

EMISSION MEASUREMENTS IN DUAL FUELED INTERNAL COMBUSTION ENGINE TESTS

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Abstract: Dual fueled engine test procedures and result interpretation are not available in the literature, This paper describes a methodology for calculating the emission mass flow rates, using the chemical reaction mass balance of the components. The experimental data were obtained from tests made at the MWM dynamometer. Starting from basic principles, the hydrocarbon (HC) mass flow rate was related to molar concentration through the molecular mass and the exhaust gas mass flow rate, and compared to the available expressions in the EPA diesel engine test standard. The dual fuel model was established by a linear combination for the hydrocarbon (HC) equivalent molecular mass, when there is 0 % and 100 % natural gas in the fuel. Finally, the paper shows that, by a similar methodology, the natural gas mass flow rate can be calculated from emission measurements.

Keywords: emissions, dual fuel, chemical reaction mass balance.

1. INTRODUCTION

Diesel fueled engine tests in Brazil follow standard ABNT 05:102.03-002 [1]. Molar concentration of the exhaust gas components (ppm) are measured to within 2,5 % and are used to calculate the emission mass flow rates (g/kWh). These values are compared to limits stipulated by the environment legislation, so that the engine can be approved for operation. Because of the fact that the emission flow rates are not directly measured, they must be calculated from the measured values of diesel (\dot{m}_{diesel}) and air (\dot{m}_{air}) mass flow rates, which are available from [1]. Dual fueled engine test procedure and result interpretation are not available in the literature, and requires additionally the natural gas (\dot{m}_{gas}) mass flow measurement. This paper describes a methodology for calculating the emission mass flow rates, using the chemical reaction mass balance of the components. Because their mass flow rates are much smaller than those for O₂, N₂ and CO₂, a care had to be exercised to numerically evaluate them with minimum discrepancy. The experimental data were obtained from 13 point tests made with MWM dynamometer.

2. COMBUSTION CHEMICAL REACTION

2.1 Air composition

In this methodology air composition is calculated from emission measurements and compared to the standard one, 21 % O₂ and 79 % N₂, which has an equivalent molecular mass of 28,84, as opposed to the real one of 28,97.

2.2 Diesel composition

An equivalent diesel composition was established from the ultimate analysis made by PETROBRAS (Brazilian oil company), resulting in C_n H_m S_p, with an equivalent molecular mass of 204,7, and n = 14,809, m = 26,926 and p = 0,00205.

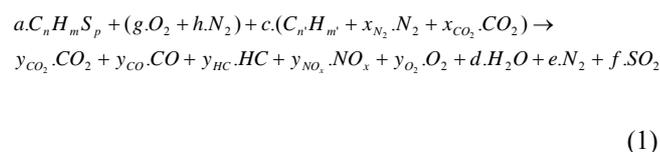
2.3 Natural gas composition

The gas chromatography molar composition was used to calculate an equivalent composition for the natural gas, resulting in, C_{n'} H_{m'} + x_{N₂} .N₂ + x_{CO₂} .CO₂, with an equivalent molecular mass of 17,8606, and n' = 1,113, m' = 4,209, x_{CO₂} = 0,0036 and x_{N₂} = 0,0049.

2.4 Exhaust gas composition in a dry basis

The HORIBA emission meter measures directly the exhaust gas molar composition (y), respectively for CO₂ (%), NO_x (ppm), CO (ppm), HC (ppm) and O₂ (%).

2.5 Chemical reaction equation



where *a*, *b*, *c*, *d*, *e*, *f*, *g* and *h* will be determined from chemical reaction mass balance. Air composition, *g* and *h*, will be determined also from mass balance.

3. EMISSION MASS FLOW RATE CALCULATION

3.1 Basic equations

The ideal gas equation relates partial pressure (P_i), mass (m_i), molecular mass (M_i), absolute temperature (T) and mixture volume (V) for each component i (NO_x , CO and HC) by the following equation:

$$P_i \cdot V = m_i \cdot \frac{\bar{R}}{M_i} \cdot T \quad (2)$$

where $\bar{R} = 8314,472 \text{ J/kmol.K}$ is the universal gas constant. Also, the molar fraction of component i , can be expressed as a function of the mixture pressure as :

$$x_i = \frac{P_i}{P} \quad (3)$$

$$\frac{m_i}{V} = x_i \cdot M_i \cdot \frac{P}{\bar{R} \cdot T} \quad (4)$$

However, at the reference conditions $P = 101325 \text{ Pa}$, and $T = 273,15 \text{ K}$. Thus,

$$\frac{m_i}{V} (\text{g} / \text{m}^3) = x_i (\text{ppm}) \cdot \frac{M_i}{22414} \quad (5)$$

According to [1], the exhaust gas specific mass (ρ_{exhaust}) is approximately the same as for air (ρ_{air}), that at the same reference conditions has the value of :

$$\rho_{\text{exhaust}} = \frac{m_{\text{exhaust}}}{V} \approx \rho_{\text{air}} = 1,293 \text{ kg/m}^3 \quad (6)$$

Combining Eq. (5) and (6) and noticing that :

$$\dot{m}_{\text{exhaust}} = \dot{m}_{\text{diesel}} + \dot{m}_{\text{gas}} + \dot{m}_{\text{air}} \quad (7)$$

$$\dot{m}_i (\text{g} / \text{h}) = x_i (\text{ppm}) \cdot C_i \cdot \dot{m}_{\text{exhaust}} (\text{kg} / \text{h}) \quad (8)$$

$$C_i = \frac{M_i}{28981} \quad (9)$$

3.2 Emissions from diesel fuelled engines

Table 1 shows the value of C_i from [1], and the calculated molecular mass from Eq. (9).

Table 1 : Emission equivalent molecular mass [1]

Emission	C_i	M_i
NO_x	0,001587	46
CO	0,000966	28
HC	0,000479	13,882

It can be seen that the test standard [1] calculates NO_x as NO_2 , as an upper limit ($M_{\text{NO}_x} = 46$). CO molecular mass calculated from [1] coincides with its actual value ($M_{\text{CO}} = 28$). For hydrocarbons (HC) however, only diesel lighter components are considered, resulting in an equivalent molecular mass (13,882) less than for natural gas (17,8606). An equivalent composition of $\text{CH}_{1,882}$ was then adopted as representative of HC composition.

3.3 Emissions from dual fueled engines

The methodology considers that unburned hydrocarbons in the exhaust gases come from two sources, (a) Diesel lighter components, from [1], with $M_{\text{HC,diesel}} = 13,882$, or $\text{CH}_{1,882}$, (b) Natural gas without CO_2 and N_2 , with $M_{\text{HC,gas}} = 17,565$, or $\text{C}_{1,113} \text{H}_{4,209}$. From Eq. (1), a fraction α of the diesel – natural gas mixture will not be burnt, or :

$$\alpha \cdot (a \cdot \text{CH}_{1,882} + c \cdot \text{C}_{1,113} \text{H}_{4,209}) \quad (10)$$

An equivalent hydrocarbon composition can be written as $\text{C}_r \text{H}_s$, where :

$$r = \frac{1}{1 + c/a} \cdot 1 + \frac{c/a}{1 + c/a} \cdot 1,113 \quad (11)$$

$$s = \frac{1}{1 + c/a} \cdot 1,882 + \frac{c/a}{1 + c/a} \cdot 4,209 \quad (12)$$

with an equivalent molecular mass of :

$$M_{HC} = 12.r + s \quad (13)$$

The linear combination of this methodology takes into account that when there is only diesel in the fuel, the hydrocarbon molecular mass is 13,882 [1]. When there is almost natural gas in the fuel [2], the hydrocarbon composition is approximately the same as natural gas. Therefore, a linear interpolation is suggested for dual fuel, based on the following expression, with the help of Eq. (1) :

$$\frac{\dot{m}_{diesel}}{\dot{m}_{gas}} = \frac{a.M_{diesel}}{c.M_{gas}} \quad (14)$$

Using $M_{diesel} = 204,7$ and $M_{gas} = 17,8606$, the following expression can be obtained :

$$c/a = \frac{\dot{m}_{gas}}{\dot{m}_{diesel}} . 11,461 \quad (15)$$

The hydrocarbon molecular mass can thus be calculated by Eq. (13), upon calculating r and s from Eq. (11) and (12), with the help of Eq. (15).

An interesting aspect of this methodology is that NO_x and CO mass flow rates are calculated the same way as when there is only diesel in the fuel, thus according to [1]. This hypothesis is supported by an EPA report [3] that indicates that the emission factors for NO_x and CO are almost the same from diesel and dual fuel, and much higher for HC from dual fuel.

In order to validate this methodology, a chemical reaction mass balance is performed with the experimental data obtained from tests in a MWM dynamometer.

4. CHEMICAL REACTION MASS BALANCE

A 13 point dynamometer test was used to supply data to the chemical reaction mass balance, which was applied to Eq. (1). That means that the number of atoms in the reactants and in the combustion products must be the same for C, H, S, O and N, which supplies 5 equations to be solved. The following data must be supplied :

- Diesel composition and its molecular mass.
- Natural gas composition and its molecular mass.

- Measured mass flow rates (in kg/h) for diesel (\dot{m}_{diesel}), natural gas (\dot{m}_{gas}) and combustion air (\dot{m}_{air}).
- Measured molar concentration (y) in the exhaust gases of CO_2 (%), NO_x (ppm), CO (ppm), HC (ppm) and O_2 (%).

From Eq. (1), the following unknowns must be calculated by solving the system of equations : a, c, d, e, f, g and h . The following 5 equations are the results of the chemical reaction mass balance :

$$C: a.n + c.(n'+x_{CO_2}) = y_{CO_2} + y_{CO} + r.y_{HC} \quad (16)$$

$$H: a.m + c.m' = s.y_{HC} + 2.d \quad (17)$$

$$O: 2.g + 2.c.x_{CO_2} = 2.y_{CO_2} + y_{CO} + 2.y_{NO_x} + 2.y_{O_2} + d + 2.f \quad (18)$$

$$S: a.p = f \quad (19)$$

$$N: 2.h + 2.c.x_{N_2} = y_{NO_x} + 2.e \quad (20)$$

Two more equations can be obtained from diesel, natural gas and air flow rates measurements :

$$c/a = \frac{\dot{m}_{gas}}{\dot{m}_{diesel}} . \frac{M_{diesel}}{M_{gas}} \quad (21)$$

$$g/a + h/a = \frac{\dot{m}_{air}}{\dot{m}_{diesel}} . \frac{M_{diesel}}{M_{air}} \quad (22)$$

The air molecular mass can be calculated from the following equation :

$$M_{air} = \frac{g}{g+h} . M_{O_2} + \frac{h}{g+h} . M_{N_2} \quad (23)$$

Eq. (16), (17), (18), (19), (20), (21) and (22) can be solved iteratively for determining a, c, d, e, f, g and h . Eq. (11) and (12), together with Eq. (21) can be used for calculating r and s . A software (SOFT 1) was developed for the calculations.

Table 2 shows the validation of the methodology against the chemical reaction mass balance and standard [1]. A 13 point test was made at MWM, using only diesel as fuel. It can be seen that the results are practically the same, thus validating both methodologies, processed by SOFT 1.

Table 3 shows the emission mass flow rates for a 13 point test at MWM, using a conversion kit (called A) for operation with dual fuel. HC emissions were calculated using the proposed methodology, processed by SOFT 1.

Table 2 : Emission Mass Flow Rate at MWM for Diesel

Point	Power kW	Consumption (kg/h)			NOx (g/h)			CO (g/h)			HC (g/h)		
		Diesel	Air	Balance	Standard	Method	Balance	Standard	Method	Balance	Standard	Method	
1	0,0	0,46	55,2	22	19	19	21	18	18	9	8	8	
2	74,9	16,49	412,1	418	416	416	47	47	47	15	15	15	
3	46,2	11,91	445,2	197	198	198	98	99	99	22	22	22	
4	69,4	17,20	497,8	284	283	283	95	95	95	20	20	20	
5	38,0	8,64	328,1	214	215	215	41	41	41	16	16	16	
6	56,6	12,61	381,4	320	322	322	31	31	31	17	17	17	
7	18,8	5,14	263,6	105	105	105	86	86	86	19	19	19	
8	91,9	21,19	521,5	476	475	475	90	90	90	18	18	18	
9	23,0	7,33	402,4	109	110	110	244	247	247	32	33	33	
10	98,3	25,01	577,1	484	485	485	138	138	138	12	12	12	
11	24,6	9,76	523,8	171	173	173	115	116	116	33	33	33	
12	74,6	20,41	559,7	314	312	312	92	92	92	20	20	20	
13	49,5	15,04	543,0	227	226	226	82	81	81	28	28	28	

Table 3 : Emission Mass Flow Rate at MWM for Dual Fuel (kit A)

Point	Power kW	Consumption (kg/h)			Substitution %	Emission Flow Rate (g/kWh)		
		Diesel	Air	Gas		NOx	CO	HC
1	0,0	1,70	148,67	1,0	39,9	-	-	
2	110,9	11,70	588,99	13,3	56,2	4,94	6,74	
3	64,8	13,77	559,36	2,7	18,1	4,04	8,07	
4	102,1	14,65	736,36	11,3	46,6	3,19	12,87	
5	53,2	11,90	386,13	0,9	7,9	5,17	1,03	
6	86,0	11,54	498,72	8,6	45,7	4,44	6,87	
7	27,7	8,73	334,71	1,0	11,5	5,27	16,78	
8	129,6	15,03	796,61	15,8	54,3	3,59	9,80	
9	33,3	11,41	478,12	1,0	9,0	4,75	19,68	
10	120,0	18,93	925,90	13,2	44,1	2,85	13,58	
11	53,0	15,84	672,45	0,8	5,4	3,70	13,16	
12	105,2	25,13	852,58	0,9	3,9	4,14	0,65	
13	69,6	17,67	716,66	0,8	4,9	3,85	2,14	

5. FLOW MEASUREMENT FROM EMISSIONS

Natural gas and air mass flow rate can be calculated from emissions measurements. It was shown in [4] that the air/fuel ratio can be calculated from exhaust gas composition. Also, the larger the flow rate, the better the accuracy. The same methodology can be applied for dual fueled engines.

Sometimes, natural gas mass flow rate measurement is not made during a test. In order to recover the information, the chemical reaction mass balance method can be used. In this case, a slight modification can be made on the proposed model. Because of the fact that there is a missing information about the gas flow rate, another hypothesis must be made, so that the system of equations can be solved. Performance simulations have shown that the calculated air composition by the proposed model is approximately equal to the standard one, that is, 21 % O₂ and 79 % N₂.

Therefore, it was decided to introduce another equation in place of Eq. (21).

$$h = 3,76. g \quad (24)$$

The system of equations to be iteratively solved is composed of Eq. (16), (17), (18), (19), (20), (22) and (24). A software (SOFT 2) was developed to perform the calculations. Its validation was made by using the same data of Table 3, calculating the natural gas mass flow rate and comparing to the measured value. Table 4 presents the results. It is shown that low gas flow rate values are not estimated correctly by the model. On the other hand, larger values are estimated to within less than 5 %. Emission mass flow rates are also estimated by SOFT 1 and SOFT 2, comparing the results to the ones obtained by the methodology proposed in this paper. The differences are less than 5 %, what validates the model.

Table 4 : Flow measurement from emissions : Validation. (kit A)

Point	Power kW	Consumption (kg/h)		Natural Gas(kg/h)		NOx (g/h)		CO (g/h)		HC (g/h)	
		Diesel	Air	Measured	SOFT 2	SOFT 1	Measured	SOFT 1	SOFT 2	Measured	SOFT 1
1	0,0	1,70	148,67	1,0	-0,4	53	28	27	137	73	69
2	110,9	11,70	588,99	13,3	13,1	563	558	548	766	760	747
3	64,8	13,77	559,36	2,7	2,5	276	273	262	551	545	523
4	102,1	14,65	736,36	11,3	10,8	339	333	326	1364	1340	1314
5	53,2	11,90	386,13	0,9	1,4	288	281	275	58	56	55
6	86,0	11,54	498,72	8,6	8,2	398	391	382	616	606	591
7	27,7	8,73	334,71	1,0	-0,2	174	154	146	555	491	465
8	129,6	15,03	796,61	15,8	15,5	478	474	465	1306	1295	1270
9	33,3	11,41	478,12	1,0	0,0	175	164	158	726	679	655
10	120,0	18,93	925,90	13,2	14,3	341	352	342	1629	1677	1630
11	53,0	15,84	672,45	0,8	-0,6	218	203	196	777	722	697
12	105,2	25,13	852,58	0,9	0,6	451	447	425	71	70	68
13	69,6	17,67	716,66	0,8	0,4	281	276	268	157	154	149

Finally, another dual fuel conversion kit (called B) was tested at MWM, without measuring the natural gas flow rate. Table 5 and 6 presents the results, respectively without and with a catalyst, processed by SOFT 2.

Table 5 : Emission Mass Flow Rate at MWM for Dual Fuel. Without catalyst. (Kit B)

Point	Power kW	Consumption (kg/h)			Substitution %	Emission Flow Rate (g/kWh)		
		Diesel	Air	Gas		NOx	CO	HC
1	0,9	1,55	147,3	0,0	0,0	65,43	19,81	6,24
2	11,4	4,63	331,6	0,0	0,0	12,27	6,74	1,43
3	28,4	4,83	346,8	3,1	42,0	7,06	19,36	38,99
4	57,4	4,94	397,0	8,0	64,6	6,78	13,47	25,83
5	85,7	9,34	473,7	8,6	51,0	7,63	8,16	11,97
6	114,3	17,48	606,0	6,5	29,6	6,79	4,93	6,15
7	1,1	1,56	146,7	0,0	0,0	56,66	20,85	6,55
8	142,6	23,51	995,2	9,1	30,4	6,41	7,57	9,50
9	107,0	14,31	887,7	12,5	49,7	6,09	16,09	23,64
10	71,5	8,37	753,2	12,8	63,3	5,57	27,91	50,64
11	36,9	6,29	616,4	7,8	58,3	6,51	36,73	79,67
12	15,5	7,94	545,6	0,0	0,0	13,83	8,32	2,38
13	0,9	1,53	147,6	0,0	0,0	66,03	24,28	8,15

Table 5 : Emission Mass Flow Rate at MWM for Dual Fuel. With catalystr. (Kit B)

Point	Power kW	Consumption (kg/h)			Substitution %	Emission Flow Rate(g/kWh)		
		Diesel	Air	Gas		NOx	CO	HC
1	0,0	1,52	145,8	0,0	0,0	-	-	-
2	11,1	4,64	327,8	0,0	0,0	12,09	0,74	0,51
3	28,0	5,19	336,6	2,5	35,6	7,45	2,24	29,89
4	55,9	5,80	376,5	7,0	57,8	7,46	0,25	19,02
5	83,7	11,13	440,2	6,9	41,3	8,02	0,12	5,99
6	112,6	19,81	542,1	5,0	22,1	6,19	0,09	0,98
7	0,0	1,50	146,5	0,0	0,0	-	-	-
8	139,5	27,00	833,2	6,3	20,8	6,50	0,32	2,06
9	103,8	15,27	726,1	10,8	44,5	7,11	0,56	6,61
10	69,2	9,10	643,1	11,2	58,1	6,49	0,88	17,83
11	34,8	6,63	557,5	7,3	55,4	8,01	8,32	54,75
12	15,1	7,67	516,6	0,4	5,8	13,90	0,86	1,03
13	0,0	1,47	146,1	0,0	0,0	-	-	-

6. UNCERTAINTY ANALYSIS

Assuming that the HC composition in the exhaust gases follows the proposed model, the uncertainty of measurements for the emission mass flow rates can be made according to [5]. Using Eq. (8) and (9), the following equation can be obtained for the combined uncertainty of measurement ($u_{\dot{m}_i}$) for each emission mass flow rate, from the standard uncertainty of molar concentration (u_{x_i}), molecular mass (u_{M_i}) and exhaust gas mass flow rate ($u_{\dot{m}_{exhaust}}$):

$$\left(\frac{u_{\dot{m}_i}}{\dot{m}_i}\right)^2 = \left(\frac{u_{x_i}}{x_i}\right)^2 + \left(\frac{u_{M_i}}{M_i}\right)^2 + \left(\frac{u_{\dot{m}_{exhaust}}}{\dot{m}_{exhaust}}\right)^2 \quad (25)$$

Molar concentration can be measured to within $\pm 2,5$ % with the HORIBA meter.

The exhaust gas mass flow rate can be measured to within approximately 2 %, which is the air mass flow rate relative uncertainty of measurement, the greatest contribution to it in Eq. (7)

Equivalent molecular mass relative uncertainties of measurement for CO and NO_x are assumed to be negligible, following what has been established by standard [1]. Therefore, using Eq. (25), emission mass flow rate uncertainty can be calculated as :

$$\frac{U_{\dot{m}_{CO}}}{\dot{m}_{CO}} = 2 \cdot \left[\left(\frac{2,5}{2} \right)^2 + 0 + \left(\frac{2}{2} \right)^2 \right]^{1/2} = 3,2\% \quad (26)$$

$$\frac{U_{\dot{m}_{NO_x}}}{\dot{m}_{NO_x}} = 2 \cdot \left[\left(\frac{2,5}{2} \right)^2 + 0 + \left(\frac{2}{2} \right)^2 \right]^{1/2} = 3,2\% \quad (27)$$

The uncertainty of HC molecular mass can be calculated from Eq. (13) :

$$u_{M_{HC}} = \left[(12 \cdot u_r)^2 + u_s^2 \right]^{1/2} \quad (28)$$

Both r and s depend only the ratio c/a , Eq. (15). However, both gas and diesel mass flow rate can be measured with an uncertainty of ± 2 %. Thus its uncertainty becomes :

$$\frac{u_{c/a}}{c/a} = \left[\left(\frac{u_{\dot{m}_{gas}}}{\dot{m}_{gas}} \right)^2 + \left(\frac{u_{\dot{m}_{diesel}}}{\dot{m}_{diesel}} \right)^2 \right]^{1/2} = 1,4\% \quad (29)$$

$$u_r = \frac{\partial r}{\partial (c/a)} \cdot u_{c/a} = \frac{1,113 - r}{1 + c/a} \cdot u_{c/a} \quad (30)$$

$$u_s = \frac{\partial s}{\partial (c/a)} \cdot u_{c/a} = \frac{4,209 - s}{1 + c/a} \cdot u_{c/a} \quad (31)$$

Then

$$u_{M_{HC}} = \frac{\left[(1,113 - r)^2 \cdot 144 + (4,209 - s)^2 \right]^{1/2}}{1 + c/a} \cdot u_{c/a} \quad (32)$$

Table 6 shows that the uncertainty of measurement of HC molecular mass is very small.

Table 6 : Uncertainty of measurement of HC mass flow rate

Point	r	s	M _{HC}	c/a	u _{o/a}	Uncertainty of Measurement		
						M _{HC}		
						Absolute (k=1)	Relative % (k=1)	Relative % (k=2)
1	1,098	3,908	17,089	6,740740	0,0953	0,00428	0,025	3,20
2	1,105	4,043	17,303	13,032850	0,1843	0,00252	0,015	3,20
3	1,078	3,492	16,431	2,246816	0,0318	0,00812	0,049	3,20
4	1,102	3,973	17,191	8,840438	0,1250	0,00348	0,020	3,20
5	1,052	2,963	15,592	0,866884	0,0123	0,00947	0,061	3,20
6	1,101	3,965	17,179	8,542068	0,1208	0,00357	0,021	3,20
7	1,064	3,203	15,973	1,312734	0,0186	0,00935	0,059	3,20
8	1,104	4,031	17,283	12,048470	0,1704	0,00270	0,016	3,20
9	1,057	3,048	15,727	1,004296	0,0142	0,00952	0,061	3,20
10	1,100	3,950	17,155	7,993530	0,1130	0,00376	0,022	3,20
11	1,041	2,735	15,232	0,578656	0,0082	0,00884	0,058	3,20
12	1,033	2,559	14,954	0,410442	0,0058	0,00786	0,053	3,20
13	1,039	2,677	15,140	0,518847	0,0073	0,00857	0,057	3,20

Therefore, the uncertainty of measurement of HC mass flow rate can be calculated as before :

$$\frac{U_{\dot{m}_{HC}}}{\dot{m}_{HC}} = 2 \cdot \left[\left(\frac{2,5}{2} \right)^2 + 0 + \left(\frac{2}{2} \right)^2 \right]^{1/2} = 3,2\% \quad (33)$$

In conclusion, emission mass flow rate can be measured to within $\pm 3,2\%$, if molar composition is measured to within $\pm 2,5\%$, and exhaust gas mass flow rate to within $\pm 2\%$.

7. CONCLUSIONS

The paper presents the methodology for calculating the emission mass flow rate from measured values of molar concentration for dual fueled diesel engines. Also it shows that gas and air mass flow rate can be accurately calculated from measured values of emissions, by using a chemical reaction mass balance. Assuming that the HC composition in the exhaust gases follows the proposed model, an uncertainty analysis shows that NO_x , CO and HC mass flow rates can be measured to within $\pm 3,2\%$, when molar emission composition are measured to within $2,5\%$, and diesel, natural gas and air are measured to within 2% .

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