

Designation: D4891 - 13

# Standard Test Method for Heating Value of Gases in Natural Gas and Flare Gases Range by Stoichiometric Combustion<sup>1</sup>

This standard is issued under the fixed designation D4891; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

- 1.1 This test method covers the determination of the heating value of natural gases and similar gaseous mixtures within the range of composition shown in Table 1, and Table 2 that covers flare components but is not intended to limit the components to be measured in flare gases.
- 1.2 This standard involves combustible gases. It is not the purpose of this standard to address the safety concerns, if any, associated with their use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

### 2. Referenced Documents

2.1 ASTM Standards:<sup>2</sup>

D1826 Test Method for Calorific (Heating) Value of Gases in Natural Gas Range by Continuous Recording Calorimeter E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

2.2 EPA Standard:<sup>3</sup>

EPA-600/2-85-106 Evaluation of the Efficiency of Industrial Flares: Flare Head Design and Gas Composition

## 3. Terminology

- 3.1 All of the terms defined in Test Method D1826 are included by reference.
  - 3.2 Definitions of Terms Specific to This Standard:
- 3.2.1 *combustion ratio*, *n*—the ratio of combustion air to gaseous fuel.
- <sup>1</sup> This test method is under the jurisdiction of ASTM Committee D03 on Gaseous Fuels and is the direct responsibility of Subcommittee D03.03 on Determination of Heating Value and Relative Density of Gaseous Fuels.
- Current edition approved May 1, 2013. Published May 2013. Originally approved in 1989. Last previous edition approved in 2001 as D4891–89 (2001). DOI: 10.1520/D4891-89R06.
- <sup>2</sup> For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.
- <sup>3</sup> Available from United States Environmental Protection Agency (EPA), Ariel Rios Bldg., 1200 Pennsylvania Ave., NW, Washington, DC 20004, http://www.epa.gov.

- 3.2.2 burned gas parameter, n—a property of the burned gas after combustion which is a function of the combustion ratio.
- 3.2.3 critical combustion ratio, n—for a specific burned gas parameter, the combustion ratio at which a plot of burned gas parameter versus combustion ratio has either maximum value or maximum slope.
- 3.2.4 combustion air requirement index (CARI), n—is the amount of air required for complete combustion of the gas being measured and can be used to index against other measured values such as the Wobbe Index or Heating Value.
- 3.2.5 *stoichiometric ratio*, *n*—the combustion ratio when the quantity of combustion air is just sufficient to convert all of the combustibles in the fuel to water and carbon dioxide.

## 4. Summary of Test Method

4.1 Air is mixed with the gaseous fuel to be tested. The mixture is burned and the air-fuel ratio is adjusted so that essentially a stoichiometric proportion of air is present. More exactly, the adjustment is made so that the air-fuel ratio is in a constant proportion to the stoichiometric ratio that is a relative measure of the heating value. To set this ratio, a characteristic property of the burned gas is measured, such as temperature or oxygen concentration.

# 5. Significance and Use

- 5.1 This test method provides an accurate and reliable procedure to measure the total heating value of a fuel gas, on a continuous basis, which is used for regulatory compliance, custody transfer, and process control.
- 5.2 Some instruments which conform to the requirements set forth in this test method can have response times on the order of 1 min or less and can be used for on-line measurement and control.
- 5.3 The method is sensitive to the presence of oxygen and nonparaffin fuels. For components not listed and composition ranges that fall outside those in Table 1 and Table 2, modifications in the method and changes to the calibration gas or gasses being used may be required to obtain correct results.

### 6. Apparatus

6.1 A suitable apparatus for carrying out the stoichiometric combustion method will have at least the following four

TABLE 1 Natural Gas Components and Range of Composition
Covered

Compound	Concentration Range, mole, %	
Helium	0.01 to 5	
Nitrogen	0.01 to 20	
Carbon dioxide	0.01 to 10	
Methane	50 to 100	
Ethane	0.01 to 20	
Propane	0.01 to 20	
<i>n</i> -butane	0.01 to 10	
isobutane	0.01 to 10	
<i>n</i> -pentane	0.01 to 2	
Isopentane	0.01 to 2	
Hexanes and heavier	0.01 to 2	

components: flow meter or regulator, or both; combustion chamber; burned gas sensor; and electronics. The requirement for each of these components is discussed below. The detailed design of each of these components can vary. Three different apparatus are shown in Fig. 1, Fig. 2 and Fig. 3. In each figure the equivalent of the four necessary components are enclosed in dashed lines.

6.2 Overview—Air and fuel enter the apparatus and the flow of each is measured. Alternatively, only one gas flow need be measured if the flow of the other is kept the same during measurement and calibration. This is illustrated in Fig. 2. Next there is a combustion chamber in which the air and fuel are mixed and burned. This can be as simple as a bunsen or meeker burner, but precautions should be taken that subsequent measurements of burned gas characteristics are not influenced by ambient conditions. Finally, there is a sensor in the burned gas which measures a property of this gas that is sensitive to the combustion ratio and has a unique feature at the stoichiometric ratio. Two such properties are temperature and oxygen concentrations, and either can be measured.

6.3 Flow Meter or Regulator, or both—The flow measurement part of the apparatus should have an accuracy and precision of the order of 0.1 %. Likewise, if the flow is to be kept constant, the flow regulator should maintain this constant value within 0.1 %. The meter or regulator for natural gas must maintain this precision and accuracy over the density and viscosity ranges consistent with the composition range in Table 1 or Table 2.

## 6.4 Combustion Chamber:

6.4.1 There are two different types of combustion chambers that may be used. In the first type the air and fuel are mixed and burned in a single burner. The apparatus shown in Fig. 1 has this type of combustion chamber.

6.4.2 In the second type of combustion chamber, the air and fuel are each divided into two streams, and combustion takes place simultaneously in two burners. The division of air flow must be such that the proportion of air going to each burner always remains the same. Likewise the division of fuel flow must always remain the same even through fuel composition changes. Another requirement is that the flow divisions be such that one burner has a mixture with a slightly higher combustion ratio than the other. The apparatus shown in Fig. 2 has this type of combustion chamber.

TABLE 2 Natural Gas Components and Range of Composition
Covered<sup>A</sup>

CO	verea
Compound	CAS Number
<del></del>	
Volatile Analytes Acetone	67-64-1
Acetonitrile	75-05-8
Acrolein Acrylonitrile	107-05-8 107-13-1
Benzene	71-43-2 2
1,3-Butadiene	106-99-0
Carbon disulfide	75-15-0
Chlorobenzene	108-90-7
Cumene	98-82-8
(isopropylbenzene)	30-02-0
1,2-Dibromoethane	106-93-4
Ethylbenzene	100-41-4 2,2,4
Hexane	110-54-3
Methanol	67-56-1
Methyl isobutyl ketone	108-10-1
Methyl t-butyl ether	1634-04-4
Methylene chloride	75-09-2
Nitrobenzene	98-95-3
Nitropropane	79-46-9
Pentane2	109-66-0
Styrene	100-42-5
Tetrachloroethene	127-18-4
Toluene	108-88-3
Trichloroethene	79-01-6
Trimethylpentane	2 540-84-1
Xylenes (mixed isomers)	1330-20-7
Trimethylpentane	2 540-84-1
Xylenes (mixed isomers)	1330-20-7
,	
Semi-volatile Analytes	
Acenaphthene	83-32-9
Acenaphthylene	208-96-8
Aniline	62-53-3
Anthracene	120-12-7
Benzidine1	92-87-5
Benz[a]anthracene	56-55-3
Benzo[b]fluoranthene	205-99-2
Benzo[k]fluoranthene	207-08-9
Benzo[g,h,i]perylene	191-24-2
Benzo[a]pyrene	50-32-8
Benzo[e]pyrene2	192-97-2
Biphenyl2,	92-52-4
Cresol (mixed isomers)	/9ea/ast 1319-77-3 1-13
Chrysene	218-01-9
Dibenz[a,h]anthracene	53-70-3
Dibenzofuran	132-64-9
Dibenzo(a,e)pyrene	192-65-4
3,3'- Dimethoxybenzidine	119-90-4
Dimethylaminobenzene	60-11-7
7,12-	57-97-6
Dimethylbenz(a)anthracene	
3,3'- Dimethylbenzidine	119-93-7
á,á-	122-09-8
Dimethylphenethylamine	
2,4-Dimethylphenol	105-67-9
Fluoranthene	206-44-0
Fluorene	86-73-7
Indeno(1,2,3-cd)pyrene	193-39-5
Isophorone	78-59-1
3-Methylcholanthrene	56-49-5
2-Methylnaphthalene	91-57-6
Naphthalene	91-20-3
Perylene2	198-55-0
Phenanthrene	85-01-8
Phenol	108-95-2
1,4-Phenylenediamine	106-50-3
Pyrene	129-00-0
o-Toluidine	95-53-4
Aldehydes	
Methanol	67-56-1
Formaldehyde	50-00-0
Acetaldehyde	75-07-0



TABLE 2 Continued

Compound	CAS Numl	CAS Number		
Propanal	123-38-6	123-38-6		
C1 to C5 Hydrocarbons				
Description	Compound	CAS Number		
C1 Alkanes	Methane	74-82-8		
C2 Alkanes	Ethane	74-84-0		
C3 Alkanes	Propane	74-98-6		
C4 Alkanes	n-Butane	106-97-8		
	Isobutane	75-28-5		
	n-Pentane	109-66-0		
C5 Alkanes	2-Methylbutane	78-78-4		
	Cyclopentane	287-92-3		
C2 Olefins	Ethylene	74-85-1		
C2 Alkanes	Acetylene	74-86-2		
C3 Olefins	Propylene	115-07-1		
C4 Olefins	1-Butene	106-98-9		
	2-Butene	107-01-7		
	Isobutene	115-11-7		
C5 Olefins	1-Pentene	109-67-1		
	Cis-2-pentene	627-20-3		
	Trans-2-pentene	646-04-8		
	2-Methyl-1-butene	563-46-2		
	3-Methyl-1-butene	563-45-1		
	2-Methyl-2-butene	513-35-9		
	Cylcopentene	142-29-0		
C3 Alkadienes	Propadiene	463-49-0		
C4 Alkadienes	1,2-Butadiene	590-19-2		
	1,3-Butadiene	106-99-0		
C5 Alkadienes	1,2-Pentadiene	591-95-7		
	1-cis-3-Pentadiene	1574-41-0		
	1-trans-3- Pentadiene	2004-70-8		
	1,4-Pentadiene	591-93-5		
	2,3-Pentadiene	591-96-8		
	3-Methyl-1,2- butadiene	598-25-4		
	2-Methyl-1,3- butadiene	78-79-5		
	Cyclopentadiene	542-92-7		
Heating Value Range				
Unit	Lower	Upper		
Btu/ft <sup>3</sup>	83	2350		

<sup>A</sup>Flare Gas Heating Value range defined in Table 2 is derived from the Evaluation of the Efficiency of Industrial Flares: Flare Head Design and Gas Composition EPA-600 /2-85-106 September 1985 Table 1-1. Agency Information Collection Activities OMB Responses EPA ICR Number 2411.01; NSPS and NESHAP for Petroleum Refineries Sector Residual Risk and Technology; OMB Number 2060-0657.

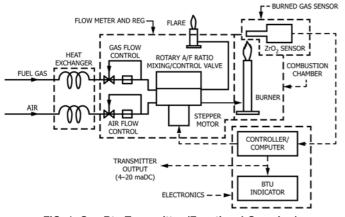


FIG. 1 Gas Btu Transmitter (Functional Overview)

6.4.3 A third type utilizes a combustion oven operating in excess of 800°C (1472°F) to assure the combustion of gases within the natural or flare gas compositions being combusted as shown in Fig. 3.

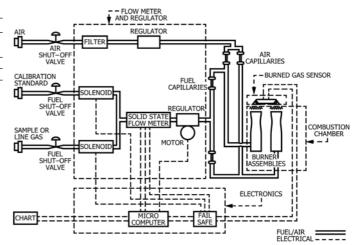


FIG. 2 Stoichiometric Combustion Apparatus

## 6.5 Burned Gas Sensor:

- 6.5.1 The burned or combusted gas sensor must measure a characteristic of the burned gas which is a function of the combustion ratio and for which there is a critical combustion ratio related to the stoichiometric ratio. A combustion chamber of the first type (Fig. 1) would have one sensor in the burned gas and its output signal would constitute the desired measurement. In a combustion chamber of the second type (Fig. 2) there would be a sensor in the burned gas from each burner. The difference between the two output signals would constitute the desired measurement. In the third type (Fig. 3), the residual oxygen is measured and the resulting oxygen value is correlated to the CARI and Wobbe Index.
- 6.5.2 There are several properties of the burned gas which are related uniquely to the combustion ratio. A burned gas sensor may be selected which provides a measure of any one of these, for example, either temperature or oxygen partial pressure.
- 6.6 *Electronics*—Electronics are used to receive the signals from the components described above to control the flow of gases into the combustion chamber in response to the signal from the burned gas sensor and to provide a digital or analog output signal, or both, which is proportional to the heating value of the gaseous fuel.
- 6.7 Temperature Stability and Operating Environment—The method is capable of operating over a range of temperatures limited only by the specific apparatus used to realize the method. It is desirable to equilibrate the air and fuel temperatures before the gases are measured. The electronics should also be stabilized against temperature changes and the burned gas sensor should be insensitive to changes in the ambient conditions.

## 7. Reagents and Materials

7.1 *Physical Contamination*—The air and gas must be free of dust, liquid, water, liquid hydrocarbons, and other entrained solids. Foreign materials should be removed by a sample line filter. To avoid any problems in the line from any liquid accumulation, pitch the line to a low point and provide a drip leg.