



an Air Liquide company

Refinery Sector Rule

Flare NHV Monitoring and Calibration



THIS DOCUMENT IS PUBLIC

4C HSE Conference
April 2018

Airgas, an Air Liquide company

Refinery Sector Rule (RSR)
Flares NHV Monitoring and Calibration

Airgas
an Air Liquide company

1

RSR for Flares - NHV Monitoring Overview

THIS DOCUMENT IS PUBLIC

2

4C HSE Conference
April 2018

| Airgas, an Air Liquide company

| Refinery Sector Rule (RSR)

| Flares NHV Monitoring and Calibration

Airgas
an Air Liquide company

RSR- NHV Btu Monitoring

- **GC- PS-9 outlines performance validation requirements**

- Component based analysis with derived NHV reporting
- Options for Calibration Standards
 - i) Based on pre-survey concentrations
 - Required and optional components
 - ii) C1 thru C5 Plus Hydrogen (and other Title V Components?)
- Mid-Range Daily (90-110 of Target)
- Quarterly Low 40-60% of Mid; High 140-160% of Mid
- Analytes (component) based
- Consent decree based Btu targets not applicable

- **New Flare Class Btu calibration standards warranted**

- Standard reference conditions defined
- Table 12 Specified NHV Btu Values (Differ from GPA/Wobbe)
- Includes **1212 Btu allowance** for Speciated Hydrogen
- RSR specified engineering reference conditions



THIS DOCUMENT IS PUBLIC

3

4C HSE Conference
April 2018

| Airgas, an Air Liquide company

| Refinery Sector Rule (RSR)

| Flares NHV Monitoring and Calibration

Airgas
an Air Liquide company

■ 37. The appendix to subpart CC is amended by adding table 12 to read as follows:

**Appendix to Subpart CC of Part 63—
Tables**

* * * * *

**“Table 12 Normalized
Certificate of Analysis”**

TABLE 12—INDIVIDUAL COMPONENT PROPERTIES

Component	Molecular formula	MW _i (pounds per pound-mole)	CMN _i (mole per mole)	NHV _i (British thermal units per standard cubic foot)	LFL _i (volume %)
Acetylene	C ₂ H ₂	26.04	2	1,404	GPA
Benzene	C ₆ H ₆	78.11	6	3,591	NHV
1,2-Butadiene	C ₄ H ₆	54.09	4	2,794	2.5
1,3-Butadiene	C ₄ H ₆	54.09	4	2,690	1.3
iso-Butane	C ₄ H ₁₀	58.12	4	2,957	2.0
n-Butane	C ₄ H ₁₀	58.12	4	2,968	1.8
cis-Butene	C ₄ H ₈	56.11	4	2,830	3000
iso-Butene	C ₄ H ₈	56.11	4	2,928	3011
trans-Butene	C ₄ H ₈	56.11	4	2,826	1.8
Carbon Dioxide	CO ₂	44.01	1	0	1.7
Carbon Monoxide	CO	28.01	1	316	∞
Cyclopropane	C ₃ H ₆	42.08	3	2,185	12.5
Ethane	C ₂ H ₆	30.07	2	1,595	2.4
Ethylene	C ₂ H ₄	28.05	2	1,477	3.0
Hydrogen	H ₂	2.02	0	1,212 ^a	1619
Hydrogen Sulfide	H ₂ S	34.08	0	587	1499
Methane	CH ₄	16.04	1	896	274
Methyl-Acetylene	C ₃ H ₄	40.06	3	2,088	4.0
Nitrogen	N ₂	28.01	0	0	909
Oxygen	O ₂	32.00	0	0	5.0
Pentane+ (C5+)	C ₅ H ₁₂	72.15	5	3,655	1.7
Propadiene	C ₃ H ₄	40.06	3	2,066	∞
Propane	C ₃ H ₈	44.10	3	2,281	1.4
Propylene	C ₃ H ₆	42.08	3	2,150	2.16
Water	H ₂ O	18.02	0	0	2.1
					2315
					2182
					2.4
					∞

^a The theoretical net heating value for hydrogen is 274 Btu/scf, but for the purposes of the flare requirement in this subpart, a net heating value of 1,212 Btu/scf shall be used.

THIS DOCUMENT IS PUBLIC

Airgas, an Air Liquide company

2

RSR for Flares - NHV Measurement Methods

THIS DOCUMENT IS PUBLIC

5

4C HSE Conference
April 2018

| Airgas, an Air Liquide company

| Refinery Sector Rule (RSR)

| Flares NHV Monitoring and Calibration

Airgas
an Air Liquide company

Analyzer Modes

Calculated NHV through Individual Components Measurement
H2 Speciation Inherent
NHV calculated through component concentrations



Gas Chromatograph (GC)
7-13 Minute Cycle



Calorimeter
Near Real Time Cycle
H2 Speciation Optional
(Additional thru GC or Module)



Mass Spectrometer
Near Real Time Cycle

RSR- NHV Btu Monitoring Analyzer Modes

- **Calorimetric Btu NHV determination**

- Direct calculation based on O2 residual
- Near real time reading/ reporting
- Optional hydrogen speciation via add-on module or GC
- Performance validation per manufacturer's guidelines

- **Gas Chromatograph (GC)**

- Table 12 Specified NHV Btu values (Differ from GPA/Wobbe)
- 7 to 13 minute reporting cycle typical
- Performance validation per PS9 (Performance Spec 9)

- **Mass Spec Analysis**

- ALT 124 adds Mass Spec as a widely accepted monitoring technology
- Near real time plus speciation (Inherent)
- Table 12 Specified NHV Btu values (Differ from GPA/Wobbe)
- Performance validation modeled per PS9



THIS DOCUMENT IS PUBLIC

| Airgas, an Air Liquide company

4CHSE Conference
April 2018

| Refinery Sector Rule (RSR)
Flares NHV Monitoring and Calibration

Airgas
an Air Liquide company

3

RSR for Flares - Validation & Calibration Modes & Gas Standards

THIS DOCUMENT IS PUBLIC

Options (i) and (ii) for Calibration Standards

Option (i)- Pre-Survey Based

Required

- Hydrogen
- Ethane
- Propane
- N-Butane
- Butene (general)
- N-Pentane
- Methane
- Ethylene
- Propylene
- Iso-Butane
- 1,3 Butadiene

Optional

- Acetylene
- Propadiene
- Carbon Monoxide
- Hydrogen Sulfide

Option (ii)- Surrogate

C1 thru C5 Normal plus Hydrogen

(Plus trace components?)

Analyte Requirements- per Either Option

Mid-point (Daily)	90-110%
Low (Quarterly)	40-60% of Mid-point
High (Quarterly)	140-160% of Mid-point

Cal Gas Option (i)

Daily Midpoint gas to be established to cover required components and allows for addition of optional components plus others

Midpoint is daily standard

Low and High are quarterlies

LOW components are to be 40-60% Midpoint

HIGH components are to be at 140-160% of Midpoint

Required Components

- Hydrogen
- Methane
- Ethane
- Ethylene
- Propane
- Propylene
- N-Butane
- Iso-Butane
- Butene (general)
- 1,3-Butadiene
- N-Pentane

Optional Components

- Acetylene
- Carbon Monoxide
- Propadiene
- Hydrogen Sulfide

Cal Gas Option (ii)- Surrogate Calibration Gas

Daily Midpoint gas to be established to cover required components and allows for addition of optional components plus others

Midpoint is daily standard

Low and High are quarterlies

LOW components are to be 40-60% Midpoint

HIGH components are to be at 140-160% of Midpoint

Required Components

- Hydrogen
- C1 through C5 Normal Hydrocarbons

(Plus trace components?)

Trends

- #1 Trend is no dominant trend

Some Sightings

- Calorimeter for Control and Reporting - H2 Speciation via either H2 Module or GC
- SOLA removed; Mass Spec for RSR Monitoring/ Control
(and also potentially Ja Compliance)
- Additional calibration components for Title V compliance
- Heated storage cabinets and/or blankets for dew point pressure limited Btu calibration standards

4

RSR for Flares - NHV Control Absent SSM Exemptions

THIS DOCUMENT IS PUBLIC

Dew Point Vapor Pressure



- Dew point vapor pressure limited means that blends contain components that are subject to liquefying (falling out of gaseous solution)
- The gaseous concentration of these components might be limited which could lead to restrictions in cylinder fill pressure
- Restricted fill pressure limits the total amount of gas contained in a cylinder
- Cylinders might also need to be kept warm in to assure that some components do not liquefy which would ruin the calibration standards if used when some components are not in gas phase

Ex: Dew point pressure limited to 40psi @ 50F

1,3 BUTADIENE	C4 Di-Olefin	1.5	%	5% (1.425 - 1.575)	2%	106-99-0
1 BUTENE	C4 Olefin	2.75	%	5% (2.62 - 2.88)	2%	106-98-9
ACETYLENE	C2	2.75	%	5% (2.62 - 2.88)	2%	74-86-2
CARBON DIOXIDE		0.85	%	5% (0.808 - 0.892)	2%	124-38-9
HYDROGEN SULFIDE		2.75	%	5% (2.62 - 2.88)	2%	7783-06-4
ISOPENTANE	C5	2.85	%	5% (2.708 - 2.992)	2%	78-78-4
N PENTANE	C5	2.85	%	5% (2.708 - 2.992)	2%	109-66-0
TRANS 2 BUTENE	C4 Olefin	2.75	%	5% (2.62 - 2.88)	2%	624-64-6
ETHYLENE	C2 (<30% desired)	2.25	%	5% (2.15 - 2.35)	2%	748-5-1
ISOBUTANE	C4	7.25	%	5% (6.887 - 7.613)	2%	75-28-5
N BUTANE	C4	7.25	%	5% (6.887 - 7.613)	2%	106-97-8
PROPYLENE	C3 (<20% desired)	7.25	%	5% (6.887 - 7.613)	2%	115-07-1
ETHANE	C2 (<30% desired)	13.8	%	13.5 - 14.1	2%	74-84-0
NITROGEN		13.8	%	13.5 - 14.1	2%	7727-37-9
PROPANE	C3 (<20% desired)	13.8	%	13.5 - 14.1	2%	74-98-6
HYDROGEN		7.55	%	7.3 - 7.8	2%	1333-74-0
METHANE		8	%	7.6 - 8.4		74-82-8

Combined C-4 on this 21.5%
Combined C-5 on this 5.7%

Desired max <10-15% on C4
Desired max <4% on C5



Blend Temperature Control During Use and In Storage

- Suggested that calibration standards stay 20+ degrees above listed Dew point
- If temperature drops below rated Dew point:
 - Do not withdraw any gas
 - Return to warm environment
 - (Dew point $+>20^{\circ}\text{F}$)
 - Keep warm for at least 72 hours
 - Return to service



THIS DOCUMENT IS PUBLIC

4

RSR for Flares - NHV Control Absent SSM Exemptions

THIS DOCUMENT IS PUBLIC

NHV CONTROL

- Startup, Shutdown & Malfunction (SSM) exemption eliminated with RSR
- “The Rule now applies at all times”
- Potentially challenging to comply during major nitrogen purge events and steam outs
- Supplemental fuel gas likely needed to maintain 270 Btu during high N₂ flow purging and steam out events
- Internal or External Supplemental Fuel Gas?





Thank you

THIS DOCUMENT IS PUBLIC