Accurate Correlations to Estimate Refinery Fuel Gas, Natural Gas, and Fuel Oil CO_2 Emission Factors and Its Uncertainty

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The quantification of Greenhouse Gas (GHG) inventories and its associated uncertainty is a relevant activity often requested by authorities. Accurate methods to calculate both inventories and the involved uncertainty are convenient for close monitoring purposes. Using Monte Carlo simulations, correlations of high accuracy between emission factors (EFs), lower heating value (LHV), and density were built for refinery fuel gas, natural gas and fuel/residual oil. In all cases, the data generated by the simulations also served the purpose of building correlations for upper and lower bounds of the EF that can be readily used to estimate the EF estimation uncertainty. The correlations were tested against actual refinery data and the results show that more accurate estimations were obtained compared with EF obtained from laboratory composition methods and from methods that estimate EF as proportional to LHV only. In the case of fuel and residual oils, the correlations developed are a function of LHV only but were improved by using a cubic polynomial. The calculation of upper and lower bounds for EF offer a convenient method to estimate EF uncertainties that are required in official GHG emissions inventory calculations. In conclusion, in addition to LHV, the use of one additional readily available fuel property, namely fuel density is sufficient to reduce uncertainty of estimation of GHG (in this case CO_2) from combustion to acceptable levels. © 2010 American Institute of Chemical Engineers *AIChE J,* 56: 2479–2488, 2010

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Introduction

As the evidence of the influence of greenhouse gas emissions (GHG) on global warming and climate change accrues, the efforts carried out to reduce GHG throughout the world escalate. Refineries and petrochemical plants, due to their considerable releasing of GHG, are prominent domains where these efforts take place. Such efforts involve strategies to abate GHG, for example, increasing the energy efficiency of sites or GHG sequestration. To assess the success of emissions reduction actions, it is necessary to quantify accurately GHG. Furthermore, the quantification of GHG inventories and their associated uncertainty is a relevant activity often requested by local governments, national governments, and by private corporations for several purposes. Among the latter are:

- Monitoring compliance with environmental regulations.
- Following the effectiveness of measures to reduce GHG.
- Assessing the labor workload and estimating the budgets necessary to achieve the necessary reductions of GHG.

In refineries and petrochemical sites, the main sources of GHG are diverse types of liquid, gaseous, or solid fuel. The

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product of the combustion of fuel is mainly water and CO_2, one of the most commonly released greenhouse gases.

The GHG from a particular fuel source can be calculated as the product of the source specific emission factor (EF) times the activity factor (AF) that describes the amount of burned fuel.[1,2] An inventory is the sum of all of the emissions for a particular facility or site. The AF is usually measured and recorded on site with adequate instruments. On the other hand, the EF is obtained from published tables and its value depends on the type of fuel combusted. In refineries and petrochemical sites, the most commonly burned fuels are natural gas, refinery fuel gas (RFG), fuel oil (FO), and coke. The EF associated to a fuel is usually correlated to the heat content of the fuel expressed as lower heating value (LHV) or high heating value (HHV). However, as most of these fuels are blends of components whose composition can change over time and have an inherent uncertainty in its combustion enthalpy values,[3] the relationship between the EF of a fuel source and its LHV or HHV is not given by a constant ratio as assumed in common practice. Therefore, the latter assumption implies some degree of uncertainty or error, which usually is not reported. A possible way to narrow down the uncertainty involved in estimating EF for fuels is to relate the EF not only to the corresponding LHV or HHV but also to additional properties routinely determined in quality control laboratories such as density.

This article describes the development of accurate correlations between the EF of specific fuels commonly used in refineries and petrochemical sites, and relevant, routinely determined fuel properties such as LHV, HHV, and specific gravity. To account for the broad variety of compositions these fuels can span, Monte Carlo simulations were used as a tool to cover the widest possible range of compositions of each component of every considered fuel.

Preliminary Background

The EF of a fuel consisting of a blend of species whose combustion generates CO_2 can be readily calculated if its composition is known as:

$$\mathrm{EF} = \sum_{i=1}^{N} \mathrm{ef}_i \cdot y_i \tag{1}$$

where, ef_i is the EF corresponding to species i in kg CO_2/mol and y_i is the mole fraction of species i in the fuel blend.

Some sites determine analytically fuel composition either on-line or in the laboratory from periodically collected samples. However, the composition of fuels is not always available. Instead, LHV or HHV and density are commonly determined. In this case, the EF of the fuel must be determined from a correlation involving fuel properties mentioned earlier.

The presence of inert species, hydrogen in gaseous fuels as well as the varying proportions of the different components in the fuel blend are some of the factors that introduce variability in the relationship between the properties of a fuel and its EF. As a matter of fact, such relationship is not a one-to-one function as will be shown later. Instead, the EF corresponding to a given LHV or set of LHV and specific gravity values will have an uncertainty band, which can be narrowed down by optimizing the parameters of the correlation among them or by including additional variables in the correlation used to estimate the EFs.

As mentioned earlier, refineries and petrochemical sites fuels are blends of species with broad concentration ranges. To develop an accurate correlation between the EF of a fuel and its properties, it is necessary to obtain data of both the dependent and the independent variables. Obviously, it would be a titanic experimental task to obtain representative samples of a fuel type and analyze them to obtain the necessary data to generate such a relationship. A much simpler approach is to use the Monte Carlo technique and generate a sufficiently abundant number of data points that would allow computing the relevant parameters of the targeted correlation. Every data point represents a randomly generated blend of species with molar fractions within the limits determined for a specific fuel. For such a hypothetical fuel sample, it is possible to calculate exactly the LHV, the specific gravity, and the EF from basic data. Multivariate regression techniques can be used afterward to obtain the relevant parameters of the correlation as well as upper and lower bounds.

In the following sections, the Monte Carlo technique will be used to generate composition, LHV, density, and EFs of random samples of fuels commonly combusted in refineries and petrochemical sites. The latter hypothetical samples will be within wide concentration ranges according to experimental data widely available. Then correlations between the EF and the calculated fuel properties will be constructed from the generated data.

Natural Gas and Refinery Fuel Gas

Natural gas is a gaseous fossil fuel whose main component is methane. Nevertheless, it contains substantial quantities of ethane, butane, propane, carbon dioxide, nitrogen, and other species. The main sources of natural gas are oil fields, natural gas fields, and coal beds. It can be classified as associated, nonassociated, and condensate gas, depending on the characteristics of the oil content of the source field and on the physical state of the gas at reduced pressures and temperatures. The composition of natural gas can vary within certain limits depending on factors such as the original characteristics and degree of depletion of the source field and treatment prior to utilization. A bibliographic search shows that the composition ranges of natural gas widely vary from source to source.[4–8] After reviewing a numerous collection of plausible natural gas composition sets, the widest composition ranges identified for components of natural gas were summarized in Table 1. The relevant properties of the individual components for the Monte Carlo simulation, namely, lower heating value and molecular weight were obtained from authoritative bibliographic sources.[9,12]

The Monte Carlo technique was next used to obtain an abundant number of theoretical natural gas samples with compositions complying with the ranges set in Table 1. The molar fraction of all components except one was obtained from a uniformly distributed random numbers generator properly scaled subsequently to the correct composition range. The remaining component molar fraction was determined, so that the total sum of compositions added up to one.

However, the resulting composition had to be within the composition limits provided in Table 1 to represent a valid

Table 1. Composition Ranges of Natural Gas Typical Components

Component	Lower Limit (mol %)	Upper Limit (mol %)
Methane	70	99
Ethane	0	20
Propane	0	5
Butane	0	5
Isobutane	0	5
Isopentane	0	0.14
Pentane	0	0.04
Nitrogen	0	5
Carbon dioxide	0	8
Oxygen	0	0.2
Hydrogen	0	0.02
Hexane	0	0.06

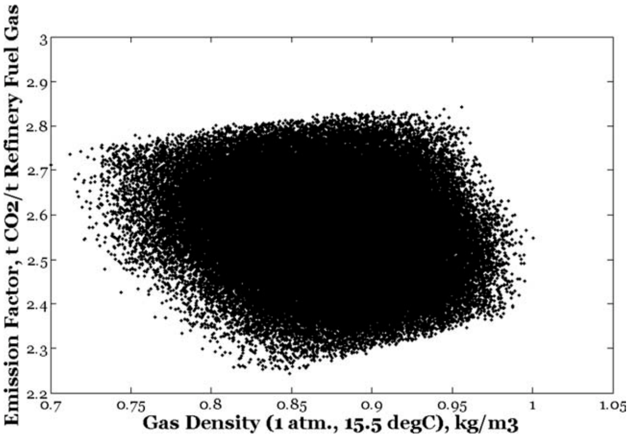

Figure 2. Emission factor of the natural gas data points generated with the Monte Carlo technique against corresponding density at standard conditions: 60°F (15.56°C) and 1 atmosphere.

natural gas sample. Otherwise, the point was rejected. This procedure is typical of Monte Carlo simulations and as long as all points have the same probability of occurring, no bias is introduced in the sampling procedure. For all the valid samples, the corresponding LHV was calculated according to its molar composition. The average molecular weight and the gas density at 15.56°C (60°F) of the blend were calculated as well. The EF corresponding to every data point was calculated according to the stoichiometry of full combustion of all components. The algorithm described earlier was used to produce 150,000 data points of plausible blends corresponding to the definition of natural gas outlined in Table 1. It was checked that a higher number of samples did not introduce significant changes in the results; hence, the number of samples was considered sufficient. It was verified graphically that the composition of the accepted points cover uniformly the composition interval of each component from Table 1. Figure 1 displays calculated EFs against its corresponding LHV values for the cluster of natural gas points. A clear trend between both variables can be observed and it is noticeable that rather than a line, the trend consists of a somewhat broad band. A graph displaying EF against density at standard conditions is shown in Figure 2. In this case, the relationship between EF and density is defined by a cluster of points and not by a linear trend. Furthermore, visual inspection shows that density alone would not be an accurate enough regressor for EF. Therefore, it was deemed necessary to verify the convenience of adding density to LHV as a regressor in a correlation to estimate EF.

One way to analyze how relevant two or more possibly correlated, independent variables are in explaining the behavior of a dependent variable is by means of principal component analysis. The theory and interpretation of principal components analysis has been the subject of many publications. See for instance.[10]

A plot of the principal components scores of the matrix formed by columns containing LHV and density against EF shows that both variables contain information to explain the behavior of EF, as shown by the linear correlation between the principal components depicted in Figure 3. The data generated via the Monte Carlo technique can be used to render initially a correlation between LHV alone and EF, as there

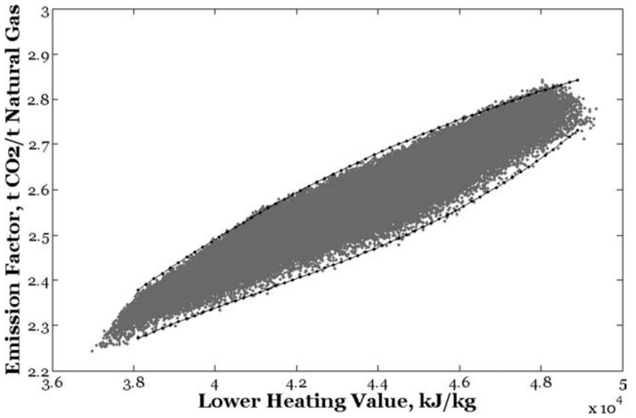

Figure 1. Emission factor of the natural gas data points generated with the Monte Carlo technique against corresponding lower heating values.

Upper and lower bounds as a function of the LHV of natural gas are included.

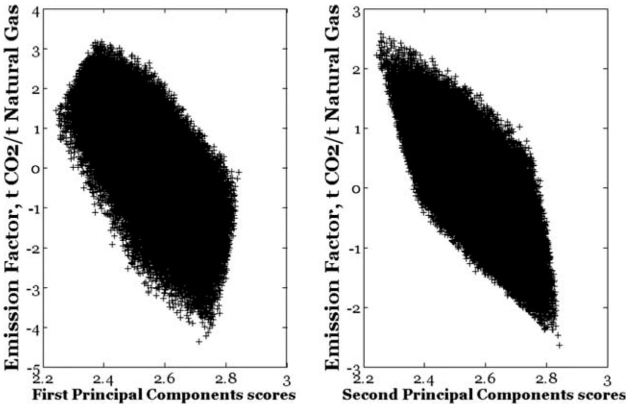

Figure 3. Emission factor of the natural gas data points generated with the Monte Carlo technique against first and second principal component scores corresponding to the LHV, standard density matrix.

Table 2. Coefficients of the Various Correlations Developed for Natural Gas LHV and its Upper and Lower Bounds

Bound Type b	$a1_b$	$b1_b$	$c1_b$	$d1_b$
Lower	−14.069	1.137E-03	−2.687E-08	2.180E-13
Upper	−5.636	4.147E-04	−6.875E-09	3.969E-14
Coefficients of the correlation between EF, LHV, and density at standard conditions	$a2$	$b2$	$c2$	–
Lower	−0.029	4.646E-05	0.666	–
	$a3_b$	$b3_b$	$c3_b$	$d3_b$
Lower	−14.445	19.614	−7.933	1.117
Upper	−2.983	4.541	−1.357	0.170

are instances in which only LHV is known from laboratory analytical determinations. A possible way to obtain a correlation between LHV and EF would be a straightforward regression between the two variables from which a confidence band could be calculated. This path, though, would not reflect the actual EF limits that a natural gas sample with a particular LHV could have. Actual limits are those corresponding to the band drawn in Figure 1 that is a representative universe of all the possible compositions constrained by the limits provided in Table 1. Therefore, to capture the EF bounds given a specific LHV as revealed by the Monte Carlo simulation, two different correlations were developed corresponding to the upper and lower bounds of the band given in Table 1. Unlike statistically defined confidence bands, these upper and lower bounds constrain the EF to an interval defined by the simulation results that, theoretically, is very close to the lowest and highest values that a natural gas blend with a specific LHV can reach, always within the constraints imposed by Table 1. These results are depicted in Figure 1, where the upper and lower bounds of EF are shown outlining the area corresponding to the domain of acceptable EF and LHV of natural gas.

The correlations for the upper and lower bound limits shown in Figure 1 have the form

$$\mathrm{EF_b} = a1_\mathrm{b} + b1_\mathrm{b}\mathrm{LHV} + c1_\mathrm{b}\mathrm{LHV}^2 + d1_\mathrm{b}\mathrm{LHV}^3 \qquad (2)$$

where the index b denotes bound type (upper or lower) and $a1$, $b1$, $c1$, and $d1$ are regression constants. The numerical values for all constants are reported in Table 2. The procedure to calculate these constants consisted of dividing the LHV range covered by the Monte Carlo simulation into subintervals or slots,

$$\mathrm{LHV_o} + (i-1)\cdot\Delta\mathrm{LHV} \le \mathrm{LHV}_i \le \mathrm{LHV_o} + i\cdot\Delta\mathrm{LHV}, \quad i = 1\ldots\mathrm{N} \qquad (3)$$

where, $\mathrm{LHV_o}$ is the lowest LHV for which the relationship applies and ΔLHV is an increment depending on the number N of slots created.

Next the minimum ($\mathrm{LowerEf}_i$) and maximum ($\mathrm{UpperEf}_i$) values of EF corresponding to each slot were found as

$$\mathrm{LowerEf}_i = \min(\mathrm{LHV}_i) \qquad (4)$$

$$\mathrm{UpperEf}_i = \max(\mathrm{LHV}_i) \qquad (5)$$

Then the mean LHV ($\mathrm{MeanLHV}_i$) values of every slot were calculated as

$$\mathrm{MeanLHV}_i = \mathrm{LHV_o} + i\cdot\Delta\mathrm{LHV} - \Delta\mathrm{LHV}/2 \qquad (6)$$

and correlated with the minimal or maximal corresponding EF values with standard linear regression techniques.

It is a straightforward exercise to show that the maximal EF difference between the lower and upper bounds occurs for an LHV around 44,300 kJ/kg. The difference between the two bounds in this case is 0.21 kg CO_2/kg natural gas. Hence, the maximum error in absolute terms expected from these correlations is 0.105 kg CO_2/kg natural gas or roughly 4%. Notice that the correlations defined by Eq. 2 have been built for the composition ranges set in Table 1. Hence, the EF of natural gas streams with composition outside these limits is not accurately estimated by the Eq. 2 and its corresponding coefficients.

An improvement on the accuracy of estimation of EF can be readily achieved if the regression between EF and fuel properties involves additional variables other than LHV, namely, density at standard conditions as suggested by the principal component plots displayed in Figure 3.

The following linear, multivariable correlation between EF, LHV, and density at standard conditions was produced

$$\mathrm{EF}^* = a2 + b2\cdot\mathrm{LHV} + c2\cdot\rho \qquad (7)$$

where ρ corresponds to the standard density of the fuel gas and EF* is the regression-estimated EF value. The regression constants for Eq. 7 are reported in Table 2, whereas the corresponding parity plot is displayed on Figure 4.

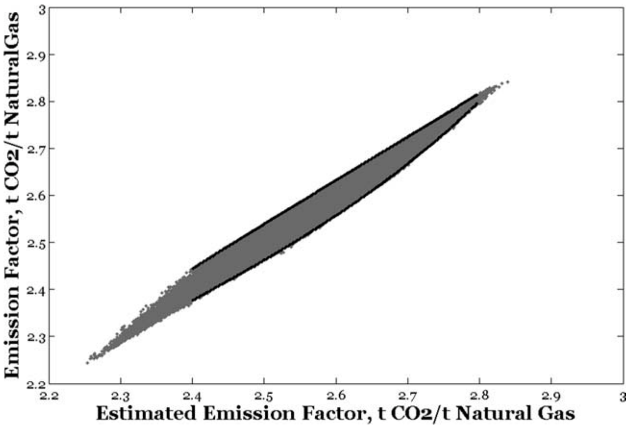

Figure 4. Emission factor as a function of the LHV and density at standard conditions: Parity plot.

Upper and lower bounds are included.

Table 3. Composition Ranges of RFG Typical Components

Component	Lower Limit (mol %)	Upper Limit (mol %)
Methane	10	53
Ethylene	0	5
Ethane	0	19
Propylene	0	8
Propane	0	20
Butylene	0	1
Butane	0	2
Pentane and higher	0	3
Hydrogen	0	36
Carbon monoxide	0	12
Carbon dioxide	0	44
Nitrogen	0	8
Water	0	1.1
Oxygen	0	2
Hydrogen sulfide	0	0

As expected, the relationship between EF and fuel properties shows a broad swarm of points rather than a line. Following a similar procedure to the one outlined earlier, upper and lower bounds can be found for EF*,

$$\mathrm{EF}_{\mathrm{b}}^{*} = a3_{\mathrm{b}} + b3_{\mathrm{b}}\mathrm{EF}^{*} + c3_{\mathrm{b}}\mathrm{EF}^{*2} + d3_{\mathrm{b}}\mathrm{EF}^{*3} \tag{8}$$

Hence, once EF* is estimated as a function of LHV and standard density, upper and lower bounds can also be estimated using Eq. 8 with constants reported in Table 2.

Again the maximal difference in EF occurs for an EF* around 2.54 kg CO_2/kg natural gas. The difference between the two bounds in this case is 0.078 kg CO_2/kg natural gas. Hence, the maximum error in absolute terms expected from these correlations is 0.039 kg CO_2/kg natural gas or roughly 1.5%, which shows the improvement in maximal error achieved with a correlation involving both LHV and standard density over one involving only LHV.

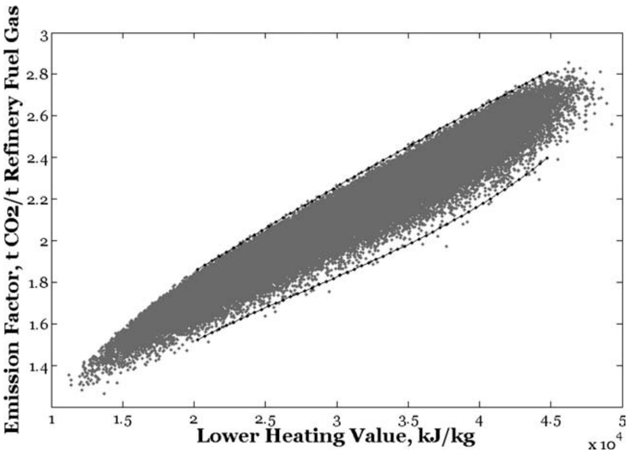

Figure 5. Emission factor of the refinery fuel gas data points generated with the Monte Carlo technique against corresponding lower heating values.

Upper and lower bounds as a function of the LHV of refinery fuel gas are included.

RFG is another fuel commonly burned in refineries and petrochemical sites, which in a similar fashion to natural gas, is a blend of gases that cannot be sold in an economically viable way produced in different refinery sections. RFG will usually include H_2, CH_4, C_2H_6, and other C_3, C_4, and higher molecular weight gases. A totally similar process to that followed for natural gas was carried out for RFG. Table 3 contains the possible components of RFG and its widest range of compositions.[5,11,12] The composition of points generated via Monte Carlo simulation was acceptable as complying with the ranges established in Table 3. As before, it was verified graphically that the samples cover uniformly the composition interval of each component. Figure 5 displays the calculated EFs against its corresponding LHV values for the population of refinery fuel gas samples. The RFG band has similar features to that obtained for natural gas, although it is noticeably broader as expected from the higher possible number of components in RFG and its wider composition ranges. Figure 6 depicts the trend of refinery fuel gas EF against the corresponding values of density of gas at standard conditions. In this case, too, the band is broader although the correlation between these two variables can be visually appreciated more noticeably than for the natural gas case. The principal components of the matrix containing the LHV and density values generated by the Monte Carlo simulation for RFG are plotted in Figure 7. The latter Figure allows reaching similar conclusions to those deduced from the natural gas results. Therefore, lower and upper EF bound correlations were obtained for the band shown in Figure 5 as a function of LHV only as follows:

$$\mathrm{EF}_{\mathrm{b}} = a4_{\mathrm{b}} + b4_{\mathrm{b}}\mathrm{LHV} + c4_{\mathrm{b}}\mathrm{LHV}^{2} + d4_{\mathrm{b}}\mathrm{LHV}^{3} \tag{9}$$

The coefficients corresponding to Eq. 9 are contained in Table 4 and the resulting bounds outlining the swarm of points that make its bandwidth are depicted in Figure 5.

A further improvement on the accuracy of estimation of the EF of RFG can also be achieved for RFG by including the standard density as a regressor. Eqs. 10 and 11

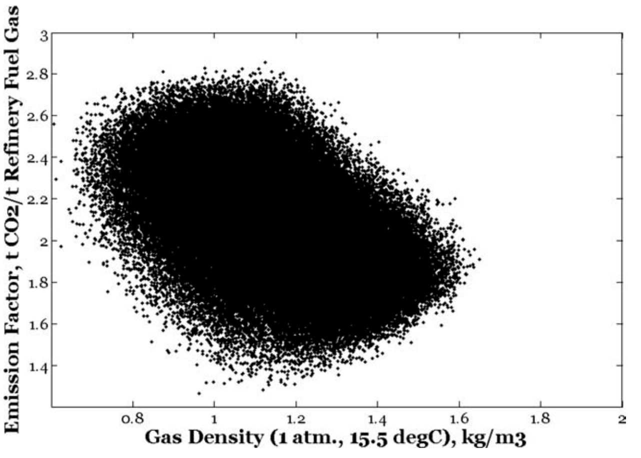

Figure 6. Emission factor of refinery fuel gas data points generated with the Monte Carlo technique against corresponding density at standard conditions: 60°F (15.56°C) and 1 atmosphere.

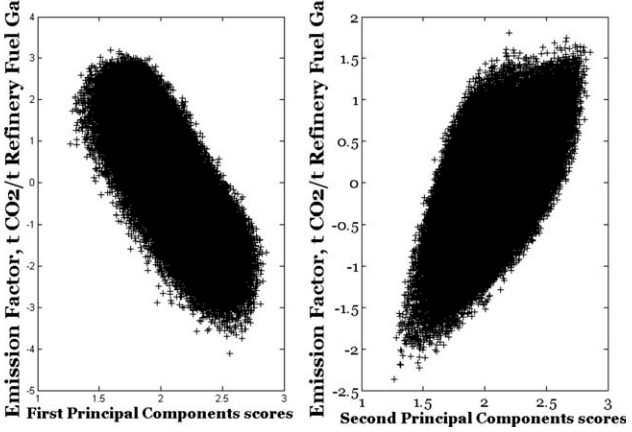

Figure 7. Emission factor of refinery fuel gas data points generated with the Monte Carlo technique against first and second principal component scores corresponding to the LHV, standard density matrix.

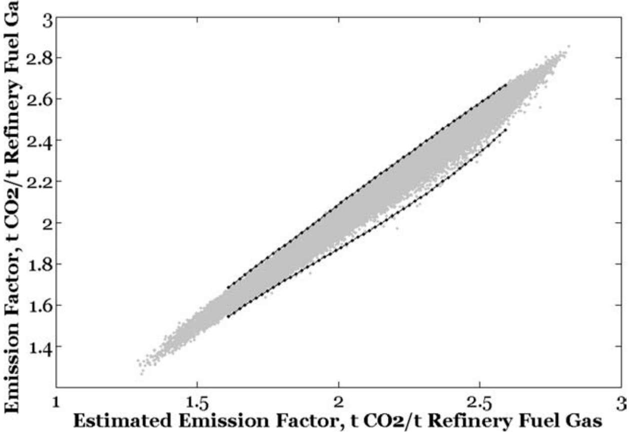

Figure 8. Refinery fuel gas emission factor as a function of the LHV and density at standard conditions: upper and lower bounds.

correspond to more accurate relationships between EF, LHV, and standard density and to the upper and lower bounds surrounding the EF values generated by the Monte Carlo simulation for RFG.

$$\mathrm{EF}^{*} = a5 + b5 \cdot \mathrm{LHV} + c5 \cdot \rho \tag{10}$$

$$\mathrm{EF}_{\mathrm{b}}^{*} = a6_{\mathrm{b}} + b6_{\mathrm{b}}\mathrm{EF}^{*} + c6_{\mathrm{b}}\mathrm{EF}^{*2} + d6_{\mathrm{b}}\mathrm{EF}^{*3} \tag{11}$$

The resulting upper and lower bounds are shown in Figure 8, whereas the coefficients of Eqs. 10 and 11 are reported in Table 4.

Notice that the correlations defined by Eq. 7 have been built for the composition ranges set in Table 3. Hence, the EF of RFG streams with composition outside these limits is not accurately estimated by Eq. 7 and its corresponding coefficients.

To test the correlations, fuel gas data from a refinery was used. The site collects periodic RFG samples and measures composition, LHV, and density among other properties. With these measurements, it is possible to calculate and compare the EF for the samples both from the gas composition, which can provide an accurate value of the EF based on combustion stoichiometry, and from the correlations with LHV and density values that was developed earlier. To assess the improvements achieved with the correlation obtained from the Monte Carlo simulation data against other methods, the EF of the samples was also estimated using a standard EF based on LHV only, namely, the method proposed in the compendium of greenhouse gas emissions methodologies for the oil and gas Industry from the American Petroleum Institute.[1] For RFG, the comparison of both approaches is summarized in Figure 9, in which the deviation (error) from the accurate EF derived from the gas composition is shown. The error was calculated as the difference between the EF of the RFG calculated from its composition and the mean value predicted by either correlation (API or present work). The improvement introduced in the accuracy of estimation of the EF compared to the estimation from the API compendium method[1] is around 50% for the data in Figure 9. Furthermore, by removing the three outliers in the data of Figure 9 for which the LHV is beyond the limits, the correlation improvement rises to almost 90%. As a consequence, the error in the EF estimation can drop from 8% to below 3% for RFG, which results in a significantly more accurate estimation of emissions.

Table 4. Coefficients of the Various Correlations Developed for Refinery Fuel Gas LHV and its Upper and Lower Bounds

Bound Type b	$a4_b$	$b4_b$	$c4_b$	$d4_b$
Lower	0.280	1.000E-04	−2.509E-09	2.974E-14
Upper	0.945	4.804E-05	−1.351E-10	−1.820E-16
Coefficient	$a5$	$b5$	$c5$	
Lower	2.634E-01	4.414E-05	4.533E-01	
	$a6_b$	$b6_b$	$c6_b$	$d6_b$
Lower	−2.700	5.352	−2.329	0.398
Upper	−0.015	1.036	0.032	−0.012

The three points in Figure 9 for which the correlation developed in this work made predictions with error larger than the API method, correspond to RFG samples which have compositions outside the ranges used to develop the correlation, leading to an unusual error. These points correspond to abnormal behavior of the refinery that led to the relatively high error.

The results for natural gas in Figure 9 show a similar comparison. Also for this case, the correlation involving density and LHV performs a better estimation of the EF than the API compendium method.[1] In average, the improvement for the data shown in Figure 9 is about 70%, although the differences in EF calculated by either method are usually below 3%. Therefore, the improvement in accuracy brought by the new correlation for natural gas is not very significant. An additional advantage of the developed correlations to the more accurate estimation of the EF is that it allows estimating the uncertainty of the EF as shown in Figure 10 for RFG data. The Figure shows how the upper and lower bounds are realistic estimations of the error made in estimating the EF.

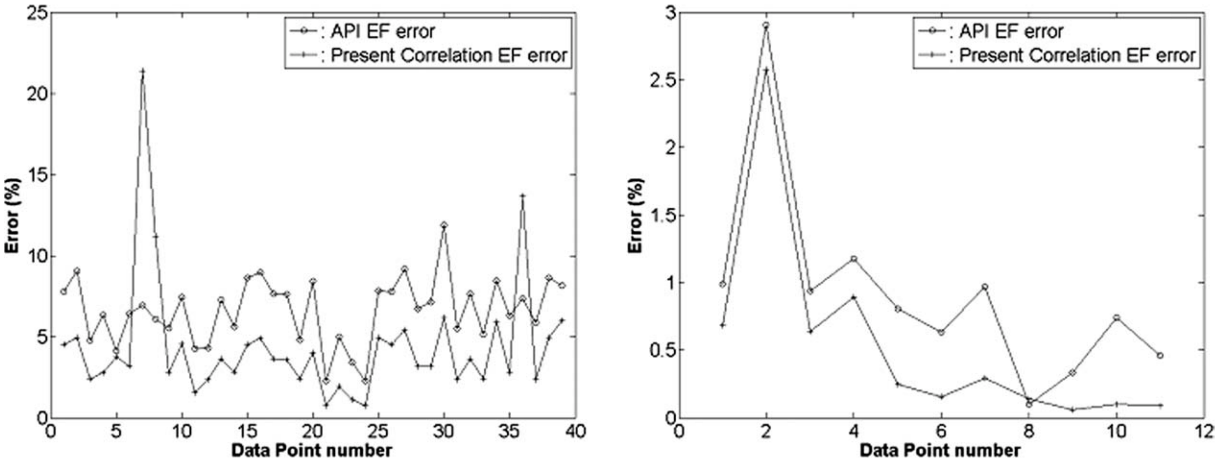

Figure 9. Comparison of error in estimating refinery fuel gas EF and natural gas EF for API method and for present correlation.

Nevertheless, the validity of the use of the earlier correlations and uncertainty estimations is given by the upper and lower bounds, outside which should not be used.

It must be mentioned that in all cases, it was assumed that the fuel is fully burned to CO_2. Although partial combustion to CO or even cases in which not all the fuel burnt, in general that is unlikely in refineries practice, where special care is taken to carry combustion to full stoichiometry as the presence of CO in flue gas involves a high risk of explosion and poisoning that is certainly avoided. Nevertheless, if the range of extent of the reaction is known, that information can be embedded in the Monte Carlo simulation, and hence, in the correlation to be developed at the cost of building higher uncertainty in the prediction. In a similar way, impurities such as H_2S can be handled if present by changing the components in the blend.

Fuel and Residual Oil

Fuel and residual oil are a more complex blend of components than RFG or NG. Although it is usually possible to determine all the components of the latter, it is an almost impossible task to determine analytically all the species present in fuel and residual oils.

As a consequence the approach followed for gaseous fuels to simulate the population of species is not practical for liquid fuels and a different method must be used.

A mixture of species families of heavy hydrocarbons composes fuel and residual oils. The most relevant ones are alkylbenzenes, cycloalkanes, naphthalenes, phenyls, alkylbenzenes, and naphthenoaromatics.[7,8,13–18] It is well-known that due to the huge number of components present in crude fractions, it is more effective to model its composition as continuum distributions rather than using discrete components. However, these distributions can occur around many properties because in fact, crude fractions can be considered as multivariate distributions in many properties.

The composition of fuel and residual oils can vary due to different factors such as processed crude oil properties, refining processes conditions, etc. Like gaseous fuels, EFs and LHV of liquid fuels will not always have a one-to-one correspondence and some variability is expected.

Monte Carlo simulations were used again to generate a sufficiently large population of samples that would allow obtaining an accurate correlation including upper and lower bounds. However, the procedure was different to take into account the earlier discussed features of fuel and residual oils, as described later. Every liquid fuel data point consisted of the convolution of subpopulations of each of the hydrocarbon families of species already mentioned. In turn, each subpopulation was modeled by a continuous distribution of LHV. The distribution of LHV of the fuel oil must comply with certain characteristics such as:

– The distribution must be defined only for positive values.

– The distribution must be able to represent both symmetric and skewed populations.

– The selected distribution must agree with experimental data.

A distribution that complies with the above requirements is the gamma distribution.[13,16–19]

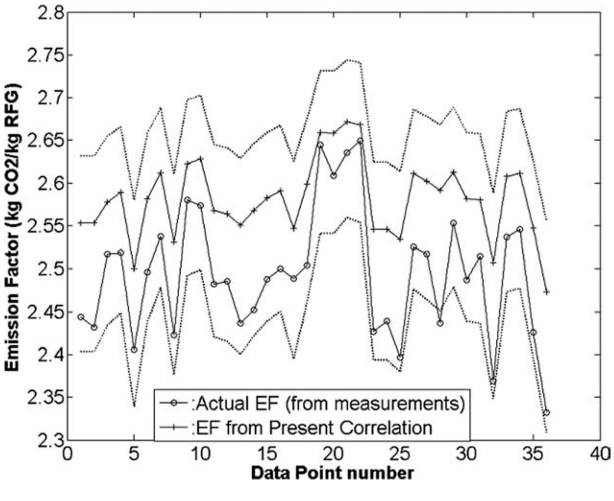

Figure 10. Refinery fuel gas EF upper and lower bounds for data from a real case.

Table 5. Molar Fraction Ranges of Heavy Hydrocarbons Families

Hydrocarbons Family	Molar Fraction Range (%)
Naphthalenes + cycloalkanes	67–100
Alkanes	0–10
Phenyls + alkylbenzenes	0–10
Naphthenoaromatics	0–13
Inert species	0–0.05
Sulfur	0–1

Gamma distributions are defined as

$$F(x;k,\theta) = x^{(k-1)}\frac{\exp(-x/\theta)}{\theta^k\Gamma(k)} \quad x > 0, k, \theta > 0 \tag{12}$$

where x is a continuous measurable variable and k and θ are shape and scale parameters of the distribution, respectively. Gamma distributions have some characteristics that make them suitable to model distributions of species, such as being asymmetric and being defined only for positive values of x.

The following steps can summarize the procedure followed to generate random liquid oil samples:
Step 1: The range of LHV of every family of species is determined taking into account that there is a molecular weight lower limit for liquid fuels. All the properties including LHV are obtained from reliable data banks.[9]
Step 2: For every subpopulation of species, shape and scale parameters for a gamma distribution are randomly generated within the following limits: $k < 6$, $\theta < 11$ to avoid unrealistically wide distributions.[13,14,16]
Step 3: A random mean LHV for every subpopulation is generated within the limits determined in Step 1. Then, the gamma distribution generated in Step 2 is scaled according to the obtained mean LHV.
Step 4: The mean EF of every subpopulation is calculated using Laguerre's integration formula.
Step 5: The weight fraction of every subpopulation is randomly generated within ranges reported for liquid fuels found in practice.

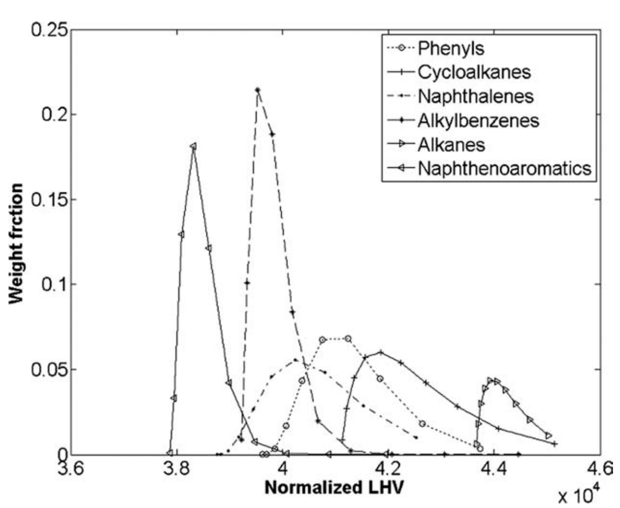

Figure 11. Example of subpopulations to be convoluted into a fuel/residual oil data point.

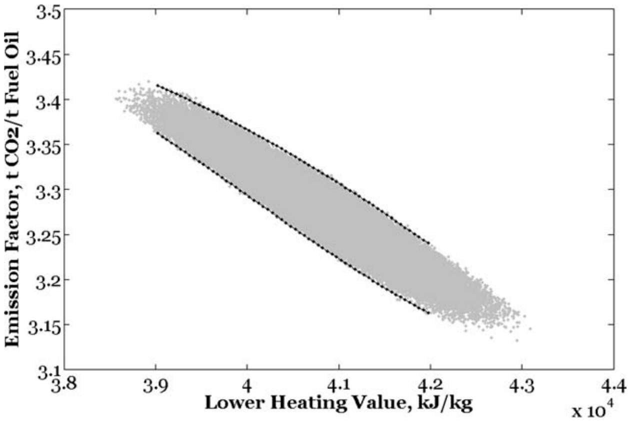

Figure 12. Emission factor upper and lower bounds as a function of the LHV of fuel and residual oil.

Step 6: The weight fractions from Step 5 are used to determine the mean LHV and EF of the convoluted population.
Step 7: A correction of the EF and LHV values is performed to take into account some weight fraction of inert and sulfur. The latter are also generated randomly within established ranges.

The molar fraction ranges set for all the families of species contained in liquid fuels are summarized in Table 5.

An example of subpopulations generated in Step 2 of the procedure above is provided in Figure 11. Once the random data points were generated, correlations for upper and lower bounds for the EF of fuel and residual oils were regressed from EF and LHV values of the form:

$$\mathrm{EF}_b^* = a7_b + b7_b\mathrm{EF}^* + c7_b\mathrm{EF}^{*2} + d7_b\mathrm{EF}^{*3} \tag{13}$$

As in the cases previously analyzed, the EF–LHV relationship is a broad band as depicted in Figure 12, which also shows the lower and upper bounds obtained. The coefficients for Eq. 13 are reported in Table 6. The maximal difference in EF occurs for an LHV around 41,000 kJ/kg, which corresponds to a difference between the two bounds of 0.082 kg CO_2/kg fuel/residual oil. Hence, the maximum error in absolute terms expected from these correlations is 0.04 kg CO_2/kg fuel/residual oil or roughly 1.3%. It should be remarked that for the liquid fuel case, the correlations obtained from LHV only are accurate enough and, therefore, no additional correlations using additional properties were developed. Notice that the correlations defined by Eq. 13 have been built for the composition ranges set in Table 5. Hence, the EF of fuel oil streams with composition outside these limits is not accurately estimated by Eq. 13 and its corresponding coefficients.

Table 6. Coefficients of the Upper and Lower Bound Correlations for EF Estimated from LHV for Fuel and Residual Oil

Bound Type b	$a7_b$	$b7_b$	$c7_b$	$d7_b$
Lower	−9.609E+01	7.560E-03	−1.918E-07	1.599E-12
Upper	−1.930E+01	1.632E-03	−3.771E-08	2.766E-13

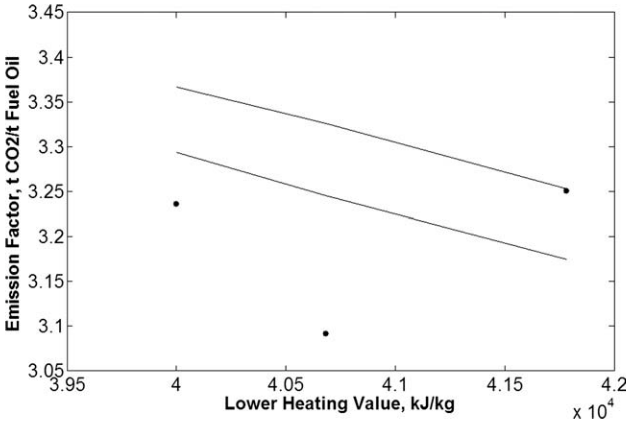

Figure 13. Comparison of emission factors as calculated with the API method against correlation results: •, API emission factors; —, upper and lower bounds calculated form correlation.

Figure 13 shows a comparison between EFs calculated following API's compendium method[1] and those obtained from the present correlation. One out of three EFs as predicted by the correlation match the API value. The other ones are below the lower bound values. This disagreement can originate from several sources. A deeper analysis shows that no single component of the different species families used in the model has a LHV and EF close to those proposed by the API method. In fact, for all the families of hydrocarbons considered to build the proposed correlation, the EF of single components corresponding to the tabulated LHV are higher than those proposed by the API compendium method.[1]

Conclusions

Given a set of components in a blend within a predefined range and whose properties are known experimentally, the method developed earlier can be used to derive a correlation among a number of properties using the Monte Carlo method to generate a significant number of points or "samples" within the predefined range of compositions as the source of data to create the desired correlation and determine its associated uncertainty. Although such method was used in this work to correlate fuels CO_2 EF values with LHV (and density in the gaseous fuels cases), similar situations can occur for other blends and its properties where then the same method can be applied. A further advantage of this method is that the narrower the known ranges of the components, the more accurate the correlation will be and the narrower its corresponding confidence intervals, as in specific contexts where the fuels in use are known to vary in composition within narrow intervals. Then a dedicated, more accurate correlation can be prepared to be applied to that specific case.

Using the method described earlier, correlations of high accuracy between EF, LHV, and density were built for RFG and NG. For fuel/residual oil, an accurate cubic correlation between EF and LHV was built. In all cases, the data generated by the simulations also served the purpose of building correlations for upper and lower bounds of the EF that can be readily used to estimate the EF estimation uncertainty. The correlations were tested against actual refinery data and the results show that indeed more accurate estimations are obtained compared with EF obtained from laboratory composition methods and from methods that estimate EF as proportional to LHV only. In the case of fuel and residual oils, the correlations developed are a function of LHV only, but were improved by using a cubic polynomial. The calculation of upper and lower bounds for EF introduces a convenient method to estimate EF uncertainties that are required in official GHG emissions inventory calculations. The use of one additional (in addition to LHV) readily available fuel property, namely, fuel density, is sufficient to reduce uncertainty of estimation of GHG (in this case CO_2) from combustion. The correlations presented earlier were developed for wide composition ranges, however, they are not meant to cover every possible case. Hence, the applicability of the correlations must be checked before applying it.

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Literature Cited

1. Shires TM, Loughran CJ. *Compendium of Greenhouse Gas Emissions Methodologies for the Oil and Gas Industry*. Washington, DC: American Petroleum Institute, 2004.
2. Chan TL, Ning Z, Wang JS, Cheung CS, Leung CW, Hung WT. Gaseous and particle emission factors from the selected on-road petrol/gasoline, diesel, and liquefied petroleum gas vehicles. *Energy Fuels*. 2007;21:2710–2718.
3. Bruno T, Smith BL. Enthalpy of combustion of fuels as a function of distillate cut: application of an advanced distillation curve method. *Energy Fuels*. 2006;20:2109–2116.
4. Guo B, Ghalambor A. *Natural Gas Engineering Handbook*. Houston: Gulf Publishing Company, 2005.
5. Baukal CE, Schwartz RE, editors. *The John Zink Combustion Handbook*. Boca Raton: CRC Press, 2001.
6. Kutz M, editor. *Mechanical Engineers' Handbook*. New York: Wiley, 1998.
7. Speight JG. *Handbook of Petroleum Analysis*. New York: Wiley, 2001.
8. Speight JG. *Handbook of Petroleum Product Analysis*. New York: Wiley, 2002.
9. Parkash S. *Refining Processes Handbook*. Amsterdam: Gulf Professional Publishing, 2005.
10. Kaspar M, Ray H. Chemometric methods for process monitoring and high-performance controller design. *AIChE J*. 1992;38:1593–1608.
11. Application Data Sheet ADS 103-800R. Measuring Hydrogen Sulfide in Refinery Fuel Gas with a Simple TCD-Based Gas Chromatograph. A01Emerson Process Management Rosemount Analytical Inc., Process Analytic Division, Houston, TX, 2004.
12. Yaws CL. *Yaws' Handbook of Thermodynamic and Physical Properties of Chemical Compounds*. New York: Knovel, 2003.
13. Park SJ, Kim CJ, Rhee BS. Fractionation of aromatic heavy oil by dynamic supercritical fluid extraction. *Ind Eng Chem Res*. 2000;39:4897–4900.

14. Al-Zaid K, Khan ZH, Hauser A, Al-Rabiaha H. Composition of high boiling petroleum distillates of Kuwait crude oils. *Fuel*. 1998;77:453–458.
15. Merdrignac I, Espinat D. Physicochemical characterization of petroleum fractions: the state of the art. *Oil Gas Sci Technol*. 2007;62:7–32.
16. Goossens GA. Prediction of molecular weight of petroleum fractions. *Ind Eng Chem Res*. 1996;35:985–988.
17. Mansoori GA, Vazquez D, Shariaty-Niassar M. Polydispersity of heavy organics in crude oils and their role in oil well fouling. *J Pet Sci Eng*. 2007;58:375–390.
18. Peramanu P, Pruden B, Rahimi P. Molecular weight and specific gravity distributions for athabasca and cold lake bitumens and their saturate, aromatic, resin, and asphaltene fractions. *Ind Eng Chem Res*. 1999;38:3121–3130.
19. Riazi MA. A continuous model for C7+ fraction characterization of petroleum fluids. *Ind Eng Chem Res*. 1997;36:4299–4307.

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