

Determination of the Gas Composition Effect in Carbon Dioxide Emission at Refinery Furnaces

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Companies that require gaseous fuel that burns in their processes, show concern for the reduction of emissions of greenhouse gases, at present, 69 % of the greenhouse gases produced by the burning of the refining processes and petrochemicals, which also generated a significant environmental impact, it shows a good performance as the world leader in the field of sustainability, as measured by the Dow Jones sustainability index, which evaluates companies in economic, environmental and social. The parameters and operating conditions for the ovens are affected by the composition of fuel gas, which may be a mixture of natural gas and process gas containing methane, ethane, propane and hydrogen. The process instability due to changes in gas composition represents a risk to industrial safety, environmental issues and structural damage due to high temperatures. In order to study this problem, the baseline emission of CO₂ generated was collected in ovens; CO₂ historical data of the process is analyzed and the relationship established with calorific value which depended on the composition of the gas. The statistical analysis of the results and the simulation of the combustion process, determined that CO₂ values have a tendency to increase when using fuels of high calorific value, which should regulate the use of mixtures containing compounds such as ethane and ethylene.

1. Introduction

The primary fuel combustion equipment can be natural gas or gas mixtures from the different processes taking place in the chemical, petrochemical and oil refining (Fonseca, 2010); the composition of these mixtures fuels varies from whom the process and characteristics of fuels used, so the present combustion equipment operating parameters and conditions that are affected continuously by the change in fuel composition, pose risks to the stability of the process, generating emissions to the environment and structural damage due to corrosion in the equipment, breakage and deformation, among others (Faruque, 2011).

From the environmental viewpoint, the refining industry has to face several challenges, in terms of reducing carbon dioxide emissions (Varga et al., 2010) it is because the combustion of large quantities of gaseous fuels increases the carbon dioxide content in the atmosphere causing an increase in global temperature of the Earth's surface known as greenhouse (Villaflor, 2008).

The environmental performance of a company is important in a price differentiation strategy because it is an indicator of the efficiency of the transformation processes used, from this point of view, pollution resulting from technological inability to use the entire matter and energy in production processes, and evidence that resources have been used incompletely, inefficient or ineffective (Nardini, 2004) and also, this lack of efficiency in process results in a non-economical behaviour in companies (Younessi, Tarighaleslami and Jafarigol, 2011).

2. Theoretical bases

2.1 Combustion process

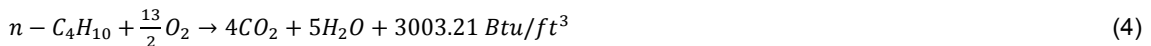
The combustion reaction study includes chemistry kinetics and gas theory, in this regard, in the area immediately after the flame, the combustion products are in chemical equilibrium or very close to equilibrium, so that it can develop methods for calculating the adiabatic flame temperature and the composition of the combustion products. Gas fuel composition is usually specified in volumetric percentage of different gases that composes it, and the calorific value is a function of the composition and calorific value of each component. Fuel gas composition in a refinery could be a mixture of compounds shown in Table 1.

Table 1: Fuel gas composition

	Natural Gas	Stream 1	Stream 2	Stream 3	Stream 4	Stream 5
Copmpound	Mol %					
Hydrogen	0.770	0	97.389	17.21	34.72	0
Carbon Monoxide	0	0	0.037	1.75	2.54	0
Methane	96.85	0	2.043	31.28	42.02	0.13
Ethane	0.375	0.001	0.036	13.34	3.50	0.40
Prophane	0.051	25.490	0.033	1.94	1.22	8.48
n-Butane	0	0.005	0.028	0.21	.037	59.85
i-Buthane	0.014	0.253	0.011	0.55	0.62	30.30
n-Penthane	0	0	0	0	0	0.21
i-Penthane	0.074	0	0.038	1.46	0.01	0.51
Ethylene	0.069	0	0	12.20	0.96	0.02
Propylene	0	74.24	0	7.71	5.18	0.10
n-Butene	0.008	0	0	0	0	0
H2S	0	0.011	0.081	3.11	0	0
Carbon dioxide	0	0	0.041	2.6	0	0
Nitrogen	1.764	0	0.263	6.64	8.86	0
Oxygen	0.025	0	0	0	0	0

2.2 Combustion reactions

The gas representative components in the network in a refinery fuel are: methane, ethane, propane, n-butane, ethylene, propylene, hydrogen and H₂S; the reactions that occur in the combustion process are:



To transform BTU/ft³ to J/m³, multiply by 3.725895·10⁴.

2.3 Law and Regulations

Environmental impact: CO₂ and other hydrocarbons (ethane, propane, butane) that are emitted to the atmosphere, impact on a rise in temperature, this is because sun rays affect the atmosphere, but some of them are unable to go out and are reflected on earth.

The environmental regulation framework is established in resolution 2153 "Protocol for the control and surveillance of atmospheric pollution from stationary sources" (Environment Ministry of Colombia, 2012) which was developed according with parameters defined by the Environmental Protection Agency US-EPA; at the same time, the ministry of environment, housing and territorial development adopts the manual for the inventory of specific sources from the national protocol for the inventory of emissions. This framework presents methods as:

Method 3: Gas analysis for determining the molecular weight dry basis

Method 3A: Determination of concentration of oxygen and carbon dioxide

Method 3B: Gas analysis for determining the correction factor of emissions or air excess

Method 3C: Carbon dioxide, methane, nitrogen and oxygen determination in stationary sources

Similarly, United Nation convention for climate change (United Nations, 2012), [Vienna Convention for the Protection of the Ozone Layer] establishes that organizations that have emissions over 25000 tons of greenhouse gases, are demanded to present annual reports to the EPA. The following technical committees of ASTM have rules to which reference is made in the EPA rule:

D02 Petroleum Products and Lubricants;

D03 Gaseous fuels;

D05 Coal and coke;

D22 Air quality;

Besides regulation present at EPA framework, ASTM committees are actually working on new regulation procedures related with climate change. This procedures include WK21096, guidelines for disclosure related to climate change and risk exposures, and WK21808, Guide for Climate Change Assessment and Risk Management.

Gases covered by these standards are: carbon dioxide, methane, nitrous oxide, hydrofluorocarbons, petrofluorocarbons, sulfur hexafluoride and other fluorinated gases such as nitrogen trifluoride and ethers hydrofluorinated

3. Methodology

In order to achieve the purpose of this research, a fired heater representative from a petroleum refining process was selected; This one consist on a heat exchanger where process fluid flows inside tubes and is heated by the radiation which comes from a combustion flame and convection coming from hot gas.

Fired heater consists in a closed steel array with an internal isolation of refractory bricks. The convective area is located in the upper side of the array and the stack. The radiation tubes are located over the walls and the flame is originated through the burners, the furnace analysed in this work have 37 tubes in the convective and 49 tubes in the radiation area. Figure 2 show a illustration of fired heater.

3.1 Selection of gas combustible mixtures

A statistical analysis of historical chromatography data was run using Statgraphics in order to obtain a representative sample of fuel gas. Results allowed eliminating some components of the refinery gas (RG) (i-pentane, butylene, acetylene, carbonmonoxide, carbondioxide, nitrogen and oxygen) from the evaluated mixtures. The criteria used to dismiss these components were:

1. Find those compounds whose contribution to the stream concentration is very low (<1 %),
2. Compounds which are not present in most of the streams,
3. Compounds which do not contribute significantly to the calorific value of the mixture.

In the case for n-butane and i-butane only one representative compound of this gas family was selected based on they represent the same Low calorific value (LCV) and the same combustion reaction.

3.2 Procedure for combustion monitoring

Monitoring data from combustion gases at refinery was collected using a portable monitoring equipment (MADUR-GAT 21). This equipment uses electrochemical cells to measure CO, O₂, NO_x, SO_x y CO₂, at the same time an oxygen analyzer was used to collect data relative to it, Figure 1 shows the structure of fired heater used to get the data. Measurement parameters are shown on Table 2.

Table 2: Measured Parameters for combustion monitoring

O ₂ (% DCS)	2.2
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Damper (% DCS)	64
Temperature Stack Gas (°F)	481
Pressure of Gas burners(psi)	12.5

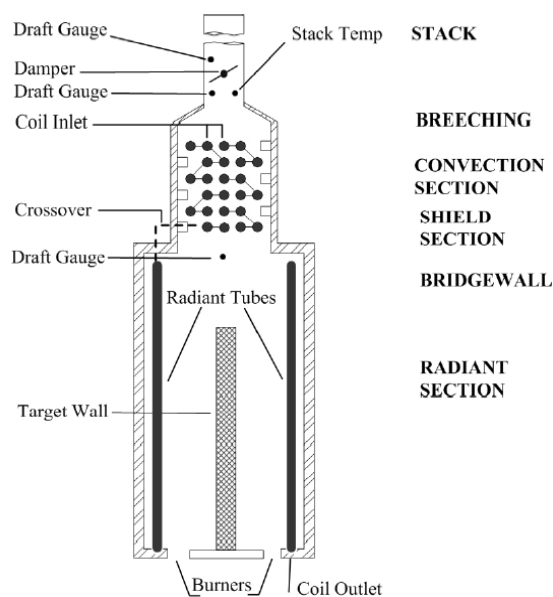


Figure 1: Illustration of fired heater

4. Results

CO₂ emissions generated in furnace were evaluated according with the composition of the gas used in the combustion process.

Using historical data from different mixtures of fuel gas it was possible to identify the interval of LCV between 800 BTU/ft³ and 2,000 BTU/ft³. Also it was possible to find the relationship between LCV and CO₂ emissions. Table 3 shows data extracted during a year of operations in furnace according to different gas compositions, LCV and CO₂ t emitted.

Table 3: Low Calorific Value of fuel gas

Fuel gas composition	LCV (BTU/ft ³)	CO ₂ emissions (t)
1	1,131.90	225.561
2	1,068.10	233.0613
3	831.8	204.0101
4	862.8	210.3843
5	937	205.1885
6	1,147.20	219.6332
7	860.1	202.3318
8	814.1	196.154
9	1,094.80	189.3512
10	1,080.60	205.7778
11	893.6	204.028
12	916.6	106.8548
13	1,103.40	190.6189

The statistical analysis done using Statgraphics allowed establishing eight main compounds that form a representative gas in the combustion network, then using Hysys to simulate the process it was possible to find four fuel mixtures that have LCV between 800 Btu/ft³ and 2,000 Btu/ft³ (C1, C2, C3 and C4).

Through computer simulations the values of the composition of the combustion gases, process efficiency and temperature and adiabatic flame fireplace were obtained, these results are consistent with historical data recorded by the process monitoring.

Oxygen excess values between 0 % to 20 % were tested and it aimed to establish the correlation between oxygen excess and the adiabatic flame temperature in order to evaluate the effect of the composition of the mixture in the adiabatic flame temperature at different values. Adiabatic flame temperature varied between 2,030 ° C to 2,110 ° C depending on the composition of fuel gas, to 0 % excess oxygen. Process efficiency shows better results for 2 % oxygen excess taking into account the variability of the fuel gas composition. Table 4 shows representative compositions of the possible mixtures and natural gas.

Table 4: Representative compositions of fuel gas

Compound	C1	C2	C3	C4	Natural Gas
CH ₄	55	70	25	35	97
C ₂ H ₆	10	0	8	3	1
C ₃ H ₈	0	16	25	35	1
C ₄ H ₁₀	4	5	10	12	0
C ₂ H ₄	5	3	10	7	0,5
C ₃ H ₆	2	0	5	8	0,5
H ₂ S	4	1	2	0	0
H ₂	20	5	15	0	0

Figure 3 shows the LCV values of the fuel mixtures and natural gas, and Figure 4 shows the concentration of CO₂ in the combustion gas at every fuel mixture analyzed, according to this it is possible to find out the rise of CO₂ emissions related to de fuel gas composition in a presence of 2 % of oxygen excess.

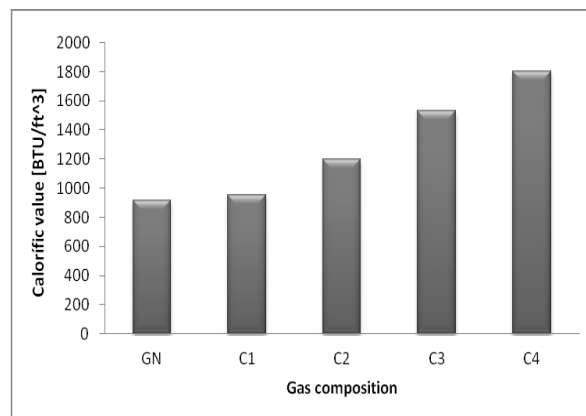


Figure 2: Calorific value of fuel mixtures and natural gas

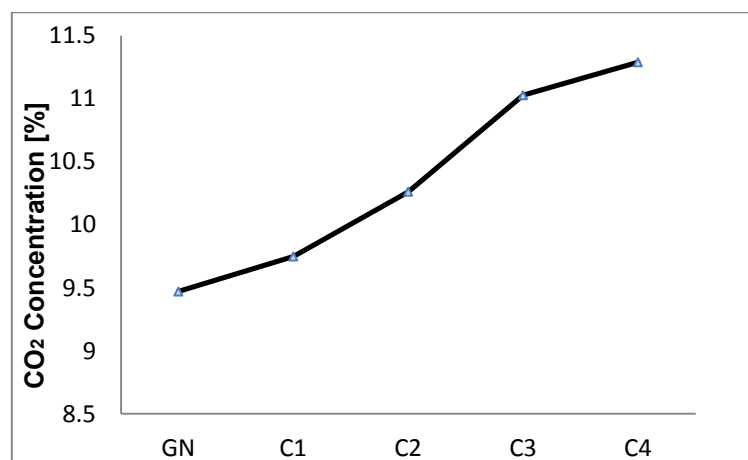


Figure 3: CO₂ concentration in combustion gas

Figure 4 evidences that when the fuel mixture receives a contribution of ethane, propane, and propylene, the LCV is incremented and the CO₂ emissions are higher.

A direct relationship between LCV of the fuel used in the furnaces and CO₂ emissions, this conclusion supports the importance of a detailed study of the fuel gas composition related with the generated emissions in order to establish operational measures and legal compliance.

Results have been compared with data presented in Refinery CO₂ Management Strategies (Hydrocarbon Publishing Company, 2010) where was tested that the data presented in this study is agree with CO₂ emission values for petroleum refining industry.

5. Conclusions

The furnaces work with typical values of 1.5 to 2.5 % excess oxygen, so that in the event of contributions from refinery gas streams to the fuel gas system, causing increased calorific value, it has the required minimum oxygen stoichiometrically for combustion.

Evidenced an increase in CO₂ emissions caused by the change in the composition of fuel gas in furnaces, in this sense we propose the use of fuel gas streams having low calorific value and similar composition to natural gas.

According to the results of the review of monitoring data and simulation data of the combustion process, the compound most significantly increase CO₂ emissions are propane and butane.

Higher adiabatic flame's temperature are obtained for mixtures where methane, propane and hydrogen represent 65 % of the mixture and also containing H₂S, which can pose risks to the structure of the equipment for high temperature damage.

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