TESTING FLARE EMISSION FACTORS FOR FLARING IN REFINERIES

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ABSTRACT

The Technical University of Madrid (UPM) and REPSOL YPF are collaborating in the improvement in the estimation of the emission factors for refinery flares. Flaring is an unavoidable process in the refining activity, both for safety reasons during upset processes (start-up, shut down, system blow-down) and when managing the disposal of waste gases with hydrocarbon from routine operations.

The official flare gas emissions in Spain are currently evaluated using the CORINAIR methodology (SNAP 090203) and surveys from the petrol companies. However, the emission factors used in CORINAIR could be non-representative for some plants in Spain.

Therefore, the aim of this study is to improve the value of the above mentioned emission factors in order to transform them into more accurate ones. The study compares the factors included in the references with factors obtained directly from flare measures and gas analyses in oil refineries.

In this case, the emission sources selected are four flares belonging to two REPSOL YPF refineries. Three of the flares considered are located at the same refinery and the fourth one is selected from another refinery in order to compare the results. This refinery has just one flare.

Several studies from other companies and institutions (US EPA, BP, OLF, Shell) are taken into account. These studies are focused on the measure of combustion efficiency, which is the indicator of a complete combustion. Different estimations of emissions have been carried out considering different combustion efficiencies.

The pollutants considered are Carbon Dioxide (CO_2) and Methane (CH_4).

INTRODUCTION

A flaring system is a compulsory safety equipment in the refining activity designed to avoid uncontrolled emissions. It is used both for safety reasons during upset processes (start-up, shut down, system blow-down) and for managing the disposal of waste gases with hydrocarbon from routine operations. However, it produces other pollutant emissions caused by combustion. In fact it is one of the air pollution sources in a refinery emission inventory.

Liquids in the waste gases can cause an irregular flame. To prevent these liquids from reaching the tip, normal flaring systems have a knock-out drum. All the stacks studied here have this equipment. Besides providing a right mixture and turbulence, all flare systems were steam-assisted. These two components are very important in order to reach high combustion efficiency.

Traditionally, the study of flaring emissions has encountered two main problems: 1) to know the exact burned gas composition since flaring is not a routine process and the gases sent to burn are

very time-varying and 2) to measure the gas composition at the end of the flare, although some important studies have been concerned with this second issue (15, 18).

Therefore, the emission factors used to calculate flaring emissions are very variable depending on the reference. One of the main differences between the factors is the activity rate considered (gas sent to flaring or refinery feed)

In accordance with the aforementioned problems, the main targets of this study are:

- To estimate the average composition of the gas sent to the flare in order to compare the values with the recommended speciation (8)
- To compare CO_2 emissions evaluated both from feed data and from gas flared data
- To compare CH_4 emissions obtained through three different approaches (8, 1, 10 respectively)

It is thus important to consider emission factor improvement because they could change both the emission inventoried and the projections. Since the results can be used for emission reduction, this part of the study is specially interesting for Industry.

1.-POLLUTANTS BY FLARING

The flaring process can produce different pollutants: SO_2, NO_X, CO, NMVOC, CH_4 and CO_2. They depend on two main factors: the waste gas composition sent to the flame and the combustion efficiency.

SO_2 may be released if there is any sulphur compound in the waste gas, such as hydrogen sulphide. NO_X is strongly temperature dependent and it is formed by the fixation of the molecular nitrogen from the air. CO is present in the emission steam because of a bad combustion. This faulty combustion is the result of not enough air in the mixing or a too low flame temperature.

Focusing the attention on Greenhouse Gases (GHG), although their emissions from flaring have a small contribution[1] (see Table 1) to total refinery inventory, it is important to check the emission factors to get fair and reliable inventories.

Table 1. Emission of GHG for flaring emission in refineries in Spain

	CH_4 (t)	CO_2 (kt)
1990	26,8 (6,8)	168,7 (1,4)
1991	26,5 (6,6)	169,9 (1,5)
1992	28,6 (6,8)	180,3 (1,5)
1993	26,9 (6.4)	170,5 (1,5)
1994	28,3 (8,7)	178,8 (1,3)
1995	27,9 (5,7)	184,5 (1,3)
1996	27,8 (5,8)	183,6 (1,3)
1997	28,6 (5,7)	181,0 (1,3)
1998	30,4 (6)	195,2 (1,4)
1999	29,9 (5,9)	192,3 (1,4)
2000	29,6 (5,8)	194 (1,3)

Ref: Spain's National Emissions Inventory CORINE AIRE 1997-2000 Vol 2. 2002.
In parenthesis, it is represented the percentage respect the total amount of emissions of that pollutant in the refinery sector

CO_2 is formed as a direct combustion product. The general industry practice accepts[2] a 98% combustion efficiency for the conversion of carbon to CO_2 for refinery flares although more recent

[1] It depends on pollutant considered, e.g. $S0_2$ represents up to 12,7% during 90´s
[2] "properly operated flares achieve at least 98 percent combustion efficiency" (EPA, AP-42 Section 13.5.2, September 1991).

studies have measured higher efficiencies in most situations. So three different values of combustion efficiencies are analysed: 98, 99 and 99.5%

In regard to CH_4, it is related to THC (Total Hydrocarbon), and they may be emitted by both vented without burning and cracking reactions in the core of the flame. So the THC emissions are very dependent on the gas composition.

2.-CALCULATION OF A FLARE GAS AVERAGE COMPOSITION

Flare emissions can vary depending on several factors. The first two steps to develop a detailed inventory of flares emissions in refineries (according to CORINAIR methodology) are:

1. To measure the real quantity of gas flared at each flare (the studied flares have volumetric flow meters, so the volume of gas flared is known)
2. To measure the average composition of flare gas
   - In three flares, located in the same refinery, 76 waste gas samples were analysed for three years and their average composition has been obtained (see tables 2, 3 y 4).
   - In the forth flare, located in a different refinery, monthly samples were taken for one year (the results from this flare have been used to contrast the values of the other flares).

Table 2 Average composition of flare gas in flare 1

	Useful samples	Average (%v)	Standard deviation	Standard error
C1	65	26,226	12,512	1,552
C2	65	9,739	3,755	0,466
-C2	66	3,227	2,706	0,333
C3	61	6,251	2,001	0,256
-C3	62	4,618	3,320	0,422
-iC4	63	0,834	0,695	0,088
iC4	60	2,083	0,994	0,128
-cC4	58	0,344	0,236	0,031
nC4	62	2,279	1,074	0,136
-tC4	65	0,581	0,540	0,067
-1C4	66	0,863	0,691	0,085
iC5	12	0,976	0,338	0,098
C5 & Sup	66	1,305	0,794	0,098
CO	66	0,205	0,169	0,021
CO_2	63	0,528	0,388	0,049
H_2S	64	0,244	0,196	0,024
O2	63	0,746	0,405	0,051
H_2	63	29,119	24,893	3,136
N2	63	6,243	3,387	0,427
LHV (kcal/Nm^3)	62	10311,6	3238,4	411,3
HHV (kcal/Nm^3)	66	11249,0	3295,9	405,7
Density (kg/m^3)	66	0,8296	0,289	0,036

Table 3: Average composition of flare gas in flare 2

	Useful samples	Average (%v)	Standard deviation	Standard error
C1	49	15,890	6,657	0,951
C2	45	6,973	1,790	0,267
-C2	41	0,6597	0,694	0,108
C3	48	7,101	3,465	0,500
-C3	45	0,783	0,756	0,127
-iC4	19	0,142	0,117	0,027
iC4	48	1,681	0,776	0,112
nC4	46	2,095	1,251	0,184
-cC4	15	0,210	0,163	0,042
-tC4	14	0,115	0,088	0,024

	Useful samples	Average (%v)	Standard deviation	Standard error
-1C4	18	0,111	0,0699	0,017
iC5	22	0,591	0,365	0,078
C5 & Sup	48	0,583	0,406	0,059
CO	47	0,193	0,156	0,023
CO_2	47	0,405	0,406	0,059
H_2S	40	0,125	0,096	0,015
O2	47	0,774	0,490	0,071
H_2	47	50,590	9,872	1,440
N2	46	6,165	3,707	0,547
LHV (kcal/Nm^3)	40	7315,3	1301,6	205,8
HHV (kcal/Nm^3)	45	7888,7	1280,9	190,9
Density (kg/m^3)	51	0,652	0,262	0,037

Table 4: Average composition of flare gas in flare 3

	Useful samples	Average (%v)	Standard deviation	Standard error
C1	76	32,673	13,201	1,514
C2	72	7,634	2,832	0,334
-C2	70	1,708	0,833	0,0995
C3	74	5,097	1,897	0,221
-C3	74	8,468	3,061	0,356
iC4	75	0,942	0,538	0,062
-iC4	69	0,516	0,256	0,031
nC4	76	1,526	0,824	0,095
-cC4	71	0,235	0,148	0,018
-tC4	72	0,292	0,182	0,021
-1C4	76	0,676	0,336	0,039
iC5	22	0,322	0,181	0,039
C5 & Sup	72	1,064	0,624	0,074
CO	69	0,416	0,261	0,031
CO_2	74	0,963	1,043	0,121
H_2S	72	1,726	1,945	0,229
O2	75	2,063	1,0297	0,119
H_2	73	12,433	5,604	0,656
N2	75	17,188	8,573	0,9899
LHV (kcal/Nm^3)	67	9394,9	1661,0	202,9
HHV (kcal/Nm^3)	73	10166,7	1804,0	211,1
Density (kg/m^3)	76	0,893	0,138	0,016

3.-CO_2 EMISSIONS

The best activity factor, mass or volume of waste gas sent to flare, to obtain a fair emission value when CORINAIR last review was done, was unavailable in most refineries so the activity rate considered was the volume of refinery feed.

The Spanish version of CORINAIR guide translates the units from volume to mass using a density of crude oil of 0,883 kg/l. CORINAIR does not give any emission factor for CO_2 but Spanish experts recommends a factor based in quantity of carbon in crude than finally becomes CO_2 (see table 5).

Table 5. Flaring emission factor for GHG

CH_4 g/t refinery feed	CO_2 kg/t refinery feed
0.5	3.14

Ref: Spain's National Emissions Inventory CORINE AIRE 1997-2000 Vol 2. 2002

As the total amount of gas sent to each flare has been available to do this project an emission factor based in this activity rate was deduced. CO_2 emission factor must consider the combustion efficiency and the amount of gas sent to flaring (eq 1). According to recent studies (16), the

efficiency in refinery flare combustion could be higher than the past-used 98% that could be too conservative. For this reason, different CO_2 emissions are evaluated depending on the combustion efficiency. The corresponding emission factors for the flares according to the efficiency of carbon burnt are shown in table 6 (calculated from data in tables 2, 3 and 4)

$E_{co_2} = V \cdot C \cdot f$ where, Equation 1

V is the amount of gas to flaring (in m^3)

C is the amount of carbon included in the gas

f is the combustion efficiency, i. e. the percentage of carbon in input gas converted to CO_2

Table 6. Emission flaring factor for CO_2 (tCO_2/t gas burnt)

	Emission (efficiency 98%)	Emission (efficiency 99%)	Emission (efficiency 99.5%)
Flare 1	2.57	2.59	2.61
Flare 2	2.33	2.35	2.36
Flare 3	2.20	2.22	2.23
Flare 4	2.60	2.63	2.64

Flares 1 to 3 are from refinery 1 and Flare 4 is from refinery 2.

As flares 1 to 3 are located in the same refinery, it is possible to obtain the emission factor for the total CO_2 emitted in the plant using the feed refinery as the activity rate. These emission factors are calculated multiplying the values from table 6 by the gas burnt in each flare and dividing their sum by the refinery feed. Then, it is possible to compare the emission factors based in feed for each refinery (Table 7)

Table 7. Emission flaring factor for CO_2 (kg CO_2/t feed refinery)

	Emission (efficiency 98%)	Emission (efficiency 99%)	Emission (efficiency 99.5%)
Refinery 1	14.80	14.95	15.02
Refinery 2	17.69	17.87	17.96

Total CO_2 emissions can be calculated from two emission factors:

1. Multiplying the amount of gas burnt for each flare (activity rate), with the corresponding emission factor from table 6 and adding the values (for 98% efficiency).
2. Multiplying the refinery feed (activity rate), by the CORINAIR emission factor (table 5).

The relations between the approaches are shown in table 8.

Table 8. Comparison of CO_2 emissions calculated with an emission factor with gas burnt as activity rate (efficiency 98%) vs. emission factor based on feed refinery

	kt CO_2 (calculated with own factor)	kt CO_2 (calculated with CORINAIR factor)
Refinery 1 2000	124.84	27.48
2001	116.57	25.40
2002	124.88	25.52
Refinery 2 (2002)	96.22	17.08

CH_4 EMISSIONS

There are several emission factors to estimate CH_4 emissions from flaring. Some of them consider the methane emissions directly and other estimate the THC and after that a speciation has to be done to obtain the CH_4 emission factor. CORINAIR recommends a speciation of 20% CH_4 and 80% NMVOCS. In this study, the average composition results in a speciation shown in table 11. This is the speciation used in the study.

Emissions are calculated using three approaches:

1. with CORINAIR emission factor: 2.5 kg of THC emitted/t feed refinery, assuming the average gas speciation of table 11. The value is shown in table 9. If it was considered a 20% of CH_4 (20), the emission factor would be the one shown in table 5.
2. assuming 0.5% unburnt CH_4 remaining in the flared gas (1) (table 9)
3. using US EPA (10) emission factor (20 kg of THC /t THC burnt) and using the developed speciation (table 11). The factor is transformed into kg of THC/ t gas burnt with the average value of HC contained in the gas (measured with the chromatography systems)

The emission factors are shown in table 9 and the corresponding emissions in table 10.

Table 9. CH_4 emission factors with different approaches

	Approach 1 (CORINAIR)	Approach 2 (API)	Approach 3 (EPA)
Refinery 1	1.17	1.015	4.06
Units	g/t refinery feed	kg/t gas flared	kg/t gas flared

The value of approach 2 is calculated multiplying the average amount of CH_4 included in the gas sent to the flares in refinery 1 times 0.5%. The approach 3 value is calculated multiplying the average amount of THC sent to flare by 0.02 (20 kg of THC/t THC burnt) times speciation (25.15% CH_4)

Table 10. Emissions of CH_4 (t) with different approaches

Refinery 1	Approach 1 (CORINAIR)	Approach 2 (API)	Approach 3 (EPA)
2000	10.259	53.664	214.657
2001	9.486	50.109	200.438
2002	9.529	53.684	214.734

The emissions in table 10 are calculated with emissions factors deduced in table 9. Each emission factor was multiplied by the correspondent activity rate.

CONCLUSIONS

According to the estimation of the emissions from the data set used in this study, actual CO_2 emissions are higher than the values obtained using CORINAIR emission factors. The CORINAIR emission factor (with the feed refinery as activity rate) is six times lower than the emission factor developed here and deduced from the amount of gas burnt.

In the methane case, the first approach could underestimate the emissions. This issue is due to the fact that the CORINAIR methodology does not take into account the speciation but only the feed refinery. In approaches 2 and 3, the high values of the emission factors are due to the high concentrations of methane in the flared gases (table 11). As this table shows, the average amount of methane contained in the gas is a 25% higher than the value recommended by US EPA.

The great differences found between the emission factor of this study and the factors included in the bibliography highlight the importance of further researches in this area.

Table 11. Methane speciation (% of the total HC in weight) in the different flares of Refinery 1

	Methane (%w)
Recommended value (EPA)	20 %
Flare 1	22.64 %
Flare 2	21.70 %
Flare 3	30.15%
Average	25.15 %

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KEYWORDS

Emission Factors
Industrial flares
Combustion efficiency
GHG emissions
Refinery
Emission Inventory
AP 42 factors
CORINAIR methodology

ACKNOWLEDGMENTS

The authors want to express their thanks to Dr. Arturo Gonzalo, Dr. José Mira and Rafael Borge for their help in the elaboration of the paper.