storage container at a point when it has an increased concentration of either of the mixture components. In this instance, a slight increase in the overall concentration of that component is seen, and conversely a dilution occurs to the component present in a lower concentration than the blend requires. In the case of DME, concentration will increase towards the end of the depletion cycle when added to propane and concentration will reduce with butane. Therefore, in the case of propane this can incrementally increase DME concentration over a number of fill cycles; a process called 'Accumulation' for the purposes of this report.

Neither Preferential evaporation or Accumulation phenomenon occur in dedicated liquid-service; they only apply where vapour-withdrawal occurs from a bulk tank or cylinder.

A wide range of literature is available on these topics:

(a) Kiwa (2022)[27] produced equation-of-state (EoS) models with pure propane/butane/DME and verified them with experimental testing.

(b) The Japanese LPG Association report[28] performed testing on blends of DME and LPG, although many of the tests were performed on 15 % Butane/ 85 % propane mix.

(c) Kiwa (2022)[17] further refined their preferential evaporation model to determine the effects of sub-zero temperatures on the DME concentration.

(d) DCC (2021[15]) performed tests by evaporating DME/Propane from a cylinder and measuring concentration throughout the cycle. They also performed tests on concentration when the cylinder is repeatedly filled.

(d) Kiwa (2023[29]) also performed modelling to determine the effect of repeated filling on potential for accumulation.

(e) WLGA/KIWA (2023[30]) modelled multiple component blends during operation to determine the combined effects of low temperature, non-propane components and accumulation.

The research demonstrated good agreement and the following conclusions were drawn:

(a) The phenomenon occurs most significantly on storage that is being operated above its' rated supply capacity (offtake) or when the storage container is less than 5 % full. For DME/propane blends at approximately 5 % (and below) the DME concentration increases until the storage container is empty.

(b) Low temperatures (at or below 5 °C degrees for propane) are worst case for increases to DME concentration. However, simulations were performed on an Isothermal model and the likelihood of sustained, very low temperatures is low.

(c) Accumulation, caused by repeat filling, leads to DME concentration peaking at different levels as the tank is cycled. Peak DME concentration occurs within the first 5 cycles, and trends down towards a stabilized figure as the storage is repeatedly filled. The peak figure reaches within 5 % of this stabilised figure after 10 fills and does not continue to rise indefinitely (verified over 20 cycles).

(d) The point during tank depletion where the fill occurs has a significant impact on accumulation. If at any time the refill takes place at higher tank levels or non-peak DME mass conditions, accumulation is 'reset', and the concentration returns to near-normal levels.

(e) Addition of small amounts of butane to propane has a mitigative effect on maximum DME concentration; it was additionally noted that preferential evaporation and accumulation applies to propane/butane blends and the effects are not considered significant.

(f)   The two phenomena are highly situation dependent, and in most instances the simulation/testing represent the worst case.

It should be noted that specific to transportation, transfer of liquid-phase DME/LPG blends, will not lead to preferential evaporation behaviour. The use of vapour-return connections during filling of vapour-service storage vessels at very low tank levels may result in very minor accumulation within the transport vehicle; however, this practice is rarely undertaken with vapour-offtake vessels, and the effect of return vapour with high DME concentration is considered negligible. This same principle applies to storage systems whereby blends are withdrawn in the liquid-phase, such as Autogas, liquid-fed grain drying, or feed-out vaporiser use.

WLGA/KIWA (2023)[31] have produced a multi-component thermodynamic model based upon NIST REFPROP data. This model, whilst Isothermal, can be used to model varying 'real-world' compositions of LPG and different operating temperatures/conditions. Different compositions have been simulated and an iterative approach has been taken to determine the bulk DME-LPG blend ratio which does not lead to higher than 20 % DME concentration in either phase during use. Worst case conditions for LPG composition and physical conditions have been used.

The result of the simulation work is that a blend of 12 % DME with a mixture of 90 % Propane and 10 % Propene (without Butane) at an isothermal temperature of –10 degrees C gives yield to a maximum liquid phase DME concentration of 19 % after 2 refill cycles, decreasing to 17 % after 10 refill cycles. Vapour phase concentration throughout was lower. This figure intends to represent worst case, filling with a lower percentage of DME, different refill levels, or changes in temperature will reduce the peak DME accumulation, and the associated risk to elastomers.

Further modelling was performed on a blend of 12wt % DME with an LPG composition of 85 % Propane, 10 Propene and 5 % Butane; this clearly showed a significant reduction in peak DME concentration caused by accumulation, and therefore offers a significant margin of safety.

Methanol is often added to LPG to act prevent freezing of free water. Hoang Vu and Shultz (2011)[32] investigated the effect of methanol in terms of inhibiting hydrate formation at mild conditions. See section D.2.3 for information relating to water and methanol content in DME. Methanol is known miscible with most polar hydrocarbons and as such, significant stratification does not occur. DME standards permit up to 500ppm (0.05 mass %) methanol. Most LPG specifications allow up to 2000mg/kg (0.2 mass %, 2000ppm) and as such, DME is unlikely to increase methanol concentration in the mixture. As Propane remains the bulk fluid, and DME is a powerful solvent, the potential for any stratification effects, are reduced.

The addition of DME to LPG effects the natural vaporisation capacity of the cylinder or tank. DME has a higher latent heat of vaporization (469kj/kg vs 428kj/kg), a unit which describes the amount of energy required to convert a unit of liquid into vapour. Thus, for the same heat input (heat taken from the atmosphere surrounding the tank) less liquid will be vaporized. However, DME has a higher expansion ratio (340:1 vs 270:1), and as such more vapour is produced per unit of DME. As such, at low blend ratio (<20 % DME/LPG), natural vaporisation effects are considered negligible.

Preferential evaporation/accumulation occurs on vapour-offtake applications but is a well-understood and manageable phenomenon. A blend ratio of 12 % provides an allowance for any increase in the vapour-phase concentration of DME based upon worst-case conditions.

D.2.3   Blend/Compositional Controls

The potential for unacceptable levels of DME in the supplied blend was identified within the full value-chain assessment. As a new process within an existing supply chain, the blending system shall be designed and delivered to ensure blends meet the required specifications. WLGA (2022)[33] investigated the rates of thermal expansion of DME and LPG across a typical temperature range (-20C to +54C). The conclusion was that volumetric metering required significant levels of compensation to account for the effects of temperature/density.

It is therefore recommended the use of mass based or temperature compensated volumetric measurement to avoid errors in blending. Fundamentally, an accurate means of blending shall be used to ensure the consistency and accuracy of DME/LPG blends.

Blending shall be undertaken using stream injection or in a dedicated blending tank, which shall be suitable for 100 % DME. Blending tank operational procedures shall ensure complete mixing of the DME and LPG. Tanks storing DME shall follow the best practices associated UN number UN1033.

Water is partially miscible in DME (up to 6wt %). Miscibility is a measure of a substance's willingness to form a homogeneous mixture with another substance. Above 6 %, water will remain 'Free water' within the mixture and can contribute to the formation of frost and freezing on valves, a critical safety concern. ISO 16861 (fuel grade DME) permits up to 0.03 % mass % water in DME or 300ppm; well below the miscibility limit, and as such it will not exist as free water. This standard has the greatest allowance for water in DME and therefore represents the worst case.

Water concentration is not limited by absolute concentration within LPG quality standards, but instead by acceptable freeze-valve test result. The Propane Education and Research Council (PERC) (Confidential report) regularly perform Carl Fischer Titration tests on propane with different water content and compare these figures with the results of valve freeze testing (the normal test methodology for LPG). Preventing freezing in valves is an essential requirement for use in LPG infrastructure. PERCs testing demonstrated water content of up to 67ppm within samples taken in the US. Water content was not directly correlated to the sample's ability to meet the valve freeze test and it was concluded that dosing with anti-freezing agent (Methanol) allowed greater content before the sample became unable to pass the valve freeze test. The Gas Processing Association[34] have similarly performed testing demonstrating that 40ppm water was sufficient for valve freeze test failures in HD5 propane not containing methanol as an antifreeze. However, research and testing has shown that the addition of DME with the maximum water content permitted by the ASTM standard (300ppm) to LPG with 60ppm water will not cause the blend to fail the freeze valve test. Ergo, it has been shown that DME also acts as an antifreeze agent by absorbing any free water up to DME's saturation point and will increase safety in this regard.

Several factors affect the way in which two liquids interact and mix, however molecular polarity has been shown to be a crucial parameter. If DME and LPG do not readily mix to form a homogenous mixture, or if they separate over time (gravitationally or otherwise) high concentration blends could occur, with potential for elastomer or appliance failure; thus, both phenomena were investigated.

With respect to mixing, Hansen Solubility Parameters (HSP) Theory shows that substances with similar polarity tend to mix well; this may be improved by proper selection of mixing temperatures, agitation, and pressure. HSP, however, is not definitive and there are examples of chemicals which are known to mix well despite having large differences in HSP. DME is slightly polar whereas propane is non-polar. DME/LPG blends have been used for decades as propellants in aerosol products. WLGA have witnessed many of these operations and can confirm that practices used to blend the products are not typically sensitive to variation nor do they suffer from inconsistent performance. DME's high solvency has been shown to require only moderate agitation to effectively blend with LPG.

DCC (2021)[15] instructed investigations into the stratification stability of blends of propane and DME, testing samples were taken from a static storage vessel over a period of 52 days. The results showed very low levels of stratification and excellent stability for the duration of the tests. High pressure storage, alongside temperature gradients within the storage vessels of tanks (stimulating a thermos-siphonic action) when in use will almost certainly contribute agitation and further improve stability. This is supported by the research undertaken in Japan (Copyright report), where a cylinder was checked for stratification after a period of 3 months (no stratification had occurred), however a prerequisite of these findings was that complete mixing of the DME and LPG occurs before it reaches the point of storage/use. Complete mixing cannot be assumed to occur if the DME and LPG are added separately, and no subsequent mixing is undertaken.

Clearly, the operating procedures used to blend the two components will have a significant effect on the accuracy achieved. No single assessment or model will eliminate the risk of operators introducing an off-specification mixture to the market and as such, further risk control methods shall be defined for utilisation by the operators, proportionate and effective relative to the risk this presents.

Given accurate mass-based metering and agitation during mixing of DME and LPG, it can be concluded that it is feasible to form a stable and good degree of homogeneity at the point of storage/blending with the addition of regular product verification/testing. Once correctly mixed, no significant effects from stratification occur.

There is strong evidence demonstrating the stability and miscibility of DME in LPG. By selecting a conservative blend ratio (below that of material transition) the risks are considered to be mitigated.

D.2.4 Equipment compatibility (regulators, valves, pressure relief valves, hydrostatic relief valves, pumps and hoses)

The determined blend ratio must be chosen to be compatible with the normal materials (metallic and non-metallic) used by the LPG industry (see section D.2.1).

All normal metallic materials (except bronze and Zamak) used by the LP gas industry are known to compatible with unblended DME. Testing has been undertaken by WLGA on both bronze and Zamak to establish their suitability for a 20 % blend. Bronze passed the test programme. Zamak exhibited a marginal softening beyond the proposed maximum level of 2 % change when immersed in a 20 % DME/Propane liquid blend. Softening of materials is considered beneficial as it generally also leads to an increase in ductility. Zamak still passed the tensile test and as such is considered suitable for the drop-in DME/LPG blend.

DME has lower lubricating properties than LPG, however any effect on gear and vane pumps will be very marginal; the drop-in blend ratio and it will have no significant effect on turbine type pumps where frictional surfaces are not present.

At the determined blend ratio, they should not have a higher incidence of leakage than when they contain commercial LPG.

Hoses and regulators (or the diaphragms and seat discs) have a finite life, the determined blend ratio should not affect that life. Routine condition-based inspection remains an adequate means of pre-empting failure.

Regulators used with bulk tanks are equipped with (or installed with separate) safety devices to prevent over pressurisation of the downstream system. These are normally over pressure shut off devices, pressure relief devices or monitoring systems with actuated shut off valves. These systems are generally used to protect against diaphragm failure which does occasionally occur in LPG service and can therefore afford similar protection when DME is blended into propane.

Conclusion: The determined 12wt % DME/LPG blend ratio will not have any significant negative safety implications. Nevertheless, information on abnormal conditions or failures shall be collated and shared with the associations for dissemination.

D.2.5 Odorant compatibility; odour fade and potency

Research[35] using an olfaction panel suggests that unblended (100 %) DME, dosed with equivalent levels of ethyl mercaptan to that used for LPG, has a marginally lower odour strength than LPG. Research recommended that dosing for 100 % DME is increased to overcome any 'masking' that occurs.

Further Research by Kiwa (2023)[36] on Propane, Butane and DME dosed with equal amounts of ethyl mercaptan, found that whilst pure DME was found to interact with the odour character of ethyl mercaptan, producing a slightly sweeter odour, the odorant levels were still considered distinctive and unpleasant on blends of up to 20 % DME in LPG.

This would require both DME and LPG to be dosed to the appropriate (LPG) levels (typically around 14 cm^3/m^3 in liquid) or for one of the blend components to be over-dosed to account for the post-blend concentration prior to blending. If odorant is added after blending, dosing can be conducted as per normal LPG practice.

The risk of adsorption of Ethyl mercaptan onto ferrous oxides was investigated, but the perceived risk is insignificant compared with that for LPG. Ferrous oxide (rust) formation in bulk storage and transport tanks is generally very low, but it is more common in cylinders with manual valves, where valves can be left open on empty cylinders. The magnitude of adsorption is highly dependent upon relative surface area; the smaller the surface area with respect to the volume stored, the lower the implications of any adsorption that occurs.

Preferential adsorption of DME onto ferrous oxide will release any previously adsorbed odorant into the DME/LPG blend, causing a slight increase in odour concentration. Odour fade would only occur if the subsequent fill was unblended LPG that was also under odorised. As such adsorption is not considered a significant risk. DME's high solubility strongly suggests that ethyl mercaptan would remain solute in any instance, other than those with conditions to promote powerful adsorption mechanisms onto the surface of the adsorbent.

To confirm this, Kiwa (2022)[37] investigated the stability of ethyl mercaptan (EM) in DME in coated and uncoated carbon steel cylinders. EM concentration was measured by GC/MS and compared to a control sample held within a stainless-steel cylinder over the same period. Whilst the results showed fluctuation in EM concentration (expected due to changing Vapour-Liquid Equilibrium conditions) throughout the 3-month test period, readings from all cylinders correlated and importantly, the uncoated cylinder did not show significant reduction. This clearly shows that EM is stable in suspension within DME, LPG and its mixtures, and as such odour fade is unlikely.

Conclusion: Evidence from testing has shown that blending DME with LPG has a minimal effect on odorization requirements, and no odour stability issues

D.2.6 **Increase in the potential net weight of static storage and transport tanks. (Increase in static loadings and also for transport applications dynamic loadings).**

At 15 °C the same volume of a blend of 12 % DME with 88 % propane is 3.06 % heavier than 100 % propane.

In most cases static storage tanks are designed for hydraulic test conditions where the net weight will be over double that for when the tank is containing LPG.

Most tank foundations are also designed with a safety margin to allow for hydraulic testing or for the tank to contain butane (at 15 °C the same volume of 100 % butane is 15.9 % heavier than 100 % propane).

Transport tanks are designed to resist lateral and longitudinal 'G' loadings, if the tanker/transport tank is being loaded by volume, then the gross weight of the vehicle/transport unit/railcar shall not be exceeded, and the net weights used in the 'G' loading calculations shall not be exceeded. Providing that the same maximum weight that is used when loading unblended LPG is not exceeded no other preventative measures are required.

In many cases transport tanks are also designed to carry butane, at the same volume a 12 % DME/88 % propane mixture weighs less than that for 100 % butane providing the maximum butane weight is not exceeded no other preventative measures are required.

At this time, insufficient evidence exists with respect to the transportation of DME in refrigerated transport. WLGA are looking to engage with operators using these forms of transport/storage to undertake the necessary research and testing. At this stage, in the absence of supporting evidence, it is not recommended to store or transport DME or DME/LPG blends in this manner.

Conclusion: Transportation should be considered carefully in respect to the additional loading from the carriage of more dense products. However, the safety margins typically employed in the design of this equipment would allow the addition of 12 % DME by mass.

D.2.7   Effects on storage practices

Effects on filling ratios and pressure relief valve flow capacity.

The thermal expansion ratios for DME/LPG blends (up to 12 % DME) and LPG are similar; DME having a marginally higher thermal expansion ratio[38], therefore when filling by volume the normal maximum filling ratio used for LPG will ensure that a safe ullage level will be maintained. When filling by mass, the higher liquid density of DME (0.676 g/cm^3 at 15 °C) compared to butane (0.573 g/cm^3 at 15 °C) and propane (0.501 g/cm^3 at 15 °C) will provide an additional margin of safety with respect to fill quantities.

Calculations have been undertaken by the WLGA[39] on the required pressure relief valve flow capacity for DME and DME/LPG blends, these show that valves sized for LPG have a minimum flow capacity of at least that required for DME and DME/LPG blends.

Conclusion: existing LPG filling ratios are suitable for DME/LPG blends and existing LPG pressure relief valves have the correct flow capacity for DME/LPG blends.

Effects on static installation separation distances.

Calculations have been undertaken by the WLGA[40] to determine how the addition of DME might affect separation/safety distance requirements. Current separation distances are based upon the protection of the storage vessel from external effects, and for the protection of people from the effect of small releases as may be considered possible normal during operation (ATEX zones or equivalent). The assessments show that the existing separation distances give equal to or better protection that those currently used for LPG by virtue of DME's lower rate of thermal expansion, increased lower flammability limit, and reduced viscosity vs LPG.

Additionally, representative dispersion and jet-flame modelling, conducted by the WLGA (2023)[1], has shown that the addition of DME to LPG reduces dispersion distances and heat flux respectively. Whilst these models are only relevant for the specific conditions used, they may be used to conclude general trends in behaviour in archetypal release scenarios.

Conclusion: The addition of DME to LPG has been found to increase the margin of safety when compared to conventional LPG separation distances

Use of Deluge/Sprinkler systems and contact with water.

Due to DME's miscibility in water, wet cavern storage is not recommended for DME without thorough assessment and systems to manage the water content of DME. Whilst DME has the capacity to become solute with large quantities of water, high water content in conjunction with low temperatures are known to increase the likelihood of hydrate formation. Chapoy et al (2011)[41] highlighted the additional dehydration requirements prior to the introduction of DME into the supply chain and also showed the mechanisms of hydrate formation at low temperatures (as experienced in underground storage).

Deluge/sprinkler systems may potentially dissolve DME during a release event. In this instance, run-off from the sprinkler system has the potential to create or extend the extents of hazardous zones as the volatile DME component is released from suspension within the water as it tracks towards any drains. There is also the potential for accumulation of a flammable atmosphere within interceptors or underground ducts.

WLGA Calculations[42] have shown that DME concentration in water at ambient conditions (15 °C) to be less than 7wt %. Water containing 7wt % DME is not flammable. The DME entrained will be released over a protracted period. The rate of release would relate to many factors and temperature increase would accelerate release. Calculations have shown for pure DME that the release rate would not significantly contribute to the escalation of the release event or post-release accumulation of DME creating flammable atmospheres. Interceptor style drainage systems are typically classed as hazardous areas and as such would not require modification. Operators are recommended to perform their own assessments specific to the draining and sprinkler systems on site prior to adopting DME in pure or blended form.

It is generally accepted that deluge/sprinkler systems be employed on above ground bulk DME storage vessels (without passive fire protection) where practicable as it forms an important control against fire/BLEVE. Other than passive fire protection, which is most effectively applied during construction, there are no known suitable alternatives to deluge/sprinkler systems, and as such the mitigative potential of sprinkler systems far outweigh the potential risk of incident escalation from DME dissolved within the cooling water. The likelihood of unblended DME interacting with deluge water is very low, lower still with DME/LPG blends, and as such standard LPG practice should be followed.

Conclusion: Wet Caverns are not suitable for the storage of DME/LPG blend without full dehydration provision; this needs to be assessed by the owner/operator of the facility. The likelihood of DME interacting with deluge water is very low, lower still with DME/LPG blends, and standard LPG practice should be followed.

Hazardous area classification

The UN classifies both LPG and DME as class 2.1 flammable gases. Comparison of fundamental physical and chemical properties show that DME and LPG can be stored under pressure as a liquid and have similar density and rates of expansion.

Areas in which a flammable atmosphere may exist are broadly defined by either the EU or US regulations 'ATEX' and National Electrical Code (NEC) respectively. Within the US and Canada, a Class/division system is utilised, whereby the nature of the hazardous material (Vapour, dust or fibres) and likelihood of a hazardous mixture (High to Low) are defined for the scenario in question. Finally, a 'Group' is assigned based upon the type of flammable or ignitable materials in the environment. Under the US regime, DME and LPG are both classified as Class I, Division 1, Group D and as such, the classification of the equipment is identical.

Within the EU, the ATEX regulations specify the specific details of the hazardous area based upon situation specifics and the properties of the flammable/ignitable mixture. Classification of (particularly electrical) equipment within these hazardous areas is relatively complex and persons selecting the equipment may require accreditation to perform the classification.

Comparing pure DME with LPG with respect to ATEX equipment classification there are two main differences: DME is Gas Group IIB and has a temperature class T3 and LPG is gas group IIA with a T2 temperature class. Group IIB gases have a lower ignition energy than group IIA gases. T3 temperature class equipment can have a maximum surface temperature lower than that of T2 Equipment. Thus, any equipment currently used for LPG and that does not exceed the minimum requirements will not be suitable for pure DME. In most instances, however, equipment will be suitable for more challenging gas groups and lower temperature requirements.

Gas group categorisation is largely based upon the ignition energy requirements, but it is also related to the range of flammability of the substance. The Minimum Ignition Energy (MIE) of DME is 0.29 mJ. The MIE of LPG is 0.2 5mJ. Zhang[43] showed, by adding 30 % DME to a mixture of propane and butane, the Lower flammability limit of 2.14 and an upper flammability limit of 11.36 was measured, therefore, even at significantly higher blend ratios than those proposed, the upper flammability limit of the mixture is only marginally increased, and the lower flammability limit is no lower than that of butane.

ISO 80079-20-1[44] provides an approach to determining the gas group based upon calculation of relative Maximum Experimental Safe Gap (MESG). Equipment group IIA, appropriate for LPG, requires MESG of the DME/LPG mixture to remain above 0.9 to remain within the same equipment group. By varying the concentration of DME in propane during calculations, it is shown that 23 % (vol, c 26 % mass) can be added without affecting the gas group classification (WLGA 2022)[45]. As such, blends of up to 23 % (which include the proposed drop-in blend) may be classified gas group IIA and no change to ATEX equipment is required in this regard.

Temperature class is determined by the autoignition temperature of the gas. WLGA (2023)[46] has undertaken testing on 20 % DME/80 % propane, 20 % DME/80 % butane and 20 % DME/60 % propane/20 % propene blends to determine their autoignition temperature (and

thus temperature class) using ASTM methodology. The findings were 20 % DME/80 % propane = 444 °C, 20 % DME/80 % butane = 384 °C and 20 % DME/60 % propane/20 % propene = 419 °C. The transition between T2 and T3 is at 300 °C and as such, temperature class is unaffected for drop-in blends.

Contact with Air / Oxygen

DME reactivity with oxygen is higher than that of LPG and oxidation can occur. Unblended DME can form dangerous peroxides, however Japanese DME Forum (JDF)[47] showed that formation was slow; taking over 6 days before any indication was seen and compared the generation of peroxides from Diethyl Ether (DEE) and Di Isopropyl Ether (DIPE). Exo-thermal auto-oxidation, the cause of explosions from peroxides, was not detected in unblended DME until above 120 °C, and only occurred very slowly. By reference, this occurs at 190 °C and over in propane, indicating that DME is more reactive with oxygen than Propane. However, DEE and DIPE both showed effects at much lower temperatures, with DIPE shown to be the most reactive.

It must be noted that in these experiments, conditions favourable for the formation of peroxides were present and that in normal conditions oxygen (air) and DME or DME/LPG blends will not coexist due to correct purging. Therefore, for blends at drop-in level, peroxide products are not a significant concern due to the timeframes and conditions for formation being unlikely. Current LPG purging methods (provided they don't involve using CO_2 or water) are acceptable.

In pre-mixed burners, DME is mixed with air prior to combustion at the burner. During appliance testing referenced by the WLGA working group, no reference to, or indication of peroxide formation caused by the temporary coexistence of DME and Air has been experienced.

Conclusion: Correct purging to remove oxygen is required as per best practices in LPG.

Leak / Gas Detection

Point detectors utilising 'Wheatstone bridge' detectors, detect the flammability of surrounding atmosphere directly are thus unaffected by introduction of DME. Other types of gas detector may require recalibration. Correspondence with manufacturers Drager and Honeywell has suggested that most Infrared and catalytic sensor types calibrated to propane or butane will alarm earlier when subjected to a DME/LPG blend than they would when subject to the relevant calibration gas, however this must be confirmed by operators appropriate to the specific gas detector type/calibration in use. Prior to issue of Gas Free Certification and vessel entry activities, two means of atmosphere testing are recommended - flammable gas in air, and oxygen. This is the same recommendation as for these operations in LPG service conditions.

Conclusion: Effects on gas detection are considered minimal, and operators must consult with the manufacturers of the gas detection equipment on the specific effect of DME/LPG blends on the sensor's efficiency and calibration. Extra precautions should be taken when entering flammable atmospheres to ensure gas readings are correct.

Jet Flame and Dispersion modelling

Duty for ensuring consequences of leakages is managed, generally falls to the operator. Guidance and codes of practice are often used to simplify the assessment of generic consequences, however, are not suitable for complex scenarios, for instance high winds, low dispersion or contained releases. WLGA (2023)[41] undertook some generic modelling using FRED software and found dispersion distances to lower flammability limit were shorter with increasing levels of DME and generally jet-flames were shorter/ with lower radiant heat flux. Whilst not conclusive for all scenarios, this modelling provides a strong indication that duty-holders will see comparable or lower risks when using DME/LPG blends.

Conclusion: with low blend ratios (<20 % DME in LPG) the effects on dispersion and jet-flames are not likely to be significant and will in general reduce dispersion distances and jet-flame length concurrently.

D.3   **Summary – Storage and Transportation**

There is sufficient available evidence to demonstrate that blending DME with LPG in a blend ratio of 12:88 % by mass is compatible with current LPG transport and storage infrastructure/equipment and will not significantly affect the metallic or non-metallic materials that are currently use.

The safety margins typically employed in storage equipment and road/rail transport equipment design will accommodate any marginal increase in weight at drop-in blend ratios, due to higher density of DME.

Blending operations shall be carefully designed to ensure the safety of the process. All blending equipment shall be purposely designed for the task of blending and shall use existing guidance relevant to service (DME, UN1033, Propane, UN 1965 etc)

To ensure mixing occurs correctly, the individual components of blend must be completely combined through agitation and recirculation; transport alone may not be sufficient to achieve effective mixing.

Evidence shows that the non-metallic material families commonly used in liquid and vapour service will not be significantly affected until the DME concentration exceeds at least 20 % by mass (vapour has a lesser affect than liquid and therefore components in the vapour phase can withstand a higher concentration).

Preferential evaporation behaviour will not cause deleterious effects to supply chain and appliance equipment from a supplied DME/LPG blend ratio up to 12:88 %.

Controls of the blend composition are critical to safe adoption and to ensure comparable feedback is gained from the industry for standardisation purposes. Blends shall be conducted utilising mass-based, or temperature compensated volumetric metering with suitable quality checking conducted post-blending.

Existing LPG pressure relief valves have sufficient flow capacity for all DME/LPG blends and unblended DME. Effects on gas detection are considered minimal. Hazardous zone distances do not increase for drop-in blends and the classification/rating of equipment remains the same.

Purging with Air, CO_2 or water is not recommended. Wet cavern storage is not suitable without special consideration of dehydration equipment. The likelihood of DME/LPG blends interacting with deluge water is very low and standard LPG practice should be followed.

Ethyl Mercaptan is considered compatible with DME. Odour fade or changes to odorant concentration through adsorption are considered minimal and should be managed through additional tests and calibration of odour dosing units. Alternative odorants are being tested however the highly subjective nature of these tests present a challenge for firm conclusions. There is no reason to believe that alternative odorants behave differently from an adsorption perspective and as such operators should ensure the specific odorant or blend of odorants still meets the requirements for sale and use.

D.4   **Conclusions and Recommendations – Storage and Transportation**

The LPG industry can introduce a drop-in DME/LPG blend with a maximum 12wt % DME content that is safe and interchangeable with conventional LPG. The proposed blend can be used in existing supply chain infrastructure and supply the existing customer base, without any additional modifications.

Wet cavern storage should not be used for DME or DME/LPG blends.

Purging with Air, Oxygen, CO_2 or water is not recommended for DME/LPG blends.

Operators are encouraged to perform simple calculations on the effects of the additional mass of DME/LPG blends on transportation equipment. WLGA's calculations show that the effect of adding 12 % DME by mass to propane will increase the mass per unit of volume by 6 % and that will remain within the normal operating envelope for the different LPG mixtures.

Operators should ensure that the water content of DME is acceptable through direct testing or by performing valve-freeze testing prior to blending. Post-blending valve-freeze testing is also recommended as an additional or alternative test.

DME-specific guidance and training for the workforce should be considered.

Operators are encouraged to be prudent as the move towards the introduction of the blend by applying appropriate controls and systematic checks.

D.5 Further Research and Testing

Significant assessment of the end-use (from the storage to the point of use) of DME/LPG blends has already been undertaken by the WLGA. This research and testing indicate that for many applications the drop-in level of 12wt % DME is acceptable, even after considering accumulation/preferential evaporation. Further research and testing is being undertaken to identify if there exists types of use where a lower blend ratio is required. The fact that the UN number will permit the addition of DME does not mean that it will be present at the maximum level, and this will be controlled by the LPG specifications and standards in the same way as non-propane/butane components such as Ethane and Propene can be assigned to UN 1075 or UN 1965 but would not be regarded as or classified as LPG. Equally, whilst these UN numbers can be used for butane or propane, controls already exist to prevent the unsafe use of butane in dedicated propane devices and vice versa. These same principles shall apply to DME/LPG blends.

D.6 Reference Documents, Reports and Standards

Any of the following documents and reports indicated with an * may be obtained from the WLGA by delegates to the UN Sub-Committee of Experts on the Transport of Dangerous Goods – please contact nxydas@WLGA.org

(1)   *WLGA (2023) - Jet flame and dispersion modelling - DME and LPG mixtures

(2)   ISO 9162 – *"Petroleum products. Fuels (class F). Liquefied petroleum gases. Specifications"*

(3)   BS 4250 – *"Specification for commercial butane and commercial propane"*

(4)   EN 589 – *"Automotive fuels. LPG. Requirements and test methods"*

(5)   ASTM D1835-22 – *"Standard Specification for Liquefied Petroleum (LP) Gases"*

(6)   ASTM 7901-20 – *"Standard Specification for Dimethyl Ether for Fuel Purposes"*

(7)   ISO 16861 – *"Petroleum products. Fuels (class F). Specifications of dimethyl ether (DME)"*

(8)   ISO 11114-1 – *"Gas cylinders. Compatibility of cylinder and valve materials with gas contents. Metallic materials"*

(9)   Kiwa (2023) - DME compatibility of bronze

(10)   ISO 11114-2 – *"Gas cylinders. Compatibility of cylinder and valve materials with gas contents. Non-metallic materials"*

(11)   Hexagon Regasco/TUV (2023) - TÜV Test report – Composite cylinders

(12)   UL – *"Underwriters Laboratory"*

(13)   ISO 1817 – *"Rubber, vulcanized or thermoplastic. Determination of the effect of liquids"*

(14)   UL Report – Preliminary Study for Material Compatibility with LPG-DME Blends

(15)   *DCC (2021) – *"A DCC study of Low ratio blends of Renewable DME in LPG"*

(16)   IDA (2017) – *"DME compatibility"*

(17)   *Kiwa (2022) – *"Dimethyl-Ether / LPG blends as fuel in gas appliances"*

(18)   *Rochester – Tests with DME

(19)   *Clesse – Clesse rubbers versus DME energy introduction

(20)   ISO DIS 1817 – "*Rubber, vulcanized or thermoplastic. Determination of the effect of liquids (draft ISO standard that includes the photographic method to measure post emersion swell*"

(21)   UL 157 – "*Standard for Safety – Gaskets and Seals*"

(22)   *WLGA (2023) - Accelerated aging testing

(23)   *Kiwa (2022) – Liquid alternative for volume change testing in dimethyl ether

(24)   *WLGA (2023) – Float gauge and float operated auto-stop valve testing

(25)   *Kiwa (2020) - Determining DME Influence on material samples

(26)   EN 751 – "*Sealing materials for metallic threaded joints in contact with 1st, 2nd and 3rd family gases and hot water*"

(27)   *Kiwa (2022) – EOS calculations for sub-zero LPG blends

(28)   Japanese LPG association report (Liquefied Petroleum Gas Center of Japan)

(29)   *Kiwa (2021) - Determining the effect of repeated filling on potential for accumulation.

(30)   *WLGA/Kiwa (2023) - Multiple component blends during operation to determine the combined effects of low temperature, non-propane components and accumulation.

(31)   *WLGA/Kiwa (2023) - multi-component thermodynamic model based upon NIST REFPROP data

(32)   Hoang Vu and Shultz (2011) - Investigations into Methanol inhibitors against hydrate formation

(33)   *WLGA (2022) – "*DME and Propane - Liquid Density v Temperature Gradient Comparisons*"

(34)   GPA 2022 - "*Summary Report of GPA Midstream Research Progress October 2022*"

(35)   *Research (Kiwa) – "*Testing ethyl mercaptan as an odorant for DME*"

(36)   *Kiwa (2023) - Revised Odor Tests

(37)   *Kiwa (2022) – "Testing the stability of ethyl mercaptan as odorant in DME".

(38)   *WLGA – Thermal expansion ratio comparisons

(39)   *WLGA - "Pressure Relief Valve (PRV) Sizing Comparison – DME vs LPG"

(40)   *WLGA – "Comparison of LPG and DME separation distances and Hazardous areas"

(41)   Chapoy et al (2011) - Potential for DME storage in underground caverns

(42)   *Calculations - "Vapor-Liquid Equilibrium (solubility) of DME And Water"

(43)   Zhang, Q. et al (2019) "Flame Dynamics and flammability limit of DME (30 %)/LPG blended clean fuel in elongated closed pipeline under multi-factors".

(44)   EN ISO 80079-20-1 - Explosive atmospheres. Material characteristics for gas and vapour classification. Test methods and data

(45)   *WLGA (2022) - Calculation of MESG for DME LPG bends

(46)   *WLGA (2023) – Auto-Ignition Temperature testing

(47)   Japanese DME Forum – Handbook

(48)   *WLGA (2023) Elastomer and Polyamide testing.

E. Appendix: DME/Propane Blend Testing Undertaken by or for WLGA

E.1 Purpose

During the preliminary research and during the risk workshops a number of types/groups of materials were identified as needing to be tested to confirm their suitability when used for transport and storage applications. Other areas that also needed to be researched/tested, including, odorization, valve freeze testing, auto-ignition temperature and jet flame behaviour.

Below are the types of materials that have been tested, the test methods, results and additional information.

For any of the following research and testing the full result/report documents may be obtained from the WLGA by delegates to the UN Sub-Committee of Experts on the Transport of Dangerous Goods – please contact nxydas@WLGA.org

E.2 Material testing

E.2.1 Accelerated aging (elastomer) testing. Summary of the results.

The changes in the materials were only marginally different to those recorded in the standard elastomer testing (single test period), with the changes recorded both in the test and control samples. All results were well within the set pass criteria and all the materials tested are suitable for operation at up to a 20 % DME/80 % LPG blend.

E.2.2 Composite cylinder testing. Composite cylinder testing results

Both the cylinders tested with the DME/LPG blend and 100 % DME passed the testing and are considered by the WLGA to be suitable for the drop-in blend (and up to 100 % DME in the future).

E.2.3 Elastomer and Polyamide material testing. Elastomer and polyamide testing results

The results of all of the materials submitted that are in current service with the LPG industry indicated that they are suitable for service at up to 20 % DME with LPG. One sample submitted for testing showed results that indicated marginal suitability for both propane and the 20 % DME/80 % propane blend, it was subsequently found that this material is not in current LPG service and that it was 'experimental' in nature.

E.2.4 Float gauge and float operated auto-stop valve testing. Float gauge and float operated auto-stop valve results.

All the float gauges, float operated auto-stop valves and separate floats passed the testing requirements and all results were well within the set pass criteria. All the float gauges, float operated valves and floats tested are suitable for operation at up to a 20 % DME/80 % LPG blend.

E.2.5 Jointing compound testing. Jointing compound testing results

All of the jointing compounds passed the testing requirements, and all results were well within the set pass criteria. All the jointing compounds tested are suitable for operation at up to a 20 % DME/80 % LPG blend.

E.2.6 Metallic material (bronze) testing. Bronze testing results

No degradation or deterioration was observed or recorded. Bronze is suitable for operation at up to a 20 % DME/80 % LPG blend.

E.2.7 Auto-ignition temperature. Auto-ignition temperature results

Unblended LPG has a temperature classification of T2 (350 to 450 °C), therefore blends of up to 20 % DME with LPG are still within the same temperature classification.

E.2.8   Jet flame behaviour. Results of the modelling

The resulting jet flames from the blends and 100 % DME were consistent in being between those for butane and propane.

E.2.9   Odorization. Results of the odorant testing

The Olfaction panel assessed that both the LPG and the 20 % DME/80 % LPG blends had the required unpleasant odour, however, as previously research the 100 % DME will require a higher dose rate of odorant.

The stain tubes indicate a very slight over indication of the odorant dosing level, however at the drop-in level the over indication is so small that it would not cause under dosing.

E.2.10   Valve freeze testing. Results of the valve freeze testing

The blend for DME and propane passed the valve freeze test without the need to add additional methanol.

Further research is going to be undertaken to see if the addition of DME will negate the need to add methanol to LPG.

F.   Endorsement

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25th March 2024
Our Ref: WLPGA-01-C-24

Subject – Risktec Endorsement of Drop-in Blend Determination Considerations, Issue 1.2 March 2024

To whom it may concern,

Please find below Risktec's endorsement of the drop in blend paper.

> Risktec confirms that the WLGA report 'Drop-in Blend Ratio Determination Considerations, Issue 1.2 March 2024 presents an rDME blend ratio which is justified, based on identification and assessment of potential risks and uncertainties. This work has been completed using a structured and systematic approach, which has been adopted to identify all reasonably foreseeable risks, with participation from a large number of subject matter experts. Where risks have been identified, suitable work has been carried out, or has been actioned, to reduce uncertainty and implement controls such that risks are managed to As Low As Reasonably Practicable (ALARP). Risktec endorses the approach taken by the WLGA for this work, which aims to ensure the safety of the industry it represents, as it attempts to find suitable low carbon solutions to address climate change in an ethical manner.

Yours sincerely

Sheryl Hurst
for Risktec Solutions Limited