SAFE PREPARATION OF COMPRESSED OXIDANT-FUEL GAS MIXTURES IN CYLINDERS

Doc 139/22

Revision of Doc 139/15

EUROPEAN INDUSTRIAL GASES ASSOCIATION AISBL

AVENUE DE L'ASTRONOMIE 30 • B – 1210 BRUSSELS

Tel: +32 2 217 70 98

E-mail: info@eiga.eu • Internet: www.eiga.eu

SAFE PREPARATION OF COMPRESSED OXIDANT-FUEL GAS MIXTURES IN CYLINDERS

As part of a programme of harmonisation of industry standards, the European Industrial Gases Association (EIGA) publication, EIGA Doc 139, "*Safe Preparation of Compressed Oxidant-Fuel Gas Mixtures in Cylinders*", has been used as the basis of an internationally harmonised gas association's publication on this subject.

This publication is intended as an international harmonised publication for the worldwide use and application by all members of Asia Industrial Gases Association (AIGA), Compressed Gas Association (CGA), EIGA, and Japan Industrial and Medical Gases Association (JIMGA). Regional editions have the same technical content as the EIGA edition, however, there are editorial changes primarily in formatting, units used and spelling. Regional regulatory requirements are those that apply to Europe.

EUROPEAN INDUSTRIAL GASES ASSOCIATION AISBL
Avenue de l'Astronomie 30 B 1210 Brussels Tel +32 2 217 70 98
E-mail: info@eiga.eu Internet: www.eiga.eu

Table of Contents

Amendments to EIGA 139/15

Section	Change
3.2	Change and addition of some definitions
5.1	Reference to appendix B and appendix B have been removed. References to literature information has been added.
	Reference to appendix C and appendix C have been removed. The list of some know unstable gases is now in Doc 39
5.2	Reference to appendix E and appendix E have been removed. The decision tree figure for manufacturing safe compressed oxidant-fuel gas mixtures is replaced with another evaluation method used in the gas industry. It included a reference to a new appendix C
5.2.1	Reference to appendix F and appendix F have been removed. New reference to the ISO standard is added
5.2.1.1	Reference to appendix G and appendix G have been removed.
7.2	Dynamic blending has been added as filling method with a reference to appendix D
10	Information that is duplicated in other publications has been removed
	Former Appendix B – Gas compatibility - has been removed
	Former Appendix C – List of unstable gases – has been removed
	Former Appendix E – Decision tree for the safe manufacturing of compressed oxidant-fuel gas mixtures – has been removed
	Former Appendix F – Limiting oxygen concentration of some flammable gases – has been removed
	Former Appendix G – Maximum explosive pressures of flammable gas-air mixtures – has been removed
Appendix C	New Appendix C: Energy limited evaluation method (Informative)
Appendix D	New Appendix D: Dynamic blending (Normative)

Note: Technical changes from the previous edition are underlined in the text

1 Introduction

Cylinders containing both oxidant and flammable components (oxidant-fuel gas mixtures) are widely used in industry, medical applications, and other fields. Typical applications include calibration of flammable gas detectors, emission monitoring equipment, and refinery process analyzers.

Due to the inherent nature of the gases used to manufacture oxidant-fuel gas mixtures, there is always the possibility of an explosive mixture being produced. To prevent the inadvertent production of explosive mixtures, strict rules and procedures shall be followed during the formulation and manufacturing processes.

Historically, during the manufacture and use of these gas mixtures, industry has experienced accidents and losses resulting in explosions that have caused injuries and death. These incidents have been caused by mixtures being manufactured that have been within the explosive range.

Compressed oxidant-fuel gas mixtures can be manufactured safely provided the principles contained in this publication are followed.

2 Scope and purpose

2.1 Scope

This publication documents the minimum requirements for the safe preparation of compressed oxidant-fuel gas mixtures in cylinders by static methods (addition of one component after another in cylinders). The publication specifically addresses:

- key principles for compressed oxidant-fuel gas mixture manufacture;
- manufacturing feasibility studies;
- gas mixing equipment, filling, and analysis; and
- the audit of oxidant-fuel gas mixture manufacturing procedures and operations.

This publication specifically describes the manufacture of compressed oxidant-fuel gas mixtures under the conditions of gas temperatures and pressures detailed within this publication. The manufacture of liquefied and liquid oxidant-fuel gas mixtures is outside of the scope of this publication.

This publication shall be used in conjunction with the information and principles contained in EIGA Doc 39, *The Safe Preparation of Gas Mixtures* [1].[1]

2.2 Purpose

The purpose of the publication is to describe practices to be used for the safe preparation of compressed oxidant-fuel gas mixtures and to ensure that they are non-explosive at the end of the manufacture.

- Safe formulation of compressed oxidant-fuel gas mixture by trained and competent personnel;
- Defined safety considerations, which are applied and maintained during the manufacturing process; and
- Overall quality system with formally approved documented procedures shall be used for manufacture and these procedures and practices shall be subject to the regular technical review and audit by technical experts independent of the routine production process.

[1] References are shown by bracketed numbers and are listed in order of appearance in the reference section.

3 Definitions

For the purpose of this publication, the following definitions apply.

3.1 Publication terminology

3.1.1 Shall

Indicates that the procedure is mandatory. It is used wherever the criterion for conformance to specific recommendations allows no deviation.

3.1.2 Should

Indicates that a procedure is recommended.

3.1.3 May

Indicates that the procedure is optional.

3.1.4 Will

Is used only to indicate the future, not a degree of requirement.

3.1.5 Can

Indicates a possibility or ability.

3.2 Technical definitions

3.2.1 Combustible gas/flammable gas/fuel

Gas able to undergo exothermic reaction with an oxidant when ignited.

3.2.2 Cylinder

Transportable receptacle that can be filled with gas under pressure, excluding small disposable cylinders.

3.2.3 Cylinder burst

Rupture of a cylinder due to the development of internal pressure from a compressed oxidant-fuel gas mixture explosion, which exceeds the cylinder burst pressure.

3.2.4 Cylinder burst pressure

Highest pressure reached in a cylinder during a burst test.

3.2.5 Cylinder working pressure

Highest pressure permitted to be developed during service (15° C [59° F] as defined by ADR) [2].

NOTE—In other jurisdictions, the referenced temperature may be defined slightly differently.

3.2.6 Cylinder test pressure

Required pressure applied during a pressure test for qualification or requalification.

3.2.7 Expert opinion

Opinion of a technically competent authority or person in the field of compressed oxidant-fuel gas mixture manufacturing who is not directly involved in commercial activity in this field or involved in oxidant-fuel mixture production.

3.2.8 Explosive pressure

Maximum pressure occurring in a closed vessel during the explosion of a gas mixture.

3.2.9 Explosive (flammable) limits

Concentration limits of the explosive range.

3.2.10 Explosive (flammable) range

Range of concentrations between the lower and the upper explosive limits where flame propagation can take place.

3.2.11 Hazard and operability study (HAZOP)

Systematic technique to identify and assess potential hazards that might arise during the operation of plant or equipment. A study is normally carried out to assess the potential effects of various malfunctions of the equipment or plant (for example, reverse flow, excessive temperature or pressure, etc.) and human error.

3.2.12 Inert gas

A gas that is non-flammable and non-oxidizing.

3.2.13 Intermediate analysis

Analysis carried out part-way through the process of filling a gas mixture in a cylinder (or cylinders). Such an analysis is normally carried out to confirm the concentrations (and sometimes the identities) of the components that have already been filled before a subsequent component is added.

3.2.14 Limiting oxygen concentration (LOC)

Maximum oxygen concentration in any mixtures of a flammable substance, air, and inert gas, at atmospheric conditions, in which an explosion would not occur.

NOTE—LOC is usually expressed as mole or volume fraction.

3.2.15 Lower explosive (flammable) limit (LEL)

Fuel lean limit of the explosive range.

3.2.16 Maximum explosive pressure

Maximum possible explosive pressure obtained by varying the concentrations of the components of a mixture (usually nearly stoichiometry).

3.2.17 Oxidant

Any gaseous material that can react with a fuel (gas, dust, or mist) to produce combustion. Oxygen in air is the most common oxidant.

3.2.18 Premix

Gas mixture that is used as one of the supply gases during the filling of a gas mixture. The use of premixes can enable low concentration components to be filled accurately and can also eliminate any potential hazards when filling certain gas mixtures containing potentially incompatible components.

3.2.19 Safety premix

Mixture of flammable gases in inert gases where the flammable gas fraction cannot react with oxidizing gases whatever their concentrations and/or mixture of oxidizing gases in inert gases where the oxidizing gas fraction cannot react with flammable gases whatever their concentrations.

3.2.20 Upper explosive (flammable) limit (UEL)

Fuel-rich limit of the explosive range.

3.2.21 Oxy-potential coefficients

Oxidizing power related to oxygen as determined by a method specified in ISO 10156, Gases and gas mixtures—Determination of fire potential and oxidizing ability for the selection of cylinder valve outlets [3].

3.2.22 Unstable gas

Gases which, under the storage and operating conditions, can be brought to an exothermic reaction by the action of energy or by the catalytic action of foreign substances, even if oxygen is excluded.

4 Key principles for the manufacture of compressed oxidant-fuel gas mixtures

4.1 Precautions to avoid risks

The following precautions should be taken to avoid risks:

- Whenever possible, consider if another mixture could be used to substitute an oxidant-fuel mixture in the proposed application since an oxidant-fuel mixture is by its very nature potentially more hazardous to produce. It is advised that this substitution is discussed with the customer;

- If there is insufficient data to enable an evaluation of the explosive limits and safety margins, the mixture shall not be manufactured;

- All employees involved in production processes shall be trained and tested for proficiency;

- All computer programs based on expert systems that are used to evaluate and formulate oxidant-fuel mixtures shall be rigorously tested, validated before use, and subject to version control. These programmes shall not be used to evaluate unknown data or to interpolate or extrapolate data;

- All computer programs shall be password protected to prevent unauthorised changes being made. Any changes to any program shall only be made by a competent authorised person and a record of these changes shall be retained. All changes shall be validated before the revised program is used;

- After one technical expert has evaluated the feasibility of safely manufacturing a new oxidant-fuel gas mixture, it is strongly recommended that this formulation should be checked by another competent person or by a computer program in order to detect any potential errors or hazards;

- Production sheet for all oxidant-fuel gas mixtures shall be formally approved following the feasibility study (for example, indication of feasibility study reference as indicated previously, signature of expert);

- Approved formulations of compressed oxidant-fuel gas mixtures shall be protected against unauthorised changes;
- Chemical incompatibility of the component gases shall be considered during the feasibility study;
- Evaluate the critical manufacturing steps that can lead to a dangerous mixture;
- Safety margins shall be introduced to avoid risks when mixing oxidant and fuel gases;
- Direct simultaneous connection of piped flammable and oxidant gases to the same manifold shall not be allowed;
- Equipment shall be regularly tested and maintained;
- Consider passive safety measures (e.g., a protection wall);
- All pipes and raw materials shall be clearly labelled;
- All cylinder connection adaptors shall be controlled (see EIGA Doc 39) [1];
- Consider backflow prevention (raw material source gas pressures greater than the pressure in the receiving cylinder); and
- Preparation of compressed oxidant-fuel gas mixtures in small size cylinders (for example, equal to or less than one litre) and, in particular, in disposable cylinders by static methods is not recommended. Small cylinders and disposable cylinders can be filled only with already prepared compressed oxidant-fuel gas mixtures.

4.2 Key steps and checks

- Check that cylinders are at room temperature to avoid condensation of components; and
- Prepare a complete production sheet before manufacturing the mixture (see Section 8.1 for requirements).

4.3 Organizational requirements

The manufacturing of a fuel/oxidizer mixture shall not be executed by the person who grants final approval of the feasibility, calculation, and preparation of instructions for the production of the mixture.

Persons involved in the feasibility, calculations, and preparation of instructions shall be trained, assessed, and formally appointed for these activities.

All manufacturing sites filling oxidant-fuel mixtures shall be formally approved by the technically competent company authority for this activity. Approvals shall be based on the:

- design and use of satisfactory filling equipment;
- completion of an audit;
- appointment of technically competent authorised personnel; and
- documented procedures and training records.

Personnel shall be formally authorised for this activity by their management. The company shall define the content of the training and shall define the minimum retraining and assessment periods.

The work instructions shall be version controlled and available at the point of use in the work area.

The organization shall record all of the information necessary to have complete traceability of the preparation and production of such mixtures.

The audit of oxidant-fuel gas mixture formulation and manufacturing should be conducted periodically by a technically competent person. The company shall establish and define this period. An example of a specimen audit check list is included in Appendix A.

Where serious hazardous conditions are found to exist following an audit, a filling plant shall cease filling oxidant-fuel gas mixtures until controls are put in place to remove these hazards.

5 Compressed oxidant-fuel gas mixture manufacturing feasibility study

The purpose of this section is to describe how to evaluate the safe preparation of oxidant-fuel gas mixtures, taking into account:

- component and cylinder compatibility (5.1);
- formulation of safe compressed oxidant-fuel gas mixtures (5.2); and
- mixture manufacturing accuracy (5.3).

5.1 Component and cylinder compatibility

The compatibility of the mixture components shall be evaluated using literature information (e.g., TRGS 407 Tätigkeiten mit Gasen - Gefährdungsbeurteilung or NOAA Expanded Chemical Reactivity Worksheet (CRW4) for determining chemical compatibility, past, present, and future) [4, 5].

The compatibility of the components with the cylinder material should also be evaluated using the information contained in ISO 11114-1, *Gas cylinders—Compatibility of cylinder and valve materials with gas contents—Part 1*: *Metallic materials* [6].

Unstable gases can strongly affect the explosive range. Only oxidant-fuel gas mixtures that are stable under the conditions of temperature and pressure existing during manufacture and use shall be produced. See EIGA Doc 39, which lists some known unstable gases [1].

A number of halocarbons have no explosive limit in air under atmospheric conditions but do have at elevated pressure in air (see Appendix B) or at atmospheric pressure in pure oxygen.

5.2 Formulation of safe compressed oxidant-fuel gas mixtures

The purpose of this section is to describe how to derive the formulation (final mixture pressure and mixture component introduction order) of safe compressed oxidant-fuel gas mixtures.

The following mixtures shall not be manufactured unless there are experimental data or an expert opinion on explosive limits at the filling pressure:

- oxidants with unknown oxy-potential coefficients with flammable gases;
- gases with unknown explosive (flammable) limits with oxidant gases;
- unstable flammable gases (for example, acetylene, butadiene, ethylene oxide) with oxidant gases; and
- pyrophoric products and other products such as organometallics, silane, disilane, trisilane, chlorosilanes, diborane, arsine, phosphine, and germane with oxidant gases.

The formulation of safe compressed oxidant-fuel gas mixtures requires the following three studies to:

- ensure non-explosive mixtures at the end of manufacture (5.2.1);

- avoid or control explosive mixtures during manufacturing (5.2.2); and
- avoid condensation during and after the manufacturing (5.2.3).

Appendix C presents an evaluation method which is used in the gas industry and applied in the absence of sufficient knowledge about the combustion behavior of a specific oxy-fuel mixture under elevated pressure conditions. The principle of the evaluation method is to limit the total combustion enthalpy of an oxy-fuel mixture, so there is not enough energy present to burst a high-pressure cylinder in case of an unintentional combustion reaction.

5.2.1 To ensure non-explosive mixtures at the end of manufacture

The uncertainty of mixture production shall be taken into account when ensuring that the compressed oxidant-fuel gas mixtures are non-explosive inside the cylinders at the end of their manufacture.

The explosive ranges of gases increase with temperature, and in most cases, with increasing pressure. Therefore, data on explosivity are required not only at atmospheric pressure and standard temperature, but also at manufacturing pressure and temperature.

The study to avoid explosive mixtures shall be based on comprehensive data considering the effect of pressure and temperature on explosive (flammable) limits.

In the absence of comprehensive data, the following rules shall be applied, taking into account:

- Lower explosive limits (LELs) in air at atmospheric pressure (see ISO 10156) [3];
- LELs in oxygen at atmospheric pressure; and
- Limiting oxygen concentrations (LOCs) of flammable gases with air as the oxidizer and nitrogen as the inert component at atmospheric pressure. For example, see ISO 10156 [3].

5.2.1.1 Mixtures containing one flammable gas in air

When data on explosivity at final filling pressures or an expert opinion is not available, the rules permitting the manufacturing of compressed gaseous mixtures of flammable gas in air below the LEL (LEL mixtures) when introducing oxygen at the end are as follows:

- Compressed oxidant-fuel gas mixtures containing one flammable gas in concentrations of less than or equal to 25% of the LEL in air at atmospheric pressure may be manufactured at a maximum pressure of the cylinder working pressure and at a maximum of 200 bar (2900 psi);
- Compressed oxidant-fuel gas mixtures containing one flammable gas in concentrations greater than 25% and less than or equal to 50% of the LEL in air at atmospheric pressure may be manufactured at a maximum pressure of the cylinder working pressure and at a maximum of 150 bar (2175 psi);
- Compressed oxidant-fuel gas mixtures containing one flammable gas in concentrations greater than 50% and less than or equal to 75% of the LEL in air at atmospheric pressure may be manufactured at a pressure which shall not exceed 1/10 of the cylinder working pressure; and
- Compressed oxidant-fuel gas mixtures containing one flammable gas in concentrations greater than 75% of the LEL in air at atmospheric pressure shall not be manufactured without data on explosivity at final filling pressure.

NOTE—Special consideration shall be given to halogenated hydrocarbons, which are not flammable at atmospheric pressure but can be flammable at elevated pressure (see Appendix B).

When data on explosivity at final filling pressures or an expert opinion are not available, the permitting the manufacturing of compressed gaseous mixtures of flammable gas in air above the upper explosive limit (UEL mixtures) when introducing oxygen diluted in an inert gas or introducing air at the end are as follows:

- Mixtures containing oxygen in concentrations of less than or equal to 50% of the LOC in flammable gases at atmospheric pressure may be manufactured at a maximum pressure of the cylinder working pressure; and

- Mixtures containing oxygen in concentrations greater than 50% and less than or equal to 75% of the LOC in flammable gases at atmospheric pressure may be manufactured at a pressure that shall not exceed $1/20^{th}$ of the cylinder working pressure. The assumption of $1/20^{th}$ of cylinder working pressure is based upon the data contained in ISO 15156 and additional safety margins necessary because of higher uncertainty on LOC values compared to the LEL.

When filling flammable gas at the end, the rules in 5.2.2 shall also be followed.

5.2.1.2 Mixtures containing one flammable gas in oxygen

When data on explosivity at final filling pressures or an expert opinion is not available, the rules permitting the manufacturing of compressed gaseous mixtures of low concentrations of flammable gas in oxygen are as follows:

- Compressed oxidant-fuel gas mixtures containing one flammable gas in concentrations of 1000 ppm or less in oxygen may be manufactured at the working pressure of the cylinder; and

- Compressed oxidant-fuel gas mixtures containing one flammable gas in concentrations greater than 1000 ppm in oxygen may be manufactured only if data on explosion at final filling pressures or expert opinion is available and following the rules of 5.2.2 when filling oxygen last.

When data on explosivity at final filling pressures or an expert opinion is not available, the permitting the manufacturing of compressed gaseous mixtures of high concentrations of flammable gas in oxygen are as follows:

- Compressed oxidant-fuel gas mixtures with flammable gas concentrations of 1000 ppm or less in oxygen may be manufactured at the working pressure of the cylinder; and

- Compressed oxidant-fuel gas mixtures with flammable gas concentrations greater than 1000 ppm gases in oxygen may be manufactured only if data on explosion at final filling pressures or expert opinion is available and following the rules of 5.2.2 when filling flammable gases last.

5.2.1.3 Mixtures containing inert gas other than nitrogen

An equivalent mixture containing the flammable gas in oxygen and nitrogen shall be defined using ISO 10156 coefficients for the equivalence between inert gases and then the following rules shall apply when data on explosion at final filling pressures or expert opinion is not available [3]:

- When the equivalent mixture has a lower oxygen concentration in nitrogen than in air, the same rules as those described in 5.2.1.1 apply; and

- When the equivalent mixture has a higher oxygen concentration in nitrogen than in air, the same rules as those described in 5.2.1.2 apply.

5.2.1.4 Mixtures containing one oxidant other than oxygen

The manufacturing of compressed oxidant-fuel gas mixtures of either low or high concentration of flammable gas with one oxidant gas other than oxygen with or without inert gas is not allowed except if experimental data or expert opinion is available. In absence of such information, the mixtures shall not be manufactured.

5.2.1.5 Mixtures containing several flammable/oxidant/inert gases

Mixtures containing one or several flammable gases in the fuel-lean range (below the flammability range and/or several inert gases and oxygen may be manufactured after studying their feasibility taking into account the following rules:

- Several inert gases:
    - Equivalent mixture containing only the major inert gas shall be defined. Using ISO 10156 coefficients and calculations to determine the major inert gas and to assimilate the other inert gases to the major inert gas [3] and
    - Depending upon the type of equivalent mixtures, the rules contained in 5.2.1.1, 5.2.1.3, or 5.2.1.4 shall apply;
- Several flammable gases:
    - Equivalent mixture containing only the major flammable gas shall be defined using ISO 10156 coefficients to determine the major flammable gas and to assimilate the other flammable gases into the major flammable gas [3];
    - LEL of the mixture may be determined using the calculation in ISO 10156 [3]; and
    - Depending upon the type of equivalent mixture or the LEL of the mixture, the rules contained in 5.2.1.1, 5.2.1.2, 5.2.1.3, and 5.2.1.4 shall apply.

For oxidant gases other than oxygen, see 5.2.1.4.

5.2.2 Study to avoid or to control explosive mixtures during manufacturing

During the manufacturing of a compressed oxidant-fuel gas mixture, an explosive mixture can exist temporarily when passing through the explosive range and before homogenization. This situation should be avoided as much as possible. The following rules shall apply.

Non-explosive oxidant-fuel gas mixtures inside cylinders during manufacturing:

- For compressed oxidant-fuel gas mixtures with a high enough concentration of inert gas such as LEL mixtures in air, the rule is never create an explosive mixture inside cylinders during manufacturing. This can be achieved if:
    - Sufficient inert gases are introduced between the flammable gases and the oxidant gases;
    - Oxidant gases or flammable gases are added to a safety premix; or
    - Mixture is homogenized before adding the excess reactive. If the cylinder is disconnected, cylinder identification is critical in preventing human error during reconnection of the cylinder.

Controlled explosive oxidant-fuel gas mixtures inside cylinders during manufacturing:

- For compressed oxidant-fuel gas mixtures with no or low concentration of inert gases, an explosive mixture can be created temporarily by passing through the explosive range during manufacture. This will be the case when all the reactive gases of the same type in minor concentration (according to the stoichiometry) are introduced into the cylinders first.
    - This temporarily created explosive mixture inside the cylinder will then become non-explosive when the concentration moves out of the explosive range. This occurs at the end of the introduction of the major concentration reactive gases of the opposite type.

- In this situation, the requirement is to calculate or have data available on the energy that will be created by a potential explosion. The calculated explosive energy shall result in potential explosive pressures less than the working pressure of the cylinder plus a safety factor taking into account any possible reaction.

- Potential maximum explosive pressure of the temporarily created explosive mixture shall be calculated assuming adiabatic conditions by subject matter experts.

- Potential explosive pressure shall never be allowed to exceed the working pressure of the cylinder.

CAUTION: *The introduction of the gas(es) of the opposite type should not be interrupted until the mixture is outside of the explosive range. The filler shall remain present during any interruptions, other than in an emergency plant evacuation.*

5.2.3 Study to prevent condensation during or after manufacturing

An oxidant-fuel gas mixture component introduced as a vapor (liquid or liquefied gas under pressure) can condense due to the exposure of the cylinder to low temperature. This can create a flammable zone inside the cylinder, which can remain unless the mixture is rehomogenized at a temperature above the vaporisation temperature of the component.

Therefore, oxidant-fuel gas mixture pressures shall be calculated to avoid condensation of components at the minimum ambient temperature to which the cylinder will be exposed, particularly during manufacture, transportation, storage, and use.

The possibility that some components of the mixture can liquefy in the cylinder during storage or transportation after manufacturing should be noted on the production sheet with indication of the temperature. The possibility that components can liquefy during storage prior to use should be stated with the temperature on documents sent to the users. The general practice is to use a standard temperature with a safety margin to calculate the mixture composition and avoid the condensation of vapours. For example, –10 °C (14 °F) for some European countries.

5.3 Mixture manufacturing accuracy

Mixtures are usually manufactured by measuring weight, pressure, or volume (syringe/ampoules) of the components into the cylinders.

The accuracy of the filling technology used shall be taken into account and incorporated into the safety margins used to calculate the pressure and/or weights of components in oxidant-fuel gas mixtures.

NOTE—To ensure precision, it is recommended that compressed oxidant-fuel gas mixtures be manufactured in cylinders large enough to allow acceptable mixture accuracy. Therefore, these mixtures should not be manufactured in small cylinders. For example, with a water capacity less than or equal to one litre or in disposable cylinders. Such small size cylinders should be filled only with already prepared compressed oxidant-fuel gas mixtures. However, direct manufacture in small cylinders is possible if safety premixes are used.

6 Gas mixing equipment

Gas mixing systems shall be designed by competent personnel and risk assessed (hazard and operability study [HAZOP]) to ensure that the systems are safe and effective. New cylinder filling manifold designs or modifications shall be reviewed and approved prior to the use of the system. The cylinder filling manifolds should be simple to operate with a logical layout to minimise the potential for operator error.

6.1 Considerations in the design of the gas mixing facility

Gas filling systems and filling areas should be segregated as far as it is practicable to eliminate the risk of the inadvertent mixing of incompatible gases. Flammable and oxidant gases or mixtures shall be stored in accordance with applicable codes and regulations.

Gas filling system components shall be compatible with the oxidants (in particular high pressure oxygen) and the flammable gases used.

The design shall take into account the prevention of feedback of gas from filling systems into supply gas systems.

The equipment shall be designed to prevent simultaneous connection of flammable and oxidant gases to the cylinder being filled.

The interconnection of incompatible supply gases shall not be possible through the various cylinder filling manifolds and mixing systems. Non-return valves and block valves shall not be relied on as the only means of protection against interconnection of incompatible gases.

Adequate provision shall be made to prevent backfeeding of partially filled cylinders into other filling systems or cylinders via supply, vent, or vacuum systems. This is particularly important where a common supply feeds different category filling areas.

Mixtures of oxidant and flammable gases shall be filled on systems engineered to minimise the risk of operator errors that could result in the formation of an explosive mixture.

The oxidant and flammable gases shall be filled either:

- on separate blending equipment; or
- using dedicated equipment with two separated supply gas manifolds, where there is no possibility of the inadvertent connection of incompatible gases at the same time.

Connections on the cylinder filling manifold system shall be designed to prevent the possibility of the connection of non-authorised products. The preparation of compressed oxidant-fuel gas mixtures in cylinders may require the use of valve outlet adaptors. Special procedures shall be put in place to control the issue and use of these adaptors.

Provision should be made for plugging or capping cylinder filling hoses, so that contamination is prevented when the hoses are not in use. The filling hoses should be dedicated to gases of the same type. Do not use hoses that have been used to fill flammable gases to fill pure oxygen because there is a possibility that the gases can be adsorbed on the internal walls of the hoses.

When oxygen is required to be added as the last component to a high-pressure fuel rich mixture, there can be a reaction that can generate sufficient heat to melt the fuse metal of the pressure relief device.

At least one of the following options shall be considered when adding oxygen to a fuel rich mixture:

- Add the oxygen at a low pressure as determined by the expert opinion;
- Avoid the use of diaphragm packless valves. If diaphragm packless valves must be used, a tied diaphragm packless valve shall be specified; or
- Install a protection device around the valve or between the cylinder and the operator in case of a reaction caused by the sudden opening of the untied diaphragm valve.

Where flammable components are to be stored and filled, consideration shall be given to the following:

- classification of electrical and mechanical equipment and safety devices (voltages, flame proofing, etc.);
- grounding of cylinder filling manifolds and associated equipment;
- sources of static discharge;
- building ventilation;
- flammable gas detection systems and alarms; and
- explosion relief for buildings.

Vent lines from cylinder filling manifolds shall be installed to enable any residual gas be vented in a safe manner. Care shall be taken to ensure that vent lines are installed in a way that avoids any reaction between incompatible products that could lead to explosive mixture formation. The vent lines should be separated with a facility to purge the lines with inert gas.

Precautions should be taken to avoid the suckback of contaminants (oil, scrubber solutions, etc.) from vacuum systems into cylinder filling manifolds and cylinders. Vacuum pumps used in oxidant service should use an appropriate oxidant compatible lubricant. (for example, fluorinated pump oils).

There should be adequate labelling to identify valves and other operating controls and equipment.

Pressure gauges, scales, and other metering equipment shall be regularly calibrated.

6.2 Oxidant and fuel gas sources

Care shall be taken to prevent the backflow of an oxidant into a fuel gas system or cylinder or vice versa as this can result in the unintentional formation of an explosive gas mixture.

To avoid such a hazard, always use reactive gas sources at pressures higher than the pressure in the receiving oxidant-fuel gas mixture cylinder.

Ensure that the gas supply systems are designed to prevent backflow. Care shall be taken to prevent an oxidant fuel gas mixture being produced inside the manifold. To avoid such a hazard:

- Use only one reactive gas source at a time;
- Do not connect flammable and oxidant gas sources to a receiving cylinder at the same time; and
- Ensure that reactive gases are effectively removed from the filling system prior to the introduction of an incompatible gas (for example, by evacuation or purging with nitrogen).

6.3 Inert gas sources

Inert gas sources should be protected against backflow by the following:

- Always use inert gas sources at pressures higher than the pressure of the mixture cylinder;
- As a minimum, protect inert gas sources with backflow protection and/or double block and bleed valves;
- Only one gas source shall be open at a time; and
- Create a vacuum inside the entire oxidant-fuel gas mixture manufacturing equipment (up to the receiving cylinder valve) prior to the introduction of inert gas.

7 Preparation methods

7.1 Choice of cylinder and valve

The materials of construction of the cylinder and the valve shall be compatible with all the components of the mixture. The use of dip tubes for homogenization is not recommended because of the potential for a dip tube to become detached and create an ignition source within the cylinder as well as resulting in a non-uniform mixture.

The inner surface of the cylinder should be clean (for example, free of rust or other potentially reactive substances, oil, grease, etc.). New cylinders and retested cylinders should be dried in an appropriate way before being used for oxidant-fuel gas mixtures. Before starting the filling procedure, the cylinder shall be evacuated.

Consideration shall be given to the potential for customers to contaminate cylinders with materials (liquids, gases, solids) that are incompatible with the components of oxidant-fuel mixtures. Preventive actions may include the examination of valve outlet for cleanliness and use of residual pressure/non-return valves.

7.2 Filling methods

In general, the following preparation methods may be used for the manufacture of gas mixtures:

- gravimetric method (component weight measurement);
- pressure method (component partial pressure and cylinder temperature measurements);
- volumetric method (syringe, intermediate capacity, etc., volume/pressure measurement); and
- dynamic method (simultaneous blending at low pressure, followed by compression).

Note that the pressure method is less precise than the 3 others as it depends on both pressure and temperature.

Dynamic blending of oxidant-fuel gas mixtures is discussed in Appendix D.

A compressed oxidant-fuel gas mixture may be produced by preparing an intermediate mixture of flammable and inert gases and then move the cylinder to a separate filling system for the oxidant addition. These measures are followed when an intermediate mixture cylinder is removed from the initial filling system:

- Status of the intermediate mixture is identified by appropriate labelling or marking;
- Intermediate mixture is homogenized; and
- Mixture composition is measured and identified prior to reconnection to complete mixture filling. Where analysis is not performed, a second person shall check the filling operation to ensure the correct component quantities are added.

It is also possible to safely manufacture oxidant-fuel gas mixtures entirely with dedicated equipment when following all the requirements contained in this publication. See 6.1.

The filling method shall be selected in order to ensure the final mixture and any intermediate mixtures are within the safety margins detailed in 5.2.

7.3 Rules for safe preparation

The filling instructions shall define the method for each step that has to be used by the operator.

Either the actual mass or the pressure and temperature of each filling step shall be recorded by the operator to ensure traceable records of the complete filling procedure.

Each step of the filling process has to be conducted in one operation. Therefore, the operator shall take care that enough of each component is available prior to starting any filling.

During the filling of fuel-rich gas mixtures containing inert gas(es), the addition of pure oxygen or other oxidants to a mixture as the final component should be avoided. It is recommended that safety premixes of oxygen or other oxidants in an inert gas should be used instead.

7.4 Filling conditions

The cylinder shall be at or above room temperature prior to filling and during the whole production process including homogenization and analysis. This will avoid condensation of components inside the cylinder. Cylinders shall not be subject to temperatures greater than 65 °C (149 °F).

The flowrate of addition of pure oxygen shall be controlled to avoid adiabatic compression and warming to avoid possible ignition sources, especially if the filling process requires going through the explosive range.

Care shall be taken when adding flammable liquids first to make sure that they are totally vaporised inside the cylinder and there is no residual liquid inside the cylinder valve prior to an oxidant being added. This is to prevent possible reaction in the cylinder valve.

7.5 Premixes

In some cases, it can be necessary to use premixes to add one or more reactive components to the mixture. The reasons for premix use are:

- to ensure that during the addition of the flammable component, the explosive range is not reached in the cylinder at any time; and
- to increase the mass or partial pressure of gas added in order to maintain filling accuracy in lower concentration components.

Premix composition shall be analyzed or measured before first use to ensure that the concentrations of all components in the premix are within the desired limits and to positively identify the balance gas.

Premix cylinders shall be identified and a control system implemented to prevent confusion with other cylinders and other premix cylinders.

If premixes are oxidant-fuel mixtures, they have to be treated according to the rules defined by this publication.

Premixes can be inert, flammable, or oxidizing and have to be treated accordingly. They include safety premixes.

Premixes should be protected from backflow when used.

8 Filling

8.1 Production sheet

The production sheet shall specify all of the relevant information necessary to produce the mixture, including safety information. The mixture shall be clearly identified as an oxidant-fuel mixture.

The production sheet shall specify, at a minimum:

- cylinder and valve type;

- order of component addition;
- quantities of gases to be added;
- any homogenization and analysis steps required; and
- identification of intermediate premix cylinders.

Additional information that may be specified on the production sheet includes:

- equipment to be used, taking into account the accuracy of weigh scales, manometers, and syringes;
- classification of the mixture;
- color of the cylinder shoulder (if applicable); and
- labelling requirement.

A system shall be put in place to avoid misuse or confusion between production sheets for different compressed oxidant-fuel mixtures.

8.2 Safe selection of raw materials

It is extremely important to ensure that the correct pure gas or mixtures are selected when manufacturing oxidant-fuel gas mixtures as incorrect selection is one of the main causes of incidents during the manufacturing process.

Pure gases, liquids, and premixes used for the manufacturing of oxidant-fuel gas mixtures shall have a defined quality and composition. Impurities should be considered to avoid the possibility of a dangerous mixture being manufactured.

There shall be adequate segregation of oxidant, flammable, and inert cylinder supply gases in the production area (i.e., pure products and premixes). These segregated areas shall be clearly identified.

Pure products and premixes shall be clearly identified with all relevant markings and current composition information using the full chemical name(s), i.e., "hydrogen" instead of "H_2," in the appropriate language for the operator. An identification system (for example, a bar code or radio frequency device) that can link the cylinder with the content is useful to enable better control.

Gas mixtures used as premix shall be labelled with the exact composition of the mixture.

When mandated by regulation, cylinders shall be labelled as required (for example, with the GHS pictogram, hazard, and precautionary statements).

8.3 Evacuation of cylinder before filling

Before filling, it is necessary to remove any residual gas from the cylinder by evacuation. Evacuation is necessary to ensure that there are no flammable or oxidant gases present that can create unexpected explosive conditions during filling or change the final mixture composition. The evacuation shall produce a vacuum in the cylinder of at least 1 mbar, abs (0.014 psia). Alternatively, completing cycles of pressurization and discharge with an inert gas and then evacuation of the cylinder to less than 10 mbar, abs (0.145 psia) is also permissible.

8.4 Single cylinder manufacture

Oxidant-fuel mixtures should be made by filling one cylinder at a time.

Batches of multiple cylinders may be manufactured only after a risk assessment has been conducted to ensure that the method employed reaches an adequate level of safety (for example, use of safety premix, double independent control of the quantity of gas introduced into each cylinder, etc.).

8.5 Topping up adjustment for out of specification mixtures

The topping up of out of specification mixtures after disconnection from the filling manifold shall not be allowed unless approval is given by a technically competent person responsible for oxidant-fuel gas mixture formulation.

8.6 Gas homogenization requirements

A mixture shall be homogeneous at the end of the filling process and prior to re-opening the cylinder valve and in some cases during the production process.

The recipe shall take into consideration the need for homogenization and shall be in writing. All homogenization steps shall be documented in the production sheet.

Before any method of homogenization is used, tests should be carried out to ensure that the method and equipment used is effective for a range of component molecular weights.

When all the preventive measures contained in this publication are taken into account, the compressed oxidant-fuel gas mixtures after homogenization are considered safe and can therefore be analyzed or used without the need for protection against explosion of the cylinder.

9 Analysis

9.1 Principles of analysis

The composition of all premixes shall be analysed or otherwise verified and the analysis results recorded and retained.

Analysis of the final mixture may be required for different reasons such as control of the accuracy of the mixture in particular for quality purpose when it contains low concentrations of reactive gases. The analysis of oxidant-fuel gas mixtures is safe provided that all of the requirements and recommendations detailed in this publication are followed. All cylinders of oxidant-fuel mixtures shall be analysed for minor component concentrations after filling.

9.2 Mixture analysis

The equipment and methods used to analyse oxidant-fuel gas mixtures shall be verified to be able to analyse the target components to an uncertainty of +/- 5% of the relative concentrations.

Before analysis, the person who conducts the analysis shall check the following:

- All masses and/or pressures are within the specified limits;
- Homogenization step has been completed; and
- All other precautions have been taken prior to the analysis, as applicable.

9.3 Mixtures out of range

If the completed mixture is found to be in the explosive range, immediately stop all actions and see Section 11 for guidance on proper handling.

10 Disposal of residual compressed oxidant-fuel gas mixtures in cylinders

For the general principles and rules relating to the disposal of gas mixtures refer to:

- EIGA Doc 30, *Disposal of Gases* [7]; and
- EIGA Doc 39 [1].

Do not simultaneously vent cylinders with incompatible gas mixtures on the same manifold. Flammable mixtures shall be separately vented from oxidizing mixtures.

11 Emergency planning

A dangerous mixture can be identified by one or more of the following methods:

- discovery of overfilling of one reactive component during the filling procedure;
- discovery of introduction of the incorrect type of gas (pure or premix);
- identification during gas analysis;
- evidence of gas component reaction; or
- review of the recipe compared to the actual component addition.

The mixture is dangerous if it is:

- inside the explosive range; or
- overpressurised.

In these cases, the following actions shall be taken:

- Identify the cylinder and inform all responsible persons;
- Do not touch the cylinder;
- Do not actuate the cylinder valve;
- Evacuate people from the immediate area;
- Evaluate the situation employing the appropriate experts; and
- Implement disposal plan as determined by the appropriate experts.

12 References

[1] EIGA Doc 39, *The Safe Preparation of Gas Mixtures*, www.eiga.eu

NOTE—This publication is part of an international harmonisation programme for industry standards. The technical content of each regional document is identical, except for regional regulatory requirements. See the referenced document preface for a list of harmonised regional references.

[2] ADR, *European Agreement concerning the International Carriage of Dangerous Goods by Road*. www.unece.org

[3] ISO 10156, *Gases and gas mixtures—Determination of fire potential and oxidizing ability for the selection of cylinder valve outlets*, www.iso.org

[4] TRGS 407, Tätigkeiten mit Gasen – Gefährdungsbeurteilung, https://www.baua.de/

[5] NOAA Expanded Chemical Reactivity Worksheet (CRW4)

[6] ISO 11114-1, *Transportable gas cylinders—Compatibility of cylinder and valve materials with contents—Part 1: Metallic materials*, www.iso.org

[7] EIGA Doc 30, *Disposal of Gases*, www.eiga.eu

NOTE—This publication is part of an international harmonisation programme for industry standards. The technical content of each regional document is identical, except for regional regulatory requirements. See the referenced document preface for a list of harmonised regional references.

Appendix A—Audit guidelines (Informative)

It is recommended that facilities manufacturing compressed oxidant-fuel gas mixtures undergo periodic audits to assess their compliance with this publication and with other recognised safe working practices. The nature and detail of such audits will be determined by the facility's level of involvement with manufacturing compressed oxidant-fuel gas mixtures and compliance with local regulations.

The following checklist of items to audit is not exhaustive; however it provides a helpful starting point. The "Ref" column gives, where appropriate, the section of this publication where more information on the checklist item can be found.

1	Compressed oxidant-fuel gas mixtures manufacturing feasibility study	Ref.
1a	Are there people designated as having responsibility for the formulation, review, and approval of recipes?	4.1 and 4.3
1b	Is there a system for approval of new recipes?	4.1 and 4.3
1c	Formulation of compressed oxidant-fuel gas mixtures shall be approved by at least 1 authorised person other than the creator of the formulation (checker).	4.1 and4.3
1d	Are approved formulations of compressed oxidant-fuel gas mixtures protected against unauthorised changes?	4.1
1e	Are oxidant-fuel formulation data sources available to personnel that create and check the recipe?	5.2 and Appendices A to D
1f	Do the rules applied for creating complex oxidant-fuel gas mixtures taking into account the rules as required for: - unstable gases; - pressure influence on the flammability of certain halocarbons; - oxidant other than oxygen and air; and - more than one flammable gas and/or more than one inert gas?	5.2
1g	Has a study been conducted for each formulation to avoid explosive mixtures or cylinder bursting during manufacturing?	5.2.2
1h	Has a study been conducted for each formulation to prevent condensation after manufacturing?	5.2.3
1i	Does the mixture composition during filling conform to the specified safety margins?	5.2
1j	Does the mixture composition conform to the safety margins with respect to the mixture accuracy?	5.3

2	Compressed oxidant-fuel gas mixtures manufacturing equipment	Ref.
2a	Is the manufacturing site approved for the manufacture of compressed oxidant-fuel gas mixtures by the technically competent company authority?	6
2b	Has a HAZOP been conducted on the complete gas mixing?	6
2c	Has the equipment been designed to prevent simultaneous connection of flammable and oxidant gases to the cylinder being filled?	6.1, 6.2, and 6.3
2d	Are gas supplies clearly labelled to avoid operator confusion?	6.1
2e	Is a manifold purge and/or vacuum available?	6.2, 6.3, and 8.3
2f	Does the filling equipment prevent backflow of gases into the supply gases? Is the system being checked on a regular basis?	6.2 and 6.3
2g	Are appropriate adaptor control systems in use?	4.1 and 6.1
2i	Are the gas filling system components compatible with the oxidants (in particular high pressure oxygen) and with the flammable gases used?	6.1

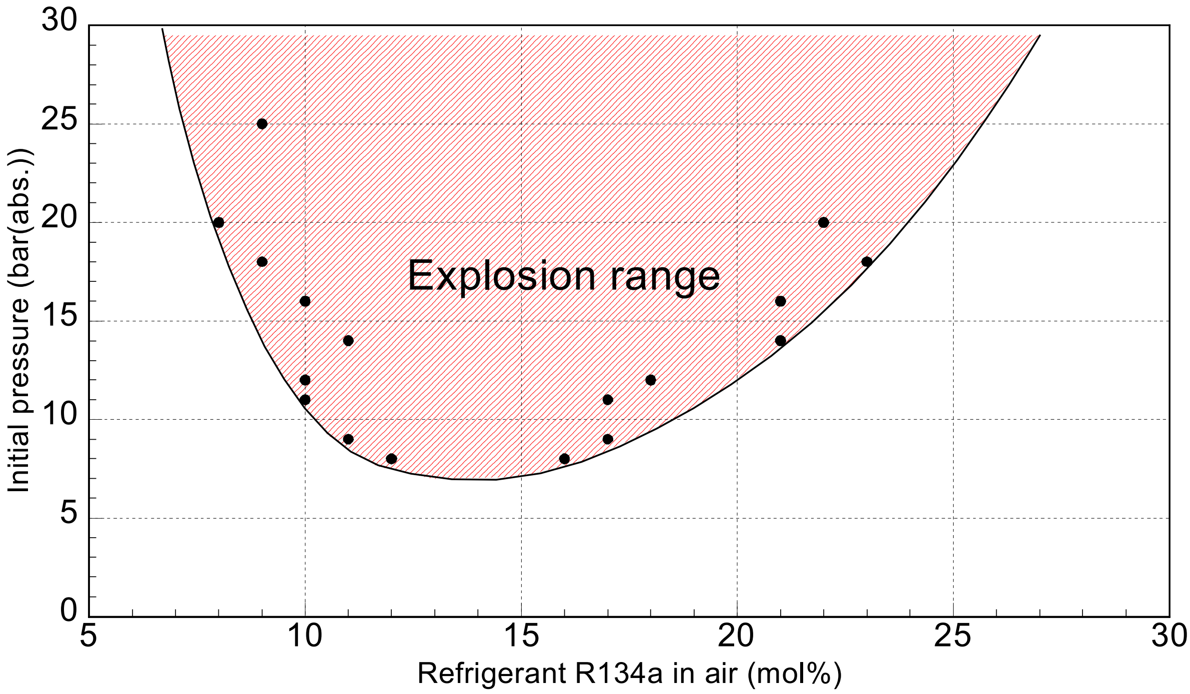
3	Compressed oxidant-fuel gas mixtures manufacturing procedures	Ref.
3a	Are compressed oxidant-fuel gas mixtures work instructions up to date and available in the work area?	4.3
3b	Are the mixtures filled to approved recipe and all associated instructions? Are the instructions followed exactly?	5.2
3c	Do the filling instructions identify the mixture as an oxidant-fuel mixture?	8.1
3d	Is the production sheet in accordance with 8.1?	8.1

3e	Has each step of filling been defined with filling amount of each component, intermediate composition confirmation (if required), and the method of mixing?	8.1
3f	Are cylinder, valve, and preparation specified?	7.1
3g	Are premixes clearly identified on the production sheet?	7.5 and 8.1
3h	Is the storage area for premixes clearly identified?	7.5
3i	Are premix cylinders analyzed and approved prior to use?	7.5
3j	Does the production sheet indicate the filling methods and the equipment to use?	8.1
3k	Are the pressure gauges, scales, and other metering equipment regularly calibrated?	6.1
3l	Are analysis records easily retrieved and retained?	4.2
3m	Is the adjustment of non-conforming mixtures controlled?	8.5
3n	Is there a procedure for the selection of the raw materials?	8.2

4	**Compressed oxidant-fuel gas mixtures manufacturing personnel qualification**	**Ref.**
4a	Are personnel involved in the formulation and in the preparation of oxidant-fuel mixtures suitably qualified, experienced, and trained?	4.3
4b	Have the operators been signed off as competent in the filling, hazards, and safety aspects of oxidant-fuel filling?	4.3

5	**Compressed oxidant-fuel gas mixtures manufacturing quality system**	**Ref.**
5a	Is a quality system in place?	2.2
5b	Does the quality system include a documentation system?	4.2, 4.3, and 8.1

Appendix B—Pressure dependence of explosive range (Informative)



Appendix C: Energy limited evaluation method (informative)

This section presents an evaluation method which is widely used in the gas industry and often applied in the following examples:

- in the absence of sufficient knowledge about the combustion behavior of a specific oxy-fuel mixture under elevated pressure conditions;

- when passing through the flammable zone during the fill process cannot be avoided; or

- when evaluating extremely complex mixtures.

The principle of the evaluation method is to limit the total potential combustion enthalpy of an oxy-fuel mixture, so there is not enough energy present to burst a high-pressure cylinder in case of an unintentional combustion reaction. The evaluation method itself does not guarantee the safety of the mixture but does limit the consequences of an unintentional combustion reaction inside the high-pressure cylinder, protecting the operators in close proximity of the cylinder.

The combustion enthalpy limit depends upon the water volume of the cylinders used for the preparation of compressed oxidant-fuel gas mixtures and the safety margin applied to the amount of energy required to bulge a high-pressure cylinder with a working pressure of 138 bar (2000 psi). The combustion enthalpy limit for a cylinder with a working pressure specification equal to 138 bar (2000 psi), and a safety margin of 5, has been set at 1290 British thermal units (BTU) per cubic foot (48.07 kJ/liter) of cylinder water volume. This combustion enthalpy limit is used for all cylinders with a working pressure greater than or equal to 138 bar (2000 psi). Cylinders with a working pressure less than 138 bar (2000 psi) shall not be filled using this method. Applying the combustion enthalpy limit is recommended for oxy fuel mixtures with LEL or LOC fractions greater than 0.5.

This evaluation method is not used for the feasibility check of oxy fuel mixtures. Rules to determine whether a mixture can be made or not, and rules on order of component addition shall be developed by a company expert and shall be used in conjunction with the energy limit calculation.

C1 Principle

First, the theoretical combustion enthalpy of the intended mixture is calculated at full cylinder working pressure. When the combustion enthalpy limit is exceeded, the maximum pressure of the oxy-fuel mixture shall be reduced (and thus reducing the total moles in the mixture) to a filling pressure, where the total combustion energy is at or below the 1290 BTU per cubic foot (= 48.07 kJ/liter) of cylinder water volume.

The final mixture recipe shall be determined by the lowest of the following calculations:

- total moles calculated based on the combustion enthalpy limit,

- total moles calculated based on the mixture vapor pressure limit if the mixture contains one or more components limited by vapor pressure,

- total moles calculated based on the mixture pressure limit due to a component’s partial pressure limit (e.g., acetylene) or due to any local rules or regulations, or

- total moles calculated based on the working pressure of the cylinder.

C2 Combustion enthalpy calculation

C2.1 Determination of energy potential

- The mixture heat of combustion is calculated by:

$$\Delta H_{c_m} = \sum_{i=1}^{n} [X_i] \Delta H_{c_i}$$

- The heat of combustion for oxygen rich mixtures is equal to the mixture heat of combustion:

$$OR\Delta H_{c_m} = \sum_{i=1}^{n} [X_i] \Delta H_{c_i}$$

- The heat of combustion of fuel rich mixtures is complicated and should be done by a company expert.

- The heat of combustion of fuel rich mixtures can be calculated by:

  - Determining the oxygen required for full combustion:

$$OCF_m = \sum_{i=1}^{n} [X_i]\, CF_i$$

  - The effective combustion factor is calculated:

$$ECF_m = \frac{[Oxidizer]}{COF_m}$$

  - and the heat of combustion is determined:

$$FR\Delta H_{c_m} = \left(\Delta H_{c_m}\right) x\ (ECF_m)$$

- The heat of combustion of fuel rich mixtures can also be calculated by:

  - Using the coefficients from the balanced reaction equation for each flammable component, calculate the BTU per cubic foot (kJ/liter) of oxygen reacted for each flammable component.

  - Starting with the flammable component that has the highest BTU per cubic foot (kJ/liter) of oxygen reacted, calculate the potential energy for the amount of the flammable component that can react before the oxygen runs out.

  - If there is any oxygen left after the first component is reacted, move to the flammable component with the next highest BTU per cubic foot (kJ/liter) of oxygen reacted, and calculate the potential energy for the amount of the flammable component that can react before the oxygen runs out.

  - Continue moving through the flammable components until the oxygen runs out and then add up the potential energy contributed by each flammable component or fraction of flammable component able to react before the oxygen ran out. The sum is the heat of combustion for the mixture.

C2.2 Sources for combustion enthalpy

Heat of combustion data should be taken from the following sources (in order of preference):

1. NIST Webbook vapor phase Heat of Combustion.
2. NIST Webbook vapor phase Heat of Formation, corrected using Hess's Law
3. NIST Webbook liquid phase Heat of Combustion

4. PubChem Web Application (NIOSH)

5. Yaws - Handbook of Chemical Compound Data for Process Safety; Carl L. Yaws

6. Calculated using Chetah ASTM Computer Program for Chemical Thermodynamic and Energy Release Evaluation

7. Calculated using the Heats of Formation of the molecules in the balanced reaction equation using the following formula where C_i is the coefficient of the molecule in the balanced equation:

$$\Delta H_c = \sum_{i=1}^{n} [C_i] \Delta H_{F\,i(products)} - \sum_{i=1}^{n} [C_i] \Delta H_{F\,i(reactants)}$$

8. Estimated value from Cameo Chemicals (NOAA)

9. If no established value for a substance can be found, its combustion energy is set to 10,000 BTU.

Appendix D—Dynamic blending (Normative)

Dynamic blending is inherently the safest method of producing fuel oxidizer mixtures. When using this process all components are added to a cylinder in the correct proportions, simultaneously, while the concentrations are monitored. This removes the most hazardous step in fuel oxidizer blending where oxidizer is added to a fuel-inert high pressure mixture or fuel is added to an oxidizer-inert high pressure mixture. Additionally, we have control over the component(s) being added and their concentrations. Many of the hazards of production of fuel oxidizer mixture are still present when using dynamic blending to produce these mixtures. The principles for fuel oxidizing mixtures contained in this publication shall be followed except where allowed in this appendix.

D1 Definitions

Excess reactant: The component(s) that is not completely consumed in a reaction with another component. If a mixture is oxygen rich, the oxygen is the excess reactant. The fuel component(s) is the excess reactant for fuel rich mixtures.

Limiting reactant: The component(s) that is completely consumed in a reaction with another component. If a mixture is oxygen rich, the fuel component(s) is the limiting reactant. Oxygen is the limiting reactant for fuel rich mixtures.

Dynamic blending: A process used to produce gas phase mixtures where controlled and monitored amounts of mixture components are blended at low pressure and compressed into high pressure target containers.

D2 Specific rules for dynamic blending

- Fill pressure used for dynamic blending of fuel oxidizer mixtures shall be determined by expert opinion.

- Fuel rich mixtures with final mixture oxygen concentrations greater than 40% of the limiting oxygen concentration SHALL NOT be produced via dynamic blending.

- Production sheet shall specify, at a minimum:

  - cylinder and valve type;

  - list all components and their concentrations

  - list the concentration targets for the limiting reactant(s) in the mixture

  - order of component addition;

  - use the identifier “dynamic blend”

  - mixture volume

  - mixture final fill pressure ; and

  - identification of intermediate premix cylinders.

- Additional information that may be specified on the production sheet includes:

  - equipment to be used

  - production plant

  - classification of the mixture; and

- labelling requirement.

D3 Mixture production

The limiting reactant concentration SHALL be set and controlled before the addition of the excess reactant.

If safety premixes are used to add the limiting reactant, the following procedure does not need to be followed:

a) For oxygen rich mixtures where the fuel(s) is the limiting reactant.

1. Set the Inert gas flow rates.
2. Start the flow of fuel(s).
3. Adjust the fuel flow(s) until the concentration(s) equal the concentration target(s).
4. Start the oxidizer flow and slowly increase to the required concentration.
5. Start compression into target cylinders.

b) For fuel rich mixtures where the oxidizer is the limiting reactant.

1. Set the Inert gas flow rates.
2. Start the flow of oxidizer.
3. Adjust the oxidizer flow until the concentration equal the concentration target.
4. Start the fuel flow and slowly increase to the required concentration.
5. Start compression into target cylinders.

c) Shut down

1. Stop the flow of limiting reactant.
2. Stop the flow of the excess reactant
3. Stop the flow of inert gas.