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Present Day Engines Pollutant Emissions: Proposed Model for Refinery Bases Impact

N. Hochart¹, N. Jeuland¹, X. Montagne¹, S. Raux², G. Belot³, B. Cahill³, R. Faucon⁴, A. Petit⁴ and S. Michon⁵

¹ Institut français du pétrole, division Techniques d’applications énergétiques,
   1 et 4, avenue de Bois-Préau, 92852 Rueil-Malmaison Cedex - France
² Institut français du pétrole, division Techniques d’applications énergétiques,
   Centre d’études et de développement industriel « René N avarre », BP 3, 69390 Vernaison - France
³ PSA Peugeot-Citroën, 18, rue des Fauvelles, 92256 La Garenne-Colombes Cedex - France
⁴ Renault, 1, allée Cornuel, 91510 Lardy Cedex - France
⁵ Renault Trucks powertrain, 99, route de Lyon, BP 310, 69808 Saint-Priest - France

Résumé — Émissions de polluants des moteurs actuels : modélisation de l’impact des bases de raffinage

L’amélioration de la qualité de l’air, tout particulièrement dans les zones urbaines, est un des principaux objectifs pour les années à venir. Dans ce contexte, les constructeurs d’automobiles, les équipementiers et les raffineurs ne cessent d’explorer de nouvelles voies compatibles avec une sévérité toujours accrue des contraintes environnementales. L’identification des pistes les plus prometteuses apparaît donc incontournable.

Un programme de recherche conduit par l’IFP, en partenariat avec le ministère de l’Industrie et les constructeurs français PSA-Peugeot-Citroën, Renault et Renault Véhicules Industriels, a donc été bâti. Celui-ci repose sur une étude de 4 ans, regroupant différentes technologies représentatives des 20 années à venir. Ce projet se scinde en 3 volets complémentaires : moteurs diesels pour véhicules particuliers, moteurs diesel de poids lourds et moteurs à allumage commandé.

L’objectif de cette étude est de caractériser l’effet de la formulation des carburants sur les émissions de polluants, de CO₂ et sur le réglage de moteurs de technologies différentes. L’originalité de ce travail réside dans le fait que les paramètres d’étude ne sont pas conventionnels dans la mesure où il s’agit directement des bases de raffinage. Ces dernières ont été sélectionnées comme étant susceptibles d’être parmi les plus représentatives du futur. Les résultats obtenus permettront aux raffineurs de disposer d’un outil concret afin d’orienter les nouveaux schémas de raffinage.

Les technologies décrites ci-après sont, pour les moteurs à allumage commandé, un moteur à mélange pauvre Euro II (Honda VTEC équipant la Honda Civic) ainsi qu’un moteur Renault Euro III 1,8 l fonctionnant à la stœchiométrie (qui équipe les Laguna), pour les moteurs diesels, un moteur à injection indirecte 2,2 l Euro II, et, pour les moteurs de poids lourds, un moteur Euro II RVI de 10 l.

Pour la formulation des carburants, une approche originale est proposée : alors que les études classiques sont essentiellement basées sur les propriétés des carburants, on retient ici directement les bases de raffinage. Pour les gazoles, six bases ont été retenues afin de construire le plan d’expériences de
mélange: un gazole straight-run, une base d’hédrocracking, un LCO, un gazole issu du procédé d’hydroconversion de résidus sous-vide, une coupe kérosène et un gazole Fischer-Tropsch. Concernant les essences, les sept bases retenues sont les suivantes: un isomérat (principalement constitué d’isoparaffines en C\textsubscript{5}/C\textsubscript{6}), un alkylat (isoparaffines en C\textsubscript{7+}), une coupe oléfinique issue du procédé d’oligomérisation, un FCC (oléfines en C\textsubscript{7+} et composés aromatiques), un réformat léger (aromatiques C\textsubscript{7}/C\textsubscript{8}), un réformat lourd (aromatiques en C\textsubscript{9+}) et un composé oxygéné (ETBE).

Pour chaque technologie, des essais ont été conduits sur banc moteur stationnaire avec des tests de variations de conditions de réglage moteur en dehors de la configuration cartographique. En parallèle, des essais avec des véhicules ont été menés sur le cycle normalisé MVEG-11s. Les émissions de polluants réglementés ainsi que les émissions de polluants non réglementés ont été étudiées.

Abstract — Present Day Engines Pollutant Emissions: Proposed Model for Refinery Bases Impact —
Air quality improvement, especially in urban areas, is one of the major concerns for the coming years. For this reason, car manufacturers, equipment manufacturers and refiners have explored development issues to comply with increasingly severe anti-pollution requirements. In such a context, the identification of the most promising improvement options is essential.

A research program, carried out by IFP (Institut français du pétrole), and supported by the French Ministry of Industry, PSA-Peugeot-Citroën, Renault and RVI (Renault Véhicules Industriels), has been built to study this point. It is based on a four years program with different steps focused on new engine technologies which will be available in the next 20 years in order to answer to more and more severe pollutant and CO\textsubscript{2} emissions regulations. This program is divided into three main parts: the first one for Diesel car engines, the second for Diesel truck engines and the third for spark ignition engines.

The aim of the work reported here is to characterize the effect of fuel formulation on pollutant emissions and engine tuning for different engine technologies. The originality of this study is to use refinery bases as parameters and not conventional physical or chemical parameters. The tested fuels have been chosen in order to represent the major refinery bases expected to be produced in the near future. These results, expressed with linear correlations between fuel composition and pollutant emissions, will help to give a new orientation to refinery tool.

The engines presented in this publication are, for spark ignition engines an Euro II lean-burn engine (Honda VTEC which equips the Honda Civic) and an Euro III 1.8 l stoichiometric-running Renault engine which equips the Laguna vehicles and, for diesel engines an Euro II Renault Laguna 2.2 l indirect injection diesel engine and an Euro II RVI truck engine.

For the fuel formulation, an original approach is proposed: while the classical studies are based on the properties of the fuel, this one is built only on a refinery bases approach. For diesel fuels, six refinery bases (a straight-run diesel fuel, an hydro-cracked diesel fuel, a LCO, a diesel fuel obtained by hydro-conversion of vacuum distillation residue, a kerosene and a diesel fuel issued from a Fischer-Tropsch process) have been selected to produce a fuel matrix which was determined according to an experimental blend design. For gasoline fuels, seven bases have been chosen, which are representative of the batch that will be used in the next years: a fuel from isomerisation process (mainly constituted of C\textsubscript{5}/C\textsubscript{6} isoparafins), an alkylate (constituted of C\textsubscript{7+} isoparafins), a fuel from olefins oligomerization process, a fuel from catalytic cracking process (mainly composed of C\textsubscript{7+} olefins and aromatic compounds), a light reformate (C\textsubscript{7}/C\textsubscript{8} aromatic compounds), an heavy reformate (C\textsubscript{9+} aromatic compounds) and an oxygenated compound (ETBE).

For each engine, tests have been run on a steady state bench with variations of some tuning parameters. Vehicle tests with the same engines have also been carried out on the European MVEG cycle, where regulated and unregulated pollutant emissions have been recorded.
The environmental legislation has become for a number of years the most important factor affecting requirements of automotive fuels, due to additional limitations caused by changes in vehicle technologies (after-treatment, etc.), but also to the growing importance of direct fuel effect (their weighting factor rising sharply as a result of a very low emission levels mandated in ecological regulations). Moreover, in order to meet the future regulation not only on pollutant emissions but also on CO₂ emissions, new technologies have appeared, such as more complex after treatment systems, or new combustion technologies such as direct injection engine.

This mutation of the engine technology and the more acute impact of fuel properties on exhaust emissions will lead to new diesel and gasoline fuel formulations. Some work has been carried out in order to study the impact of fuel composition on pollutant emissions (Auto/Oil Air Quality Improvement Research Program [1-3], EPEFE [4, 5], but even if a lot of theoretical data are available, the fuel formulation becomes more and more complex year by year. In this context, it is crucial to have an excellent knowledge of the relative impact of the different refinery bases available for the blending of future fuels on modern engines operation and emissions.

The results presented here are coming from a large study done at IFP with the support of the French Ministry of Industry, PSA, Renault and Renault VI. This study aims to quantify the impact of refinery bases which we identified as the major components in the gasoline and diesel fuel pool in the next years for engines using technologies which will be widespread in the future. Seven gasoline bases (alkylate, isomerate, FCC, a fuel from olefins dimerisation (dimate), a light reformate, an heavy reformate and ETBE) will be tested on four vehicles and engines (two PFI engines (one stoichiometric and one lean burn) and two DI engines (one stratified running)). As far as diesel technology is concerned, six diesel bases (straight-run, hydro-cracked diesel fuels, LCO, hydro-converted vacuum distillation residue, kerosene and Fischer-Tropsch base) will be tested on four passenger car engines (one indirect injection, and three high pressure direct injection) and three heavy-duty (Euro II, Euro III and Euro III with EGR) diesel engines.

The results of the first step of the study are presented in this paper, devoted to the two PFI engines and two diesel engines.

1 CONTEXT

In the early 90’s, in Europe, the wide investigation EPEFE program has been carried out to determine the role of
physical and chemical fuel parameters on pollutant emissions. It was an essential part of the European Auto/Oil 1 Program which aimed at defining the 2000 step for emission and fuel specification standards. For diesel fuels, EPEFE focused on density, poly-aromatics, cetane number and back-end volatility (T95) [1], while it focused on sulfur content, aromatic compounds rate and distilled fraction at 100°C (“E100”) for gasoline.

The original work reported here has a radically different view: instead of trying to determine the influent physical parameters of the fuel with often very complex dedicated fuel matrix, the chosen option was to try to directly determine the influence of fuel composition in terms of refinery bases. The goal of this study is to calculate linear correlations between pollutant emissions and fuel composition and thus give a pragmatic tool for choosing fuel blending components which ensure the lowest vehicle emissions. The literature does not provide much information about the use in engines of some of the bases selected here (LCO and hydro-converted vacuum distillation residue for diesel fuels, isomerate for gasoline fuels for instance). Besides, many technical points have changed since EPEFE: new engine technologies arise, such as high pressure injection diesel systems, new after-treatment solutions, lean-burn spark-ignition engines, spark-ignition stratified direct-injection engines, etc., the operation of which will require new fuel specifications such as lower fuel sulfur contents, and interest in fuel reformulation techniques grows as emissions standards are reduced. The program takes into account all of these points: new engine technologies are represented, reformulated Fischer-Tropsch fuel is included in the diesel experimental fuel matrix, oxygenated compounds are included in the gasoline fuel matrix, fuel sulfur contents are low, etc.

2 EXPERIMENTS

2.1 Gasoline Fuel Formulation

In order to study the impact of fuel composition with no interference of other physical properties, the study was led using a fuel matrix based on an experimental blending design. The first step of the work was to build this matrix and especially to define the factors used (number and type of refinery basis), the variation ranges of each factor and the characteristics of the blends (number of blends, physical properties, etc.).

2.1.1 Factors Identification (Number and Nature)

In order to give information and orientation for future fuel formulation in terms of refinery composition, seven bases have been chosen, which are representative of the batch that will be used in the next years:

- an alkylate (noted “ALK”), constituted of C7+ isoparafins;
- a fuel from olefins oligomerization process (noted “DIM”);
- a fuel from catalytic cracking process (noted “FCC”), composed of C7+ olefins, but also from aromatic compounds;
- a C7/C8 reformate (light reformate, noted “LR”);
- a C9+ reformate (heavy reformate, noted “HR”);
- an oxygenated compound: ETBE.

2.1.2 Determination of Variation Range for Each Factor

Two objectives were considered while defining variation ranges for each parameter:

- to obtain the largest experimental range;
- to ensure the correct operation of the engine.

The resulting compromise is quoted in Table 1.

| Parameters (refinery bases) | Theoretical range of variation (% volume) |
|-----------------------------|------------------------------------------|
| Heavy reformate              | 0-30                                     |
| Light reformate              | 0-30                                     |
| FCC                         | 0-20                                     |
| Dimate                      | 0-20                                     |
| Alkylate                     | 0-40                                     |
| Isomerate                    | 0-40                                     |
| ETBE                         | 0-20                                     |

2.1.3 Fuel Selection (Number, Formulation and Properties)

The minimum number of blends in order to calculate all the factors of the correlations is equal to the number of factors (7 in our case). In order to maximize the p-value for these calculation, eleven blends were produced: ten fuels for the limits of the experimental field and a center fuel. This center fuel is used for three main aims:

- to extend the mathematical model obtained to the complete experimental field described by the matrix (and not only to the border of this experimental field);
- to calculate emissions measurement repeatability. Actually, in order to obtain statistical and significant trends, it is essential to quantify this repeatability. A general isovariance hypothesis has been chosen, assuming that the repeatability does not depend on the blend composition;
- to evaluate the eventual bias of the study during the tests with the same center fuel. That is why this fuel is tested at the beginning, at the middle and at the end of the program.

Moreover, this center fuel represents a typical fuel composition for the next years.
2.1.4 Complementary Constraints

In order to stay close to present regulation and to ensure good cold engine start and driveability, two more constraints have been imposed:

- the total olefinic content (dimate and FCC) must stay below a 20% vol. limit, in order to be close to the Euro III regulation on olefinic content (18% vol.);
- the Reid vapor pressure must be above 35 kPa in order to avoid engine stalling at the beginning of the MVEG cycle.

The main properties of the selected refinery bases are detailed in Table 2.

### TABLE 2

| Refinery bases properties |
|---------------------------|
| Parameters (refinery bases) | Density (at 15°C) (kg/m³) | Octane number (RON, measured twice on a CFR engine) | RVP (kPa) |
| Heavy reformate            | 877                        | 110                                     | 1.3       |
| Light reformate            | 829                        | 103                                     | 6.6       |
| Dimersol                   | 682                        | 96.2                                    | 68.5      |
| FCC                       | 755                        | 88.5                                    | 14.8      |
| Isomerate                  | 649                        | 82.5                                    | 50.8      |
| Alkylate                   | 701                        | 95.2                                    | 101.4     |
| ETBE                      | 750                        | 115                                     | 38.8      |

In this table, the low vapor pressure of the FCC and reformate bases are to be outlined: in order to ensure the RVP limitation each blend of the calculated experimental design contains alkylate or isomerate (high volatility). This blend matrix is represented in Table 3.

### TABLE 3

| Experimental design (% volume) |
|-------------------------------|
| Isom. | Alk. | Dim. | FCC | Reformate C₃/C₄ | Reformate C₅ | ETBE |
| 1     | 0.300 | -    | -   | 0.200         | -            | 0.300 | 0.200 |
| 2     | 0.300 | -    | 0.200 | 0.300        | -            | 0.300 | 0.200 |
| 3     | 0.400 | -    | -   | -             | 0.300        | 0.300 | -    |
| 4     | 0.400 | 0.400 | 0.200 | -            | -            | -    | -    |
| 5     | 0.400 | 0.400 | -   | -             | -            | 0.300 | 0.200 |
| 6     | 0.300 | 0.400 | -   | -             | -            | 0.300 | 0.200 |
| 7     | 0.100 | 0.400 | 0.200 | 0.300        | -            | -    | 0.200 |
| 8     | 0.400 | 0.400 | -   | -             | 0.200        | -    | 0.200 |
| 9     | -    | 0.300 | 0.200 | -            | -            | 0.300 | 0.200 |
| 10    | 0.035 | 0.400 | -   | -             | 0.300        | 0.065 | 0.200 |

* C: Center blend.

Furthermore, due to the FCC high sulfur content (200 ppm), some variations of the blends effect on engine running and pollutant emissions could be linked to blends sulfur content variations and not to fuel composition, as outlined in the EPEFE program [6]. In order to avoid this phenomenon, the sulfur content of all the blends has been adjusted to a level close to 60 ppm by DMDS (dimethyldisulfide) addition.

The main physico-chemical properties of the 11 fuels are presented in Table 4.

The Table 4 shows that large differences exist between the blends properties: the RON values are between 94 and 104, the density between 676 and 775. Nevertheless, the correlation matrix, presented on Table 5, shows that the only
This decorrelation between fuel composition and physical properties ensures that the effects measured on pollutant emissions are not due to physical properties of the blends but mainly to refinery base effects.

The detailed chemical composition of these different fuels is given in Table 6. Measurements were achieved by gas chromatography.

| TABLE 5 |

| Correlation matrix between fuel composition and physical properties |

|         | HR | LR | Dim. | FCC | Alk. | Iso. | ETBE | RON | Dens. | RVP | IBP | FBP | H/C |
|---------|----|----|------|-----|------|-----|------|-----|-------|-----|-----|-----|-----|
| HR      |    |    |      |     |      |     |      |     |       |     |     |     |     |
| LR      |    |    |      |     |      |     |      |     |       |     |     |     |     |
| Dim.    |    |    |      |     |      |     |      |     |       |     |     |     |     |
| FCC     |    |    |      |     |      |     |      |     |       |     |     |     |     |
| Alk.    |    |    |      |     |      |     |      |     |       |     |     |     |     |
| Iso.    |    |    |      |     |      |     |      |     |       |     |     |     |     |
| ETBE    |    |    |      |     |      |     |      |     |       |     |     |     |     |
| RON     |    |    |      |     |      |     |      |     |       |     |     |     |     |
| Dens.   |    |    |      |     |      |     |      |     |       |     |     |     |     |
| RVP     | 0.87 | | | | | | | | -0.87 | | | |
| IBP     | | | | | | | | | | | | | |
| FBP     | 0.85 | | | | | | | | | | | | |
| H/C     | | | | | | | | | | | | | |

| TABLE 6 |

| Fuel matrix detailed chemical composition |

|  | 1   | 2   | 3   | 4   | 5   | 6   | 7   | 8   | 9   | 10  | Center |
|---|-----|-----|-----|-----|-----|-----|-----|-----|-----|------|--------|
| n-paraffin | 5.20 | 5.96 | 6.82 | 8.31 | 8.37 | 5.88 | 5.72 | 8.23 | 1.66 | 3.91 | 4.86 |
| i-paraffin | 25.59 | 30.74 | 28.66 | 71.05 | 62.31 | 51.78 | 50.67 | 52.03 | 29.50 | 39.02 | 36.3 |
| Naphthenic compounds | 5.63 | 2.72 | 3.38 | 4.10 | 4.00 | 2.95 | 4.75 | 7.56 | 0.35 | 1.21 | 3.21 |
| Aromatic compounds | 40.10 | 27.78 | 60.98 | 2.53 | 2.42 | 39.13 | 34.52 | 6.51 | 36.12 | 39.40 | 36.3 |
| Olefinic compounds | 4.56 | 12.77 | 0.12 | 13.75 | 1.13 | 0.05 | 4.12 | 5.11 | 12.20 | 0.41 | 6.21 |
| Oxygenated compounds | 18.92 | 20.02 | 0.04 | 0.26 | 21.76 | 0.22 | 0.22 | 20.56 | 19.22 | 19.33 | 10.02 |
| C₂ | 0.78 | 0.79 | | | 0.84 | | | 0.79 | 0.76 | 0.76 | 0.40 |
| C₃ | 0.14 | 0.10 | 0.09 | 0.16 | 0.16 | | | 0.16 | 0.16 | 0.16 | 0.07 |
| C₄ | 0.62 | 0.63 | 0.32 | 2.42 | 2.75 | 1.89 | 1.91 | 1.69 | 1.73 | 2.22 | 1.54 |
| C₅ | 14.18 | 14.58 | 17.52 | 22.34 | 22.26 | 15.36 | 6.32 | 21.30 | 1.74 | 3.47 | 8.76 |
| C₆ | 31.10 | 48.75 | 13.68 | 37.38 | 37.83 | 11.99 | 7.55 | 38.82 | 36.39 | 20.99 | 23.13 |
| C₇ | 7.97 | 13.80 | 12.90 | 3.52 | 3.27 | 2.93 | 23.51 | 10.28 | 2.15 | 15.19 | 12.65 |
| C₈ | 8.31 | 20.52 | 19.55 | 30.89 | 29.44 | 27.84 | 55.26 | 23.68 | 19.77 | 45.66 | 30.24 |
| C₉ | 30.63 | 0.80 | 29.50 | 1.48 | 1.44 | 31.96 | 3.55 | 2.47 | 30.09 | 8.49 | 18.71 |
| C₁₀ | 5.95 | 5.78 | 0.39 | 0.42 | 6.39 | 0.45 | 0.26 | 6.11 | 1.25 | 3.70 | 3.70 |
| C₁₁ | 0.36 | 0.42 | 0.40 | 0.42 | 0.88 | 0.40 | 0.19 | 0.52 | 0.43 | 0.36 | 0.36 |
| C₁₂ | 0.07 | 0.04 | 1.08 | 1.15 | 0.71 | 1.04 | 0.50 | 0.56 | 1.38 | 0.41 | 0.41 |
| C₁₃ | 0.03 | 0.02 | 0.01 | 0.01 | | | | 0.03 | 0.01 | 0.03 | 0.03 |
| C₁₄ | | | | | | | | | | | 0.1 |
| C₁₅ | | | | | | | | | | | |
2.2 Diesel Fuel Formulation

For diesel fuels formulation, the same methodology than for gasoline fuels have been used.

2.2.1 Factors Identification (Number and Nature)

As for gasoline fuel matrix, the main objective was to select the refinery bases that could be the most interesting and the most suitable among those of the next twenty years in the refinery possibilities. In this context, the factors of the diesel fuel matrix (the parameters of the study) are different refinery bases. Six of them have been selected to build the experimental blending design:

- a straight-run (noted SR): it is a direct distillation diesel fuel;
- a hydro-cracked product (noted HDC);
- a light cycle oil (noted LCO);
- a diesel fuel issued from hydro-conversion of vacuum distillation residues (noted HCVDR);
- a kerosene (noted kero.);
- a diesel fuel coming from a Fischer-Tropsch process (noted FT).

2.2.2 Determination of Variation Range for Each Factor

The range of variation of each basestock, chosen in order to be the largest while maintaining the correct operation of the engine, is quoted in Table 7.

| Parameters (refinery bases) | Theoretical range of variation (% volume) |
|-----------------------------|------------------------------------------|
| Straight-run                | 50-100                                   |
| Hydro-cracked product       | 0-50                                     |
| LCO                         | 0-30                                     |
| Hydro-conversion of vacuum distillation residue | 0-50 |
| Kerosene                    | 0-50                                     |
| Fischer-Tropsch             | 0-50                                     |

All the fuels of the experimental matrix are blended with at least 50% vol. of straight-run in order to obtain a “classic” distillation range for each diesel fuel. The other bases content evolved between 0 and 50% vol., except for the LCO (0-30% vol.).

2.2.3 Complementary Constraints

Furthermore, in order to be representative of fuels of the over next twenty-years and to anticipate as far as possible the Euro IV specifications, two other objectives were assigned to the blending, resulting in certain constraints on some parameters:

- the cetane number measured on a CFR engine had to be higher than 54.0 for the eleven diesel fuels;
- the sulfur content had to be lower than 100 ppm for the eleven diesel fuels (the 50 ppm limit for Euro IV had not been decided when this value was chosen. However, in fact the average sulfur content obtained was lower than 50 ppm). This is the reason why four of the six bases have been hydro-desulfurised to pass the 100 ppm maximum requirement (Table 8). The sulfur content ranged from lower than 5 ppm to 85 ppm. However, no adjustment was required since all the fuels contain at least 50% of the SR base, thus ensuring a rather small variation of sulfur content.

The main properties of the selected refinery bases are detailed in Table 8.

| Refinery bases properties |
|---------------------------|
| Parameters (refinery bases) | Density (at 15°C) | Cetane number (measured on a CFR engine) | Sulfur content (ppm) |
|-----------------------------|-------------------|-----------------------------------------|---------------------|
| Straight-run                | 0.844             | 49.5                                    | 65                  |
| Hydro-cracked product       | 0.817             | 62.6                                    | < 5                 |
| LCO                         | 0.885             | 23.3                                    | 85                  |
| Hydro-conversion of vacuum distillation residue | 0.852 | 44.4 | 60 |
| Kerosene                    | 0.790             | 46.5                                    | 50                  |
| Fischer-Tropsch             | 0.761             | 82.8                                    | < 5                 |

It must be pointed out that, except for the hydrocracked and the Fischer-Tropsch fuels, the base cetane numbers remained quite low in spite of a rather severe hydro-desulfurization.

In this context, the experimental design is represented in the Table 9.

| Experimental design (% vol.) |
|-----------------------------|
| Parameters | SR | HDC | LCO | HVDR | Kero. | FT |
|-------------|----|-----|-----|------|-------|----|
| G1          | 0.5|     |     |      |       |    |
| G2          | 0.5| 0.5 |     |      |       |    |
| G3          | 0.5|     | 0.204|      |       | 0.296|
| G4          | 0.865|     |      | 0.316|       | 0.135|
| G5          | 0.5|     |      |      | 0.335| 0.165|
| G6          | 0.5|     |      |      |       |    |
| G7          | 0.5| 0.474| 0.026|      |       | 0.068|
| G8          | 0.761| 0.172|      | 0.231| 0.083|    |
| G9          | 0.5| 0.186|      | 0.072| 0.077| 0.107|
| G10         | 0.5| 0.201| 0.043|      |       |    |
| Center      | 0.552| 0.205| 0.026| 0.043| 0.046| 0.128|
The previous mentioned constraint on the cetane number led to the following variation ranges:
- straight-run: 50-86.5% vol.;
- hydro-cracked product: 0-50% vol.;
- LCO: 0-20.4% vol.;
- diesel fuel issued from hydro-conversion of vacuum distillation residue: 0-31.6% vol.;
- kerosene: 0-33.5% vol.;
- diesel fuel coming from a Fischer-Tropsch process: 0-50% vol.

These variation ranges are a little less extensive than the theoretical ones.

The main physico-chemical properties of the 11 fuels are presented in Table 10.

Furthermore, with the low sulfur contents obtained by hydro-desulfurization, it appeared necessary to add 150 mg/l of a lubricity improver additive in every fuel (from Octel) to comply with the HFRR test specification of wear scar diameter under 460 µm.

The detailed chemical composition of these different fuels is given in the Table 11. Measurements were achieved by mass spectrometry.

### 2.2.4 Additional Diesel Fuels Tested

To complete the diesel fuel matrix, three other fuels have also been blended outside the main matrix:

- a fuel containing 80% vol. of the matrix “center” diesel fuel and 20% vol. of rapeseed methyl ester (RME);
- a fuel containing 80% vol. of the matrix “center” diesel fuel and 20% vol. of a naphthenic base;
- a diesel fuel issued from the Fischer-Tropsch process without any blending with another product or base.

The main physico-chemical properties of these three complementary diesel fuels are presented in Table 12.

### 2.3 Engines and Vehicles Characteristics and Test Procedures

#### 2.3.1 Spark-Ignition Engines

**Vehicle Characteristics**

Two engines and corresponding vehicles have been tested, whose main characteristics are described in the two following subsections.

The first tests were carried out on a Honda VTEC-E engine, whose main characteristics are:

- engine type: lean burn PFI gasoline engine, fitted on passenger car;
- 4 cylinders, 4-stroke;
- displacement: 1493 cm³;
- bore × stroke = 75 × 84.5 mm;
- compression ratio: 9.6/1;

### 2.3.2 Diesel Engines and Vehicles

**Vehicle Characteristics**

Three diesel engines and corresponding vehicles have been tested, whose main characteristics are described in the two following subsections.

The first tests were carried out on a Ford FTEC-E engine, whose main characteristics are:

- engine type: direct injection PFI diesel engine, fitted on passenger car;
- 4 cylinders, 4-stroke;
- displacement: 1800 cm³;
- bore × stroke = 73 × 84.5 mm;
- compression ratio: 20/1;

### Table 10

|                  | G1     | G2     | G3     | G4     | G5     | G6     | G7     | G8     | G9     | G10    | Center |
|------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Density (at 15°C)| 0.8021 | 0.8304 | 0.8266 | 0.8320 | 0.8310 | 0.8115 | 0.8317 | 0.8331 | 0.8192 | 0.8278 | 0.8267 |
| Cetane number    | 68.0   | 52.2   | 53.6   | 53.7   | 55.8   | 54.2   | 54.0   | 53.5   | 53.1   | 53.8   | 53.9   |
| Sulfur content (ppm wt) | 23    | 24    | 41    | 54    | 47    | 43    | 30    | 41    | 31    | 36    | 36    |
| Distillation curve: |       |        |       |        |        |        |        |        |        |        |        |
| BP (°C)          | 197.4  | 188.2  | 179.3  | 188.9  | 192.4  | 160.6  | 184.4  | 188.6  | 166.1  | 179.7  | 182.7  |
| % 5% (°C)        | 215.0  | 218.6  | 205.5  | 217.9  | 216.4  | 185.7  | 215.4  | 218.1  | 192.5  | 204.4  | 210.5  |
| % 50% (°C)       | 247.9  | 266.1  | 246.9  | 258.7  | 261.2  | 235.5  | 264.8  | 261.7  | 247.4  | 256.6  | 257.4  |
| % 95% (°C)       | 302.3  | 343.0  | 307.0  | 316.7  | 326.5  | 303.5  | 339.3  | 328.4  | 324.4  | 329.4  | 327.2  |
| FBP (°C)         | 323.3  | 350.1  | 326.6  | 330.5  | 337.5  | 317.7  | 351.2  | 341.3  | 338.5  | 344.8  | 336.1  |
| Viscosity (40°C, mm²/s) | 2.139 | 2.838  | 2.062  | 2.509  | 2.528  | 2.269  | 2.784  | 2.649  | 2.110  | 2.392  | 2.447  |
| LHV* (kJ/kg)     | 43.187 | 43.284 | 42.504 | 43.278 | 43.164 | 43.314 | 43.249 | 43.068 | 43.247 | 42.794 | 43.165 |
| wt% C            | 85.6   | 86.1   | 86.4   | 86.5   | 86.7   | 85.4   | 85.8   | 85.8   | 86.0   | 85.7   | 86.0   |
| wt% H            | 14.2   | 13.6   | 13.6   | 13.3   | 12.8   | 13.6   | 13.2   | 13.3   | 13.4   | 13.6   | 13.5   |
| wt% O            | <0.2   | <0.2   | <0.2   | <0.2   | <0.2   | <0.2   | <0.2   | <0.2   | <0.2   | <0.2   | <0.2   |
| “H/C” ratio      | 1.977  | 1.882  | 1.876  | 1.832  | 1.759  | 1.898  | 1.833  | 1.847  | 1.857  | 1.891  | 1.870  |

* LHV = Low heating value.
**TABLE 11**

Fuel matrix detailed chemical composition

|                  | G1   | G2   | G3   | G4   | G5   | G6   | G7   | G8   | G9   | G10  | Center |
|------------------|------|------|------|------|------|------|------|------|------|------|--------|
| Paraffins        | 67.6 | 38.6 | 49.1 | 41.8 | 44.0 | 49.9 | 37.8 | 39.3 | 44.1 | 12.5 | 43.7   |
| Naphthenes (1 cycle) | 5.0  | 26.2 | 8.1  | 17.6 | 14.1 | 14.5 | 25.2 | 21.5 | 19.9 | 18.0 | 18.8   |
| Naphthenes (> 1 cycle) | 12.3 | 15.2 | 10.9 | 14.9 | 13.6 | 12.8 | 15.1 | 15.1 | 13.7 | 13.8 | 13.9   |
| Naphthenes      | 17.3 | 41.4 | 19.0 | 32.5 | 27.7 | 27.3 | 40.3 | 36.6 | 33.6 | 31.8 | 32.7   |
| Alkylbenzenes   | 5.6  | 8.3  | 12.0 | 9.7  | 11.7 | 12.1 | 8.8  | 9.2  | 10.9 | 10.8 | 9.8    |
| Indanes/tetralines | 6.2  | 7.9  | 12.3 | 10.0 | 9.5  | 7.1  | 8.5  | 9.5  | 7.5  | 9.3  | 8.9    |
| Indenes         | 1.3  | 1.3  | 1.8  | 2.3  | 2.2  | 1.3  | 1.4  | 2.0  | 1.2  | 1.8  | 1.5    |
| Monoaromatics   | 13.1 | 17.5 | 26.1 | 22.0 | 23.4 | 20.5 | 18.7 | 20.7 | 19.6 | 21.9 | 20.2   |
| Naphthalenes    | 1.3  | 1.7  | 4.5  | 2.2  | 2.3  | 1.7  | 2.1  | 2.1  | 1.8  | 2.5  | 2.2    |
| Acenaphthenes/diphenyles | 0.5  | 0.5  | 0.9  | 1.0  | 1.6  | 0.5  | 0.7  | 0.8  | 0.5  | 0.8  | 0.9    |
| Acenaphthylenes/fluorenes | 0.2  | 0.2  | 0.3  | 0.4  | 0.8  | 0.1  | 0.3  | 0.4  | 0.3  | 0.4  | 0.2    |
| Di-aromatics     | 2.0  | 2.4  | 5.7  | 3.6  | 4.7  | 2.3  | 3.1  | 3.3  | 2.6  | 3.7  | 3.3    |
| Tri-aromatics    | 0.0  | 0.1  | 0.1  | 0.1  | 0.1  | 0.0  | 0.1  | 0.1  | 0.1  | 0.1  | 0.1    |
| (di)benzo-thiophenes | 0.0  | 0.0  | 0.0  | 0.0  | 0.1  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0    |
| Polyaromatics (> tri) | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0    |

**TABLE 12**

Main physico-chemical properties of complementary tested fuels

|                        | Center | Centre 80% vol. | Centre 80% vol. | Fischer-Tropsch |
|------------------------|--------|-----------------|-----------------|-----------------|
| Density (at 15°C)      | 0.8267 | 0.8373          | 0.8327          | 0.7608          |
| Cetane number measured on CFR engine | 53.9  | 56.6            | 50.8            | > 73.7          |
| Sulfur content (ppmwt) | 36     | 40              | 39              | < 5             |
| Distillation curve:    |        |                 |                 |                 |
| IBP (°C)               | 182.7  | 184.8           | 190.1           | 203.7           |
| T 5% (°C)              | 210.5  | 215.6           | 215.9           | 214.3           |
| T 50% (°C)             | 25.74  | 274.0           | 254.6           | 232.6           |
| T 95% (°C)             | 327.2  | 338.6           | 322.4           | 265.0           |
| FBP (°C)               | 336.1  | 344.6           | 331.0           | 272.9           |
| Viscosity (40°C, mm²/s) | 2.447  | 2.748           | 2.483           | 1.770           |
| LHV (kJ/kg)            | 43165  | 42.547          | 42.657          | 44.237          |
| wt% C                  | 86.0   | 84.3            | 86.6            | 84.6            |
| wt% H                  | 13.5   | 13.4            | 13.4            | 15.0            |
| wt% O                  | < 0.2  | 2.3             | < 0.2           | 0.3             |
| “H/C” ratio            | 1.870  | 1.894           | 1.844           | 2.113           |
maximum power: 84kW at 6500 rpm;
maximum torque: 138 N·m at 5200 rpm.

Vehicle tests were carried out using a Honda Civic 1.5 Lsi, whose mileage was 12 000 km.

The second tested engine was a Renault F4P. The characteristics of this engine are:
- engine type: stoichiometric PFI gasoline engine, fitted on passenger car;
- 4 cylinders, 4-stroke;
- displacement: 1783 cm³;
- bore x stroke = 82.7 x 83 mm;
- compression ratio: 9.8/1;
- maximum power: 88 kW at 6500 rpm;
- maximum torque: 165 N·m at 3750 rpm.
- depollution level: Euro III.

Vehicle tests were carried out using a Renault Laguna whose mileage was 9000 km.

Test Procedure
On an engine bench, all the tests were performed at steady state engine conditions on different operating points:
- Running conditions 1 (Pt1): 2000 rpm - BMEP = 3 bar, standard tuning: \( R^1 = 1 \), spark advance = 33°CA, w/o EGR.

At each test point, engine running parameters variations have been conducted. These variations are adapted from the engine map (Table 13).
- Running conditions 2 (Pt2): 3000 rpm - BMEP = 5.0 bar, standard tuning: \( R^1 = 1 \), spark advance = 45°CA, w/o EGR

Engine running parameters variations (Table 14).

For each operating condition, all the engine parameters were set to their map values and the BMEP was maintained to its original set-up by variations of the throttle opening.

1 In the whole paper, \( R \) refers to the equivalence ratio i.e. \( 1/\lambda \).

Engine-out pollutant emissions (CO, HC, NOx), CO₂ emissions, fuel consumption were recorded for each point.

For the vehicle, all the tests were performed over the MVEG-11s driving cycle (Euro III).

2.3.2 Passenger Car Compression-Ignition Engine

Engine Characteristics

Engine tests were carried out on a turbocharged Renault G8T engine, equipped with EGR but without catalytic converter, whose main characteristics were:
- engine type: indirect diesel engine, fitted on passenger car
- 4 cylinders, 4-stroke;
- displacement: 2188 cm³;
- bore x stroke = 87 x 92 mm;
- compression ratio: 22/1;
- maximum power: 82 kW at 4000 rpm;
- maximum torque: 240 N·m at 2500 rpm.
- depollution level: Euro III.

Vehicle tests were carried out on a Laguna model 1997 car (equipped with the G8T engine), with the following characteristics:
- vehicle inertia: 1590 kg;
- mileage of the vehicle at the beginning of the tests: approximately 9000 km;
- equipped with an oxidation catalytic converter.

Test Procedure
On an engine bench, all the tests were performed in steady state engine conditions on different operating points:
- a complete full-load curve, from 1500 to 4000 rpm with a step of 500 rpm, in the standard tuning conditions of the mapping;
- 2 partial loads running conditions:
  * running conditions 1 (Pt1): 2000 rpm - BMEP = 2.0 bar, with different levels of injection timings (–4, –2, +0, +2,

### TABLE 13

| Test procedure (for running conditions 1) |
|------------------------------------------|
| VTEC engine | F4P engine |
|--------------|------------|
| Equivalence ratio variations (0.65 \( \rightarrow \) 1), without EGR | Equivalence ratio variations (0.95 \( \rightarrow \) 1.05) |
| EGR rate variation \( (0\% \rightarrow 15\%) \)* | Spark timing variation for each equivalence ratio \( (–25° \rightarrow –40°) \)* |
| Spark timing variation \( (–20° \rightarrow –40°) \)** | Injection timing variation \( (–100° \rightarrow –200°) \), ** |
| End of injection timing variation \( (–100° \rightarrow 200°) \)** | End of injection timing variation \( (–100° \rightarrow 200°) \), ** |

* at stoichiometric conditions
** variation conducted for two conditions: stoichiometric running with EGR (20%) and lean-burn running without EGR
*** for injection timing variations, the angle is given compared with intake TDC.

### TABLE 14

| Test procedure (for running conditions 2) |
|------------------------------------------|
| VTEC engine | F4P engine |
|--------------|------------|
| Equivalence ratio variations (0.65 \( \rightarrow \) 1), without EGR | Equivalence ratio variations (0.95 \( \rightarrow \) 1.05) |
| EGR rate variation \( (0\% \rightarrow 15\%) \)* | Spark timing variation for each equivalence ratio \( (–25° \rightarrow –40°) \)* |
| Spark timing variation \( (–20° \rightarrow –40°) \)* | End of injection timing variation \( (–100° \rightarrow –200°) \), ** |
| End of injection timing variation \( (–100° \rightarrow 200°) \)** | End of injection timing variation \( (–100° \rightarrow 200°) \), ** |

* at stoichiometric conditions
** for injection timing variations, the angle is given compared with intake TDC.
+4 and +6 °CA from the standard tuning conditions of the mapping) and of EGR rate (15, 30, 35, 40 and 50%);

- running conditions 2 (Pt2): 3000 rpm - BMEP = 4.0 bar in the mapping conditions, with different levels of start of injection (–4, –2, +0, +2 and +4°CA from the standard tuning conditions of the mapping).

For the vehicle, all the tests were performed over the MVEG-11s driving cycle (Euro III).

2.3.3 Heavy Duty Engine Characteristics

Engine Characteristics

The heavy-duty engine used in this part of the study was a MIDR 062045 manufactured by Renault Véhicules Industriels, certified to Euro II (1996) pollutant emission level. A detailed description of the engine is provided in Table 15.

| Type | MIDR 062045 |
|------|-------------|
| Displacement | 9.8 l |
| Number of cylinders | 6 |
| Compression ratio | 17/1 |
| Bore × Stroke | 120 × 145 (mm) |
| Max. power output | 190 kW (at 2100 rpm) |
| Maximum torque | 1040 N·m (at 1400 rpm) |
| Injection type | Direct, inline pump |
| Other information | Intercooled turbo-charging |
| | No exhaust-gas recirculation |
| | No after treatment device |

Heavy Duty Engine Test Procedures

The tests have been carried out using mainly two certification test cycles of the next step of the European regulation on exhaust-gases regulation called Euro III. These cycles are ESC, for European steady-state cycle, that will replace the ECE R49 13 modes on 1/1/2000, and ELR for European load response, in use at the same date.

Both cycles use mainly three engine speeds (noted A, B, C), and are described as follows. A domain of engine speeds is defined for each engine type. The lower limit N1 is the speed below the rated speed that gives half the maximum power. The upper limit N2 is the speed above the rated speed that leads to a 30% loss of power compared with the maximum power. This domain is divided into four equal parts, delimited successively by N1, A, B, C and N2.

ELR is a transient cycle, used to characterize dynamic response black smoke opacity (Fig. 1). During ELR, torque is raised from 10 to 100% within less than two seconds, three times consecutively for each engine speed A, B and C as described on Figure 2.

ESC is used to measure particulate, NOx, HC and CO emissions throughout the mean measures of thirteen steady-state conditions. Idle is one of these conditions. The others are defined by the engine speed (A, B and C) and the torque: 25, 50, 75 and 100% of the maximum available torque at the corresponding engine speed.

Last, full load conditions over the entire range of speed from 900 up to 2100 rpm and five of the most important points of this cycle were also studied. The five points are A100, B50, B75, C25 and C100, each tested with five different injection timings. Beside the measurement of regulated pollutants, smoke opacity, combustion noise, specific fuel consumption and carbon dioxide emissions were also evaluated.
Differences in heating value and specific gravity of the 11 blends do not lead to any significant variation in the maximum torque, so similar torque levels were used for all blends over the entire range of test conditions.

### 2.4 Gas Analysis Methods

For engine tests, raw exhaust gases were sampled through a 180°C heated line equipped with a heated filter. Five analysis tools were used:
- a flame ionization detector (FID) for total hydrocarbon emissions;
- two nondispersive infrared detectors (NDIR) for CO and CO₂ emissions;
- a chemiluminescence detector for NOx emissions;
- a paramagnetic analyzer for oxygen.

For vehicle tests, car emissions and fuel consumption were measured on a chassis dynamometer using the modified MVEG cycle with the initial 40 s idle period removed. The test emissions used for exhaust dilution, sample collection and sample analysis diluted gases conforms to the specifications of directive 70/220/EEC and its amendments. Diluted gases were sampled in bags and analyzed with a Horiba Mexa 9000. Nonregulated pollutant emissions were analyzed using gas chromatography of samples taken in specific bags (HC) or HPLC with UV detector of gases collected on sample cartridges (oxygenated compounds).

### 2.5 Test Methodology and Principle of Results Exploitation

The main objective of the statistical analysis of this study is to determine a model for each pollutant based on mathematical relationships of this form:

$$ A = \sum_{i=1}^{N} \alpha_i \times C_i $$

where $A$ is either:
- the regulated pollutant emissions (CO, HC, NOx and particles mass for diesel tests);
- the unregulated pollutant emissions for vehicle tests (ozone forming potential, aldehyde identification, and individual unburned hydrocarbons);
- the CO₂ emissions and the fuel consumption on the driving cycle, and the BSFC of the engine;
- each refinery base of the program;
- concentration of the “$i$” refinery base in the fuel (% vol.);
- contribution of the “$i$” refinery base to emissions, expressed in % ($i = 100\%$ within each model);
- total number of basestocks (6 for diesel blend matrix, 7 for gasoline blend matrix).

These models give mathematical linear regressions. Interactions between the different parameters of the matrix are not taken into account, since their effects are second-order in an experimental blending design. For each model, the correlation factor $R^2$ and the $p$-value of the model are given. Only the models characterized by a “$100 \times (1-p$-value)” higher than 80% have been selected to define the impact of the fuel formulation. In the following pages, the results are given in terms of contribution of each base (expressed in percentage) in the model for each pollutant, as shown in the following example, for gasoline tests (Table 16).

#### TABLE 16

| 1-p-value | Correlation example: ozone formation potential (g/km) for the Laguna vehicle on the MVEG cycle |
|-----------|-----------------------------------------------------------------------------------------------|
| 90 < 95   | $R^2$                                                                  |
|           | HR 23% (0.300)                                                                    |
|           | LR 20% (0.261)                                                                    |
|           | Dim. 20% (0.267)                                                                   |
|           | FCC 0% (0)                                                                         |
|           | Alk. 5% (0.060)                                                                    |
|           | Isom. 22% (0.290)                                                                   |
|           | ETBE 10% (0.132)                                                                   |

In this table, the values between brackets represent the coefficient of each base in the linear correlation. For example, the ozone formation potential in this case can be expressed as:

$$ \text{OFP (g/km)} = 0.3 \times X_{HR} + 0.29 \times X_{\text{isom}} + 0.261 \times X_{LR} + \ldots $$

with $X_i$ proportion of the base in the blend.

The results are also expressed in terms of percentage contribution of each base to the pollutant emissions. As the blends are composed with 7 refinery bases, the mean value of this contribution is around 14%. A base with a contribution higher than this mean value is designed as a high contributor, which means that adding such a base to a blend will tend to raise the emissions of the pollutant.

It must be outlined that those correlations, calculated according a blend design, are valid only inside the limits defined during the creation of the blend matrix.

### 3 RESULTS

#### 3.1 Spark-Ignition Engines

##### 3.1.1 First Engine: Lean-Burn PFI Engine

All the blends were tested on the map point and with the engine running parameters variations described above.

The study of the results lead to curves such as the one presented in Figure 3. The HC emissions (g/kWh) obtained
for the three tests with center blend and for the test with blend 3 are presented.

The differences observed between the three center blend tests give an evaluation of the repeatability of the method. As a general isovariance hypothesis has been chosen, the differences between the three center tests represent the repeatability for all the blends, including blend 3. As the HC emissions obtained with blend 3 are out of the repeatability interval, it can be concluded that there is a significant fuel effect.

Nevertheless, as the blends are formulated according to an experimental design, no conclusion can be drawn from the comparison of 2 blends: only statistical calculation can describe the effect of each refinery base on pollutant emissions.

**Carbon Monoxide Emissions**

On the vehicle (transient running), the influence of olefinic bases (FCC and dimate) on CO emissions *(Table 17)* is

| TABLE 17 |
| CO emission model: influence of each base (contribution in g/km or g/kWh) |
| | Vehicle test | Engine test |
| CO emissions | MVEG-11s cycle | ECE phase | EUDC phase | Pt1 (standard tuning) | Pt2 (standard tuning) |
| 1-\(p\)-value | 95% < 99% | 99 < 99.9 | – | – | 81% |
| \(R^2\) | 0.85 | 0.93 | – | – | 0.76 |
| HR | 2% (0.11) | 0% (–0.13) | – | – | 15% (15.9) |
| LR | 17% (0.88) | 17% (1.82) | – | – | 19% (19.9) |
| Dim. | 24% (1.23) | 26% (2.87) | – | – | 11% (12.1) |
| FCC | 18.7% (0.96) | 19% (2.09) | – | – | 13% (13.7) |
| Alk. | 15% (0.77) | 15% (1.65) | – | – | 14% (15) |
| Isom. | 21.4% (1.1) | 23% (2.49) | – | – | 15% (16) |
| ETBE | 1.6% (0.08) | 0% (–0.36) | – | – | 13% (14.1) |

| TABLE 18 |
| HC emission model: influence of each base (contribution in g/km or g/kWh) |
| | Vehicle test | Engine test |
| HC emissions | MVEG-11s cycle | ECE phase | EUDC phase | Pt1 (standard tuning) | Pt2 (standard tuning) |
| 1-\(p\)-value | 99 < 99.9 | 99 < 99.9 | 99 < 99.9 | > 99.9 | 99 < 99.9 |
| \(R^2\) | 0.95 | 0.99 | 0.9 | 0.99 | 0.96 |
| HR | 26% (0.19) | 28% (0.487) | 16% (0.022) | 26% (8.6) | 40% (9) |
| LR | 22% (0.16) | 23% (0.398) | 15% (0.021) | 17% (5.5) | 15% (3.4) |
| Dim. | 7% (0.05) | 7% (0.126) | 0% (–0.014) | 15% (4.8) | 9% (2) |
| FCC | 15% (0.11) | 16% (0.281) | 0% (–0.013) | 11% (3.5) | 6% (1.4) |
| Alk. | 15% (0.11) | 14% (0.249) | 25% (0.034) | 12% (3.8) | 10% (2.3) |
| Isom. | 12% (0.09) | 12% (0.216) | 17% (0.024) | 10% (3.1) | 12% (2.7) |
| ETBE | 4% (0.03) | 0% (–0.016) | 27% (0.038) | 10% (3.2) | 8% (1.8) |
strong (around 20%), when the heavy reformate contribution is very low. On the engine, only the correlation calculated on the second test point is significant, and the differences between bases are less acute.

**Unburned Hydrocarbons Emissions**
Unlike for CO emissions, unburned hydrocarbons (Table 18) are mainly produced by aromatic products (reformate), and the contribution of FCC and dimate are very low, especially in warm conditions (EUDC cycle and Pt2).

**Nitrogen Oxides Emissions**
The correlations calculated for NOx emissions (Table 19) are close to those calculated for HC emissions: the reformates are the greatest contributors to NOx emissions while ETBE has the lowest contribution for most running points.

**Carbon Dioxide Emissions**
The contributions of the refinery bases on CO2 emissions (Table 20) are closely linked to H/C ratio and are similar on each phase of the MVEG cycle. ETBE has a higher contribution on CO2 emissions, due to its low heating value.

**Unregulated Pollutant Emissions**
For each blend, a set of more than 150 molecules concentration has been measured on MVEG cycle, including the TAP (toxic air pollutant). The calculation results for TAP are presented in Table 21.

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**Table 19**
NOx emission model: influence of each base (contribution in g/km or g/kWh)

| NOx emissions | Vehicle test | Engine test |
|---------------|--------------|-------------|
|               | MVEG-11s cycle | ECE phase | EUDC phase | Pt1 (standard tuning) | Pt2 (standard tuning) |
| l-p-value     | 99 < 99,9     | 99 < 99,9  | 95 < 99     | –               | 82%  |
| R²            | 0.89          | 0.97       | 0.88        | –               | 0.78  |
| HR            | 22% (0.16)    | 29% (0.153)| 20% (0.167) | –               | 8% (13.5) |
| LR            | 20% (0.14)    | 19% (0.101)| 19% (0.155) | –               | 18% (29.5) |
| Dim.          | 11% (0.08)    | 13% (0.065)| 13% (0.110) | –               | 23% (38.8) |
| FCC           | 10% (0.07)    | 13% (0.067)| 9% (0.077)  | –               | 18% (30.6) |
| Alk.          | 15% (0.11)    | 11% (0.057)| 15% (0.120) | –               | 7% (11.5)  |
| Isom.         | 14% (0.1)     | 10% (0.054)| 16% (0.132) | –               | 10% (17.5) |
| ETBE          | 7% (0.05)     | 4% (0.021)| 7% (0.057)  | –               | 15% (24.5) |

**Table 20**
CO₂ emission model: influence of each base (contribution in g/km)

| CO₂ emissions | Vehicle test |
|---------------|--------------|
|               | MVEG-11s cycle | ECE phase | EUDC phase |
| l-p-value     | 99 < 99,9     | 99 < 99,9  | 99 < 99,9  |
| R²            | 0.98          | 0.96       | 0.97       |
| HR            | 16% (162.9)   | 16% (213.6)| 16% (135.7)|
| LR            | 16% (160.9)   | 16% (211.8)| 15% (130.5)|
| Dim.          | 14% (140.4)   | 14% (186.4)| 13% (115.8)|
| FCC           | 14% (140.9)   | 14% (186.9)| 13% (116.6)|
| Alk.          | 13% (136.1)   | 13% (175.1)| 13% (112.5)|
| Isom.         | 13% (135.8)   | 13% (179.3)| 13% (110.6)|
| ETBE          | 14% (144.8)   | 14% (180.0)| 14% (117.9)|

**Table 21**
TAP emission model: influence of each base (contribution in mg/km, vehicle results)

| TAP emissions | Buta-1,3-diene | Benzene | Formaldehyde | Acetaldehyde |
|---------------|----------------|---------|--------------|--------------|
| l-p-value     | 90 < 95        | 95 < 99 | –            | 95 < 99      |
| R²            | 0.81           | 0.93    | –            | 0.95         |
| HR            | 24% (0.7)      | 38% (7.86)| –           | 13% (1)      |
| LR            | 6.8% (0.2)     | 34% (7.03)| –           | 1% (0.1)     |
| Dim.          | 24% (0.7)      | 4% (0.8) | –           | 8% (0.6)     |
| FCC           | 24% (0.7)      | 20% (4.07)| –           | 9% (0.7)     |
| Alk.          | 6.8% (0.2)     | 0% (0)  | –           | 3% (0.2)     |
| Isom.         | 0.7% (0.02)    | 3.9% (0.8)| –           | 4% (0.3)     |
| ETBE          | 13.7% (0.4)    | 0% (0)  | –           | 62% (4.8)    |
TAP emissions are directly linked to fuel chemical composition: for instance, more than 90% of benzene emissions are due to high aromatic content bases (HR, LR and FCC), 50% of the buta-1,3-diene come from olefinic basestocks and 62% of acetaldehyde emissions are due to ETBE.

**Effect of Engine Parameters Variations on Bases Contribution to Pollutant Emissions**

The correlation calculations have been led for all the engine running parameters. The main results of those calculation are summarized in Table 22. Each arrow indicates the effect of the engine parameter modification on each base contribution.

**TABLE 22**

Summary of engine running parameters variation on basestocks contributions

|          | ↓ Equivalence ratio | ↑ EGR | ↓ Spark advance |
|----------|---------------------|-------|----------------|
|          | HC                  | CO    | NOx            |
| HR       | ↓↓                 | ↑↑↑   | ↑↑↑            |
| LR       | ↓↓                 | ↓     | ↑              |
| Dim.     | ↑                  | ↓     | ↓              |
| FCC      | ↑↑                 | =     | ↓↓↓↓           |
| Alk.     | ↓                  | =     | ↑↑↑↑↑↑↑↑      |
| Isom.    | ↓↓                 | ↑↑     | =             |
| ETBE     | ↑↑↑↑               | =     | =             |

n.s.: not significant.

**Discussion on the Lean-Burn PFI Engine**

The results obtained on the Honda VTEC engine can be summarized as followed.

- For HC emissions, the heavy reformate and the light reformate have the strongest contribution, with up to 40% for HR in stabilized conditions. All the other refinery bases have an intermediate or low contribution. The case of olefinic bases (FCC and dimate) and of ETBE present some particularities: the contribution of dimate to HC emissions seems very sensitive to engine running conditions, with in particular a very low contribution in high temperature conditions. This phenomenon is particularly acute in transient conditions: the contribution of FCC to HC emissions is 16% on the ECE cycle and 0% in the EUDC cycle (as the blend matrix contains 7 fuels, the "mean value" for each fuel contribution is around 14%).

- For CO emissions, less information is available, due to the low p-value of most of the correlations. Nevertheless, it can be concluded from the tests that, unlike for HC emissions, aromatic bases induce low CO emissions in transient running conditions. The main contributor to carbon monoxide emissions is the fuel from olefin dimerization process (dimate), with a contribution up to 26%. Some effect of engine running conditions can also be found on ETBE behavior: the comparison of the results obtained on ECE and MVEG cycle seems to show that ETBE is one of the main contributor to CO emissions on the EUDC cycle (The results can be compared to those found on HC emissions were the contribution of ETBE on EUDC cycle is 27% while it is only 4% on MVEG cycle).

- For NOx emissions, the calculated correlations are close to those found on HC emissions: strong influence of aromatic bases, little influence of ETBE and increase of dimate and ETBE contribution in hot running points (EUDC cycle). The steady-state running point results are however quite different from those calculated on HC emissions, in particular with regard to the high contribution of dimate and FCC.

All the tests carried out on this engine have shown the influence of refinery bases choice on pollutant emissions for a lean-burn PFI engine. The main conclusions are following.

The strong link between NOx emissions and CO/HC emissions show that the main parameter to explain NOx emissions is not only the flame temperature of each base, but also the quality of the combustion. Indeed, if we compare results obtained for NOx and HC + CO emissions, the bases classification according to their contribution is inverted, which induces that a low contribution of a refinery base to NOx emissions is mainly due to incomplete combustion.

Heavy reformate is the strongest contributor to unburned hydrocarbons emissions, with a contribution up to 40% in hot running conditions (Pt2). Moreover, differences can be outlined in the combustion of aromatic bases (reformates) and olefinic bases (dimate): when incomplete combustion of dimate leads to CO emissions, the same phenomenon with reformates leads to HC emissions. Those two types of refinery bases lead to combustion difficulties. Moreover, the high contribution of dimate on NOx emissions seems to indicate that the combustion of olefinic bases is very fast (high combustion temperature peak) but incomplete. This phenomenon is particularly acute in transient running.

ETBE seems to have a relatively poor oxidation in low temperature conditions: a decrease of the equivalence ratio or an increase of the EGR rate induce an important growth of the ETBE contribution to HC emissions. The important increase of the impact of ETBE on HC emissions during the EUDC cycle shows that those oxidation difficulties are not linked to thermodynamic but kinetic considerations: unlike for olefinic
bases, the combustion of ETBE seems to be slow. The effect of a lowered spark advance on ETBE contribution to HC and CO emissions has to be linked to a drastic growth of exhaust temperature: as the combustion of this base is slow, decreasing the spark advance induces post-combustion of this base.

Unregulated pollutant emissions are closely linked to fuel composition, showing that the main source of hydrocarbon emissions is unburned fuel. On the other hand, some effects such as ETBE contribution on buta-1,3-diene indicate the existence of other hydrocarbon emission sources, such as partial burn or in situ synthesis.

### 3.1.2 Second Engine: Stoichiometric Lean Burn Engine

The same study as for the lean-burn engine has been carried out on the Renault F4P. The main results are summarized in Tables 23 to 28.

#### Carbon Monoxide Emissions

The correlations calculated for CO emissions are very similar to those calculated for the first engine, with a high contribution of olefinic bases (dimate) and a very low contribution of heavy reformate and ETBE. Moreover, it must be outlined that, as for the VTEC engine, the correlations calculated in steady state and under transient running are very different: in steady state conditions, the heavy reformate is one of the most important contributor to CO emissions.

#### Unburned Hydrocarbons Emissions

As for carbon monoxide emissions, the main conclusion of the calculations led on HC emissions is the highly different results found on steady state and transient running: in steady state conditions (Pt1 and Pt2), heavy reformate is the most

| CO emissions | Vehicle test | Engine test |
|--------------|--------------|-------------|
| 1-p-value    | MVEG-11s cycle | ECE phase | EUDC phase |
|              | 99 < < 99.9   | 99 < < 99.9 | 80 |
| $R^2$        | 0.94          | 0.94        | 0.7 |
| HR           | 0% (–0.51)    | 0% (–1.43)  | 26% (0.02) |
| LR           | 17% (0.59)    | 16% (1.51)  | 36% (0.03) |
| Dim.         | 27% (0.97)    | 28% (2.62)  | 10% (0.01) |
| FCC          | 9% (0.30)     | 9% (0.82)   | 14% (0.01) |
| Alk.         | 15% (0.55)    | 16% (1.47)  | 8% (0.01)  |
| Isom.        | 31% (1.1)     | 31% (2.95)  | 0% (0)    |
| ETBE         | 1% (0.03)     | 1% (0.10)   | 6% (0.01) |

| HC emissions | Vehicle test | Engine test |
|--------------|--------------|-------------|
| 1-p-value    | MVEG-11s cycle | ECE phase | EUDC phase |
|              | 83           | –           | –           |
| $R^2$        | 0.7          | –           | –           |
| HR           | 13% (0.05)   | –           | –           |
| LR           | 20% (0.07)   | –           | –           |
| Dim.         | 15% (0.05)   | –           | –           |
| FCC          | 0% (0)       | –           | –           |
| Alk.         | 13% (0.05)   | –           | –           |
| Isom.        | 30% (0.11)   | –           | –           |
| ETBE         | 9% (0.03)    | –           | –           |
important contributor to unburned hydrocarbons emissions, while it is one of the lowest in transient conditions. On the contrary, we can outlined the high contribution of isomerate on vehicle tests.

Nevertheless, due to the low HC emission level, the signification of most correlations on the MVEG cycle are low.

**Nitrogen Oxides Emissions**

As for HC emissions, transient running has a great effect on all the contributions to NOx emissions: ETBE is the greatest contributor with 30% on the MVEG cycle, when its contribution on the steady-state points stays around 10%.

**Carbon Dioxide Emissions**

The correlations calculated on CO₂ emissions confirm the results found on the VTEC engine: the fuel composition (in terms of refinery bases) doesn’t have a great influence on CO₂ emissions. However, even if all the contributions are very close (between 13 and 16%), it can be observed on those results that the crucial point for carbon dioxide emissions is the “H/C” value. As for the VTEC engine, the ETBE has a different behavior: despite its low “H/C” value, its contribution to CO₂ emissions is quite high because of its low heating value. Indeed, on the MVEG cycle the correlation calculated on fuel consumption gives the following results.

Fuel consumption (l/100 km) = 8.5 \( X_{ETBE} \) + 8.0 \( X_{isom} \) + 7.9 \( X_{dim} \) + 7.6 \( X_{alk} \) + 7.3 \( X_{FCC} \) + 6.7 \( X_{LR} \) + 6.4 \( X_{HR} \) (1-\( p \)-value = 99.2%).

The contribution of ETBE to fuel consumption is the highest of the 7 refinery bases. Its contribution to CO₂ emissions is then a compromise between this high fuel consumption (low heating value) and its low “H/C” ratio.

**Unregulated Pollutant Emissions**

The correlations calculated on TAP for the Laguna on the MVEG cycle are presented in Table 27.

The results obtained for this engine are closed to those obtained with the VTEC engine. Nevertheless, the study of the correlations shows that the combustion of the dimate is incomplete: this phenomenon, outlined during the study of

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### TABLE 25

| NOx emissions | Vehicle test | Engine test |
|---------------|--------------|-------------|
|               | MVEG-11s cycle | ECE phase | EUDC phase | Pt1 (standard tuning) | Pt2 (standard tuning) |
| 1-\( p \)-value | 90 < < 95 | 85 | 95 < < 99 | 95 < < 99 | 88 |
| \( R^2 \) | 0.77 | 0.72 | 0.85 | 0.93 | 0.76 |
| HR | 8% (0.018) | 10% (0.046) | 3% (0.002) | 16% (20.6) | 18% (26.9) |
| LR | 2% (0.004) | 2% (0.007) | 7% (0.005) | 19% (25.4) | 16% (13.4) |
| Dim. | 20% (0.043) | 20% (0.095) | 17% (0.011) | 16% (20.6) | 16% (14) |
| FCC | 18% (0.039) | 21% (0.096) | 11% (0.007) | 16% (21.2) | 12% (17.5) |
| Alk. | 9% (0.019) | 7% (0.034) | 15% (0.010) | 11% (13.8) | 14% (21.2) |
| Isom. | 13% (0.027) | 13% (0.059) | 14% (0.009) | 12% (16) | 12% (17.9) |
| ETBE | 30% (0.063) | 28% (0.130) | 32% (0.021) | 10% (12.5) | 12% (17.5) |

### TABLE 26

| CO₂ emission model: influence of each base (contribution in g/km) |
|-------------------|-----------------|-----------------|
| CO emissions | Vehicle test |
| MVEG-11s cycle | ECE phase | EUDC phase |
| 1-\( p \)-value | 95 < < 99 | 95 < < 99 | 99 < < 99.9 |
| \( R^2 \) | 0.89 | 0.89 | 0.9 |
| HR | 16% (193.3) | 16% (256.9) | 16% (155.9) |
| LR | 15% (185.6) | 15% (243.5) | 15% (150.8) |
| Dim. | 14% (164.1) | 14% (214.8) | 14% (134.3) |
| FCC | 14% (172.0) | 14% (225.8) | 14% (139.5) |
| Alk. | 14% (164.3) | 14% (215.5) | 14% (133.8) |
| Isom. | 13% (158.4) | 13% (206.6) | 13% (130.1) |
| ETBE | 14% (168.6) | 14% (224.2) | 14% (136.8) |
CO emissions is confirmed here with the high contribution of dimate to the emissions of acetaldehyde.

**TABLE 27**

| TAP emissions | Buta-1,3-diene | Benzene | Formaldehyde | Acetaldehyde |
|---------------|----------------|---------|--------------|--------------|
| 1-p-value     | 95 < < 99     | 95 < < 99| –            | 99 < < 99.9  |
| $R^2$         | 0.88          | 0.89    | –            | 0.93         |

| HR            | 13% (0.19)    | 32% (3.24)| –            | 9% (0.28)    |
| LR            | 9% (0.13)     | 40% (4.13)| –            | 2% (0.07)    |
| Dim.          | 44% (0.67)    | 9% (0.91)| –            | 20% (0.66)   |
| FCC           | 19% (0.29)    | 3% (0.29)| –            | 2% (0.05)    |
| Alk.          | 6% (0.09)     | 0% (~0.54)| –            | 2% (0.06)    |
| Isom.         | 9% (0.13)     | 16% (1.65)| –            | 9% (0.28)    |
| ETBE          | 1% (0.01)     | 0% (~0.78)| –            | 57% (1.86)   |

**Effect of Engine Parameters Variations on Bases Contribution to Pollutant Emissions**

As for the lean-burn PFI engine (Honda VTEC), the main results of correlations calculation according to engine running parameters variations for the Renault F4P are presented in Table 28.

**TABLE 28**

| ↓ Equivalence ratio | ↓ Spark advance |
|---------------------|-----------------|
| HC                  | CO   | NOx | HC | CO | NOx |
| HR                  | =    | ↓   | ↓  | =  | ↓   |
| LR                  | =    | ↓   | ↓  | =  | ↓   |
| Dim.                | =    | ↓   | ↑↑ | =  | ↑   |
| FCC                 | ↑    | ↑↑  | ↑  | ↓  | ↑   |
| Alk.                | ↑    | ↓   | =  | ↑  | ↓   |
| Isom.               | =    | ↑↑  | ↓  | =  | ↑   |
| ETBE                | ↑    | ↑↑  | ↓  | ↑  | ↓   |

It has been observed that the Renault F4P engine was less sensitive to parametric variations (equivalence ratio, spark advance). Nevertheless, it must be pointed out that the variation ranges were less wide than for the VTEC, due to the map characteristics of this second engine (stoichiometric running, knock sensitivity).

Some effects are consistent with the results obtained for the first engine, and especially the growth of the contribution of ETBE to HC emissions in less favorable conditions (lean burn, lower spark advance), due to oxidation difficulties of this base.

**Discussions on the Stoichiometric PFI Engine**

All the tests carried out on the Renault F4P engine indicate a less acute influence of refinery base on pollutant emissions than that which was measured on the VTEC engine. In fact, as the F4P is designed to run under homogeneous stoichiometric conditions without EGR, the parametric variations were more restricted: for instance, the minimum tested equivalence ratio was 0.95, while it was 0.65 for the VTEC engine.

Nevertheless, significant fuel effects can be outlined, most of the time quite similar to those which were observed on the lean-burn engine:

- Aromatic and olefinic/parafinic bases have an opposite effect on CO emissions: dimate and isomerate are the most important contributors to CO emissions in cold transient emissions, while their influence on CO in steady-state running and on the EUDC cycle is low. On the contrary, HR contribution is low under cold transient conditions (ECE) and high under steady-state conditions. The key parameter in order to explain the CO emissions seems to be the density: in cold conditions, a high density is linked with low CO emissions, while in hot running conditions the higher the density is, the higher the contribution to CO emissions is. Many hypotheses can be ventured to explain this phenomenon, linked to the air/fuel mixture.

- The study of HC emissions, although more difficult because of the low significance of the correlations, shows differences between vehicle and engine tests. Density seems to have an influence during transient running (high contribution of isomerate, low contribution of HR), but less acute than for CO emissions.

- Correlations on NOx emissions are quite different than those calculated for the VTEC engine: the most important contributor is ETBE, with up to 30% on the EUDC cycle. This result is consistent with the Auto/Oil program results [2], who noticed an increase of NOx emissions (+5.5%) when using a gasoline with 17% ETBE. This result can be explained by the fact that with the VTEC engine, low equivalence ratio induced combustion difficulties for ETBE and consequently high CO emissions. As far as the F4P is concerned, the contribution of ETBE to CO and HC emissions is always very low (6% for the CO on the EUDC cycle). The complete combustion of this refinery base induces higher cycle temperatures and higher NOx emissions. It can be outlined that the equivalence ratio variation done on the engine tend to confirm this fact: in lean-burn conditions, ETBE induces higher CO and HC emissions and lower NOx emissions.
3.1.3 Discussion/Comparison of the Two Engines

It has been shown that significant differences between refinery bases can be outlined, not only with regard to pollutant emissions, but also to combustion conditions. The main results are the following:

1. The main precursor of unburned hydrocarbon is the heavy reformate. The combustion difficulties of this base may be due to its high aromatic content or its high density.

2. The olefinic bases (fuel from FCC and fuel from olefin dimerization process) are characterized by a very fast and violent combustion, which impacts on pollutant emissions with incomplete combustion (high CO emissions) and a high sensitivity to engine running conditions.

3. On the contrary, ETBE seems to have a slow combustion, particularly under more difficult conditions (low spark advance, high EGR). This phenomenon is visible on HC emissions, with a drastic growth of ETBE contribution in the EUDC cycle (high engine speed). Moreover, a post-combustion phenomenon in the exhaust line can be observed when lowering the spark advance. The effect of EGR is acute for the VTEC engine, while the effect of spark advance is important for the F4P engine. Nevertheless, ETBE is a low contributor to NOx and CO emissions.

From this first test phase, it can be concluded that ETBE can reduce CO, HC and NOx emissions for a PFI engine, provided the engine running conditions are favorable to a good oxidation of this base (little or no EGR, hot running condition, etc.).

The main results for both engines are summarized in Tables 29, 30 and 31. In those tables, the contribution of each base to HC, CO and NOx emissions are compared for VTEC and F4P engine (for each contribution, the results are presented under the format VTEC/F4P).

3.1.4 Conclusions on Spark-Ignition Engine Tests

This work has shown that significant refinery base effects can be outlined on pollutant emissions. Most of those effects are common to both PFI engines:

1. HR has a high contribution to HC emissions.
2. The nonregulated pollutant emissions are closely linked to fuel chemical composition. Moreover, two other ways of UHC production at the exhaust of the vehicle can be outlined: partial oxidation and in situ synthesis.
3. Both engines are very sensitive to transient running and show quite different results between engine and vehicle tests.

Those tables show that most of the effects are common to both engines: high contribution of HR to HC emissions in steady-state conditions and of dimate and isomerate in ECE cycle. Nevertheless, as outlined in a previous paragraph, the main differences observed between engines concern NOx emissions with a high contribution of ETBE in transient running (ECE and EUDC cycles) for the F4P engine. Indeed, the main differences between the two engines, only visible in transient running, seem to come from oxidation difficulties of ETBE in lean-burn conditions with EGR.
3.2 Compression-Ignition Engines

3.2.1 Passenger Car Diesel Engine and Vehicle Results

An example of the bench test results obtained with the diesel engine is given in Figure 4. It represents the smoke/NOx trade-off measured at the bench. The operating conditions are “2000 rpm - BMEP = 2.0 bar” with different EGR rates (from 15% to 50%).

We observe that the G1 fuel gives a better smoke/NOx trade-off than the centre diesel fuel at each EGR level. This is essentially due to the G1 formulation, including 50% vol. of Fischer-Tropsch product, while the centre diesel fuel contains only about 12.8% vol. of this high potential emissions reduction product.

![Figure 4](https://via.placeholder.com/150)

Smoke/NOx trade-off measured on the engine bench.

### TABLE 32
CO emission model: influence of each base (contribution in g/km or g/kWh)

| CO emissions | Vehicle test | Engine test |
|--------------|--------------|-------------|
|              | MVEG-11s cycle | ECE phase | EUDC phase | Pt1 (standard tuning) | Pt1 (EGR = 15%) |
| 1-\(p\)-value | 95% < < 99% | 95% < < 99% | 95% < < 99% | 99% < < 99.9% | 95% < < 99% |
| \(R^2\)     | 0.79 | 0.80 | 0.75 | 0.86 | 0.78 |
| SR          | 16% (0.29) | 16% (0.64) | 14% (0.08) | 16% (0.73) | 22% (0.73) |
| HDC         | 15% (0.28) | 15% (0.61) | 16% (0.09) | 18% (0.82) | 12% (0.41) |
| LCO         | 34% (0.63) | 33% (1.36) | 36% (0.21) | 15% (0.71) | 17% (0.56) |
| HVDR        | 20% (0.38) | 20% (0.80) | 22% (0.13) | 20% (0.95) | 11% (0.36) |
| KERO        | 14% (0.26) | 14% (0.57) | 12% (0.07) | 25% (1.15) | 29% (0.95) |
| FT          | 1% (0.02) | 2% (0.08) | 0% (0.00) | 6% (0.31) | 9% (0.29) |

### TABLE 33
HC emission model: influence of each base (contribution in g/km or g/kWh)

| HC emissions | Vehicle test | Engine test |
|--------------|--------------|-------------|
|              | MVEG-11s cycle | ECE phase | Pt1 (EGR = 50%) | Pt2 (standard tuning) |
| 1-\(p\)-value | 87.5% | 82.8% | 95% < < 99% | 95% < < 99% |
| \(R^2\)     | 0.65 | 0.61 | 0.77 | 0.82 |
| SR          | 15% (0.022) | 18% (0.064) | 15% (0.13) | 18% (0.06) |
| HDC         | 18% (0.028) | 16% (0.059) | 13% (0.11) | 12% (0.04) |
| LCO         | 27% (0.041) | 34% (0.126) | 25% (0.21) | 22% (0.07) |
| HVDR        | 14% (0.021) | 15% (0.056) | 14% (0.12) | 18% (0.06) |
| KERO        | 16% (0.025) | 11% (0.042) | 26% (0.22) | 27% (0.09) |
| FT          | 10% (0.015) | 6% (0.022) | 7% (0.06) | 3% (0.01) |
Carbon Monoxide Emissions
The results are described in Table 32.
On the vehicle, the LCO is the strongest contributor (approximately 35% whatever the phase) to CO emissions, while the Fischer-Tropsch is the smallest (around 1%). On the engine, the Fischer-Tropsch is always the smallest (responsible for 5 to 10%) while the strongest is the kerosene fuel (25 to 30%).

Unburned Hydrocarbons Emissions
For HC emissions (Table 33), LCO is the strongest contributor, as for CO emissions, on vehicle and on engine tests. Fischer-Tropsch fuel is always the weakest contributor. The kerosene fuel is also a potent contributor, but only in the bench experiment, as for CO emissions.

Nitrogen Oxides Emissions
Diesel fuel formulation impact on NOx emissions (Table 34) is weaker than on CO or HC emissions. Nevertheless, LCO appears to be the strongest contributor, with a relative weight around 25%, while the other bases have similar contributions.

Particulate and Smoke Emissions
The calculated models on particulate (Table 35) and smoke (Table 36) emissions are quite similar: LCO and HVDR fuels are the strongest contributors (between 20 and 45%). Fischer-Tropsch fuel (and kerosene fuel in the case of particulate and smoke emissions) are the smallest contributors (about 5 to 10%).

### Table 34
| NOx emissions | Vehicle test | Engine test |
|---------------|--------------|-------------|
|               | ECE phase | 2500 rpm full load | 4000 rpm full load | Pt2 (standard tuning) |
| 1-p-value     | 88.1%       | 90.1%         | 91.3%           | 95% < < 99% |
| $R^2$         | 0.65        | 0.67           | 0.69            | 0.76 |
| SR            | 17% (0.82)  | 14% (2.71)     | 14% (3.73)      | 16% (6.15) |
| HDC           | 16% (0.81)  | 15% (2.83)     | 14% (3.86)      | 16% (5.93) |
| LCO           | 18% (0.88)  | 25% (4.69)     | 24% (6.46)      | 26% (9.79) |
| HVDR          | 18% (0.87)  | 14% (2.55)     | 13% (3.68)      | 18% (7.08) |
| KERO          | 17% (0.85)  | 17% (3.25)     | 19% (5.23)      | 12% (4.66) |
| FT            | 14% (0.68)  | 15% (2.93)     | 16% (4.40)      | 12% (4.70) |

### Table 35
| Particulate emissions | Vehicle test | Engine test |
|-----------------------|--------------|-------------|
|                       | MVEG-11s cycle | ECE phase | 2500 rpm full load | Pt2 (standard tuning) |
| 1-p-value             | 95% < < 99%   | 94.7%      | 95% < < 99%         | 95% < < 99% |
| $R^2$                 | 0.75          | 0.74        | 0.83                | 0.76 |
| SR                    | 17% (0.06)    | 19% (0.10)  | 17% (0.29)          | 15% (0.08) |
| HDC                   | 17% (0.06)    | 15% (0.08)  | 8% (0.13)           | 2% (0.01) |
| LCO                   | 25% (0.09)    | 27% (0.15)  | 38% (0.64)          | 45% (0.24) |
| HVDR                  | 19% (0.07)    | 19% (0.10)  | 24% (0.40)          | 19% (0.10) |
| KERO                  | 14% (0.05)    | 11% (0.06)  | 12% (0.20)          | 11% (0.06) |
| FT                    | 8% (0.03)     | 9% (0.05)   | 1% (0.01)           | 8% (0.04) |
TABLE 36
Smoke emission model: influence of each base
(contribution in FSN number, engine bench measurements only)

| Smoke emissions | Engine test | Vehicle test |
|-----------------|-------------|--------------|
| Pt2 (standard tuning) | 2500 rpm full load | 2000 rpm full load |
| 1-p-value | 95% < < 99% | 95% < < 99% |
| R² | 0.81 | 0.72 |
| SR | 18% (2.42) | 10% (0.09) |
| HDC | 13% (1.77) | 17% (0.15) |
| LCO | 28% (3.87) | 25% (0.22) |
| HVDR | 25% (3.51) | 20% (0.18) |
| KERO | 11% (1.57) | 17% (0.15) |
| FT | 5% (0.68) | 11% (0.10) |

TABLE 37
CO₂ emission model: influence of each base
(contribution in g/km)

| CO₂ emissions | Vehicle test |
|---------------|--------------|
| MVEG-11s cycle | ECE phase | EUDC phase |
| 1-p-value | 95% < < 99% | 99% < < 99.9% | 82.6% |
| R² | 0.83 | 0.91 | 0.60 |
| SR | 16% (176) | 16% (236) | 17% (141) |
| HDC | 16% (177) | 16% (237) | 17% (142) |
| LCO | 17% (178) | 17% (245) | 16% (138) |
| HVDR | 17% (178) | 17% (241) | 17% (141) |
| KERO | 18% (196) | 19% (275) | 17% (149) |
| FT | 16% (170) | 15% (226) | 16% (137) |

TABLE 38
Fuel consumption model: influence of each base
(contribution in l/100 km)

| Fuel consumption | Vehicle test |
|------------------|--------------|
| MVEG-11s cycle | ECE phase | EUDC phase |
| 1-p-value | 99% < < 99.9% | > 99.9% | 95% < < 99% |
| R² | 0.91 | 0.95 | 0.82 |
| SR | 16% (6.6) | 16% (8.9) | 16% (5.3) |
| HDC | 17% (6.9) | 16% (9.2) | 17% (5.5) |
| LCO | 15% (6.4) | 16% (8.9) | 15% (4.9) |
| HVDR | 16% (6.6) | 16% (9.0) | 16% (5.3) |
| KERO | 19% (7.8) | 19% (11.0) | 18% (6.0) |
| FT | 17% (7.0) | 17% (9.4) | 18% (5.7) |

TABLE 39
TAP emission model: influence of each base
(contribution in mg/km, vehicle results)

| TAP emissions | Buta-1,3-diene | Benzene | Formaldehyde | Acetaldehyde |
|---------------|----------------|---------|--------------|--------------|
| 1-p-value | – | 85.7% | 84.5% | 79.4% |
| R² | – | 0.63 | 0.62 | 0.58 |
| SR | 22% (1.00) | 16% (15.21) | 16% (7.33) |
| HDC | 17% (0.81) | 16% (15.19) | 17% (7.80) |
| LCO | 18% (0.83) | 32% (29.21) | 29% (13.42) |
| HVDR | 16% (0.72) | 15% (13.66) | 16% (7.52) |
| KERO | 19% (0.88) | 13% (11.83) | 13% (6.20) |
| FT | 8% (0.37) | 8% (7.26) | 9% (3.99) |

TABLE 40
PAH emission model: influence of each base
(contribution in µg/km, vehicle results)

| TAP emissions: particulate PAH | Benzo(a)anthracene | Chrysene | Pyrene |
|-----------------------------|---------------------|----------|--------|
| 1-p-value | 95% < < 99% | 79.6% | 78.8% |
| R² | 0.84 | 0.58 | 0.58 |
| SR | 15% (0.06) | 15% (0.06) | 14% (0.52) |
| HDC | 34% (0.13) | 12% (0.05) | 29% (1.11) |
| LCO | 24% (0.09) | 45% (0.18) | 15% (0.55) |
| HVDR | 24% (0.09) | 15% (0.06) | 25% (0.94) |
| KERO | 3% (0.01) | 3% (0.01) | 8% (0.29) |
| FT | 0% (0.00) | 10% (0.04) | 9% (0.34) |

**Carbon Dioxide Emissions and Fuel Consumption**
As for NOx emissions, the fuel formulation impact on CO₂ emissions (Table 37) and on fuel consumption (Table 38) is weak. On the engine bench, no models were statistically significant. Nevertheless, on the vehicle, it seems that the kerosene fuel has a marginally stronger influence on CO₂ emissions and on fuel consumption than the other parameters.

**Unregulated Pollutant Emissions**
The unregulated emissions measured on vehicle in this study are now presented: there are toxic air pollutants such as buta-1,3-diene, benzene, formaldehyde and acetaldehyde (Table 39), some PAH (Table 40) and OFP (Table 41).
Considering these unregulated emissions measured on vehicle, the models are very similar one another. LCO is the strongest contributor (about 30%) and Fischer-Tropsch fuel has the smallest influence (about 10%).

The hydro-cracked product and the fuel issued from vacuum distillation residue are also strong contributors to the PAH emissions while the kerosene fuel is characterized by low factors.

For the buta-1,3-diene, the model was not significant. The ozone forming potential is calculated with the Carter’s factors in the range C1-C13.

Those results, obtained on the bench engine and with the vehicle can be summarized as follows.

For CO, HC, aldehydes (formaldehyde, acetaldehyde), PAH emissions and for ozone formation potential, the results are almost the same. While the Fischer-Tropsch fuel is the weakest contributory base (from 5 to 10%, according to the engine operating conditions), LCO has the strongest impact (from 25 to 35%). The kerosene fuel is also a potent contributor (from 25 to 30%), in steady-state engine conditions for CO and HC emissions.

LCO is also the most influential base on NOx emissions on steady-state engine conditions: this product is characterized by a factor of about 25%. The Fischer-Tropsch has the lowest factor in transient conditions of the vehicle in the urban phase: 14%.

For particulate emissions, two different behaviors can be identified:
- kerosene and Fischer-Tropsch fuels are low contributors (from 5 to 10%);
- LCO is a strong contributor (from 25 to 45%).

For smoke emissions, there are also two different behaviors:
- Fischer-Tropsch fuel is a low contributor (from 5 to 10%);
- LCO and the fuel obtained through hydroconversion of vacuum distillation residue are high contributors (from 20 to 30%).

CO₂ emissions show two types of results: while the kerosene is the main contributor (18%), the Fischer-Tropsch product is the weakest with 16%. The same result is found considering fuel consumption: the kerosene fuel is the most potent product with 19%.

It must be pointed out that the range of CO₂ emission percentages is naturally lower than the regulated pollutant emission range, and that a single percentage on CO₂ emissions reveals a notable impact from the fuel base.

In conclusion, each refinery base selected for this experimental design contributes to the emissions of the indirect injection diesel engines (IDI). Nevertheless, these contributions are very different from each other. They can be classified in three main groups:

1) Bases characterized by the strongest contributions:
- LCO fuel for CO, HC, NOx, particulate, smoke, SOF, IOF, PAH and aldehydes emissions, for ozone forming potential and for BSFC;
- The diesel fuel produced by vacuum distillation residue hydroconversion, for CO, particulate, smoke and PAH emissions.

2) The kerosene fuel:
- It increases CO, HC and CO₂ emissions and fuel consumption;
- It is a low contributor to particulate, SOF, IOF and PAH emissions.

3) The Fischer-Tropsch product:
- It is characterized by the smallest contribution to CO, HC, particulate, smoke, SOF, IOF, PAH, aldehydes and benzene emissions, and also to ozone forming potential.
- The straight-run and the hydrocracked products are characterized by intermediate contributions.

All these results are available for the different steady-state engine operating conditions (such as engine speed, engine torque, injection timing and EGR rate) and in transient vehicle conditions on the MVEG-11s cycle.

The Table 42 synthesizes the main diesel fuel formulation effects.

LCO and the vacuum distillation residue hydroconversion fuels are the strongest contributors. These two bases are characterized by:
- the highest aromatic contents;
- a very low “H/C” ratio;
- a high density;
- and a low cetane number (particularly for the LCO). That is why the EPEFE program has found a very strong influence of these parameters on engine emissions.

The kerosene is characterized by a medium cetane number and by its high volatility. This result can also be expressed in terms of high CO and HC emissions.
On the opposite, the low density and the low aromatic contents induce low particulate, smoke and PAH emissions.

The specific composition of the Fischer-Tropsch fuel, with 95% of linear alkanes, leads to very peculiar properties: a very high “H/C” ratio, a very low density and a very high cetane number. These characteristics, together with the absence of aromatic compounds, give this refinery base the weakest contribution to the pollutant emissions considered.

Considering the hydrocracked fuel, contradictory effects are observed. The low density, the high cetane number and the low aromatic content could probably compensate the possible effect of the naphthene content and lead to intermediate emission levels.

Besides, for the complementary diesel fuels, the main results are the following:
- RME, incorporated at a 20% vol. level in the centre diesel fuel, had no significant impact on engine emissions.
- The naphthenic product, added at a level of 20% vol. in the centre diesel fuel, increases CO emissions from 25 to 45%, HC emissions from 25 to 35% and particulate emissions by around 5%.
- The diesel fuel issued from the Fischer-Tropsch process without any blending with another product or base leads to the lowest CO, HC, NOx, particulate, benzene, formaldehyde, acetaldehyde, PAH (polycyclic aromatic hydrocarbons) emissions and to the lowest ozone forming potential.

3.2.2 Heavy Duty Results

Each parameter studied was modeled. About 30% of the models reach a significant level which complies with the criteria. Results show that models are mostly independent from the engine running condition.

### Black Smoke Opacity and Smoke Emissions

ELR tests reveal the characteristics of the combustion with reduced excess air. Two bases, LCO and hydro-converted vacuum distillation residue, are major contributors to this kind of emission, but at different engine speeds: the first one at high speed, weighing 33%, the second one at low speed, weighing 27%.

Fischer-Tropsch is represented in the model by the smallest coefficient, weighing only 2 to 8% of total emissions. Kerosene also is a minor contributor, with relative coefficients about 11 or 13%.

The results obtained in stabilized running conditions are globally similar to those observed during transient conditions, despite a higher air/fuel ratio. Once more, the dependence on engine speed of the two major contributors is verified.

### Particulate Emissions

The model, obtained with ESC test, points out three bases. LCO appears to be a major contributor to particulate emissions, while Fischer-Tropsch synthetic gas-oil and kerosene base are represented by low coefficients.

\[
PM (g/kW-h) = 0.087 \times [\%LCO] + 0.069 \times [\%HVDR] + 0.066 \times [\%straight-run] + 0.060 \times [\%hydrocracked] + 0.052 \times [\%Fischer-Tropsch] + 0.047 \times [\%kerosene]
\]

The trends observed prove the role of the base chemical composition. LCO and hydro-converted vacuum distillation residue bases contain a high percentage of heavy aromatic species known to be involved in the classic schemes describing particulate formation. On the opposite, synthetic Fischer-Tropsch fuel, containing exclusively saturated molecules, has a weak contribution to emissions [2-4].

Kerosene also appears to be a minor contributor to particulate emission, as already mentioned by Akasaka et al. [3, 6].

#### TABLE 42

|               | CO  | HC  | NOx | Particulate | Smoke | Benzene | Aldehydes | Ozone |
|---------------|-----|-----|-----|-------------|-------|---------|-----------|-------|
| LCO           | ++++| +++ | +++ | +++         | ++++  | ++      | ++++      | ++++  |
| HVDR          | ++  | ++  | ++  | +++         | ++++  | ++      | ++        | ++    |
| KERO          | +++ | +++ | ++  | +           | +     | ++      | ++        | ++    |
| FT            | +   | +   | ++  | +           | +     | +       | +         | +     |

- : contribution < 15%
++ : 15% < contribution < 20%
+++ : 20% < contribution < 25%
++++: contribution > 25%.
Nitrogen Oxides
An important result is that the Fischer-Tropsch fuel contributes weakly to NOx emissions, while it also contributes to reduced smoke and particulate emission levels [2]. Constant relative factor from 12 to 14% is found in the models. The specificities of this base are its low density, near 0.760, resulting in a low fuel mass introduction rate into the cylinder, and a high cetane number, about 80, resulting in a short self-ignition delay. Thus, the fuel mass concerned by self-ignition is reduced, as is the temperature peak level reached during the premix phase [5].

Kerosene [3, 6], at heavy loads, and hydro-cracked base, at low loads, also do not lead to high emission coefficients. The first one is characterized by a low specific gravity, the second one by a high cetane number.

For opposite reasons, products with high density but low cetane number (LCO and hydro-converted vacuum distillation residue) lead to the highest contributions, weighing about 20%.

Combustion Noise and Maximum Heat Release
Models have been calculated using the acoustical output of the combustion noise, and are significant over the entire range of conditions tested. Differences in weightings between the bases are extremely important, from 3 to 50%. The results are in accordance with what could be expected considering the cetane number of pure bases measured on CFR engine.

Thus, major contributors are LCO (25 to 50%) and kerosene (16 to 31%), while minor contributors are Fischer-Tropsch fuel (3 to 8%) and the hydro-cracked base (5 to 11%).

Models obtained for the maximum heat release only concern low loads, where the heat release peak value occurs during premix combustion (for loads higher than 50%, maximum heat release occurs during the diffusion phase of the combustion). So, at low loads, highest weightings are those of LCO and kerosene, while the lowest are those of Fischer-Tropsch [5] and hydro-cracked bases. On these points, correlation with combustion noise is excellent.

Brake Specific Fuel Consumption and Carbon Dioxide Emissions
Since heating values of the few bases do not reveal any significant difference, the results given by the models are essentially governed by the physical properties of the bases, such as cetane number and specific gravity, which both determine self-ignition delay and combustion duration. Models are strongly dependent on the engine load. The Table 43 sums up the trends observed for the specific fuel consumption.

Carbon dioxide trends only differ from previous results by taking into account hydrogen to carbon ratio. H/C of Fischer-Tropsch and hydro-cracked base, which contain exclusively or essentially saturated compounds, are about 2 while those of LCO and hydro-converted vacuum distillation residue, essentially composed of aromatic molecules, are about 1. Thus, trends concerning Fischer-Tropsch, hydro-cracked and hydro-converted vacuum distillation residue bases are stressed. Unlike these examples, kerosene which had the highest weighting for BSFC at high load, is no longer the major contributor to carbon dioxide emissions due to a rather high hydrogen to carbon ratio.

| TABLE 43 |
| --- |
| | High load | Low load |
| Strongest weight | Kerosene | Hydro-converted vacuum distillation residue |
| Weakest weight | Fischer-Tropsch | Hydro-cracked |

Unburned Hydrocarbons Emissions
Though unburned hydrocarbons content of exhaust gases is rather low, about 80 ppm, trends could have been drawn from the tests. Over the entire range of test conditions, LCO and to a certain extent kerosene [6] are the major contributors to these emissions. The characteristic temperatures of the distillation curves are particularly low. The temperature corresponding to the initial point is about 90°C, and the one corresponding to 5 percents distilled is about 150°C.

On the other hand, lowest weightings are those of bases with rather high initial temperatures of distillation curve, such as hydro-cracked and hydro-converted vacuum distillation residue bases, except in full load conditions, where Fischer-Tropsch surprisingly appears to contribute strongly to emissions.

For example, the model drawn from European steady-state cycle describes unburned hydrocarbons emissions as follows:

\[ \text{HC (g/kW·h)} = 0.51 \times [\% \text{LCO}] + 0.44 \times [\% \text{kerosene}] + 0.34 \times [\% \text{Fischer-Tropsch}] + 0.32 \times [\% \text{straight-run}] + 0.31 \times [\% \text{HVDR}] + 0.27 \times [\% \text{hydrocracked}] \]

Carbon Monoxide Emissions
Like unburned hydrocarbons emissions, carbon monoxide emissions are quite low, about 120 ppm. Results concerning LCO appear extremely dependent from the load conditions: weighting of LCO is the highest coefficient in partial load running, but the weakest while running full load.

Whatever the engine running condition may be, hydro-converted vacuum distillation residue remains a rather strong contributor to carbon monoxide emissions, as well as kerosene to a certain extent.

Synthesis
The main results obtained on the heavy duty engine can be summarized as follows (Table 44).
TABLE 44
Main diesel fuel formulation effects (contribution in %)

|         | CO  | HC  | NOx | Particulate mass | Smoke/Opacity | Combustion noise |
|---------|-----|-----|-----|------------------|----------------|------------------|
| LCO     | +++ | +++ | +++ | +++              | +++           | +++              |
| HVDR    | +++ | ++  | +   | +                | +             | ++               |
| KERO    | +++ | +++ | +   | +                | +             | +++              |
| HDC     | ++  | +   | ++  | ++               | ++            | +                |
| FT      | ++  | +   | +   | +                | +             | +                |

3.2.3 Conclusions of Diesel Tests

The diesel tests show that the contributions are very different from one base to another. The bases can easily be identified out as potentially high emissions precursors, or, on the other hand, as emissions reducing elements. So, these bases can be classified in four significantly different categories:

1) Products characterized by strong contributions, among others to NOx, particulate and smoke emissions, in steady state and in transient conditions: fuels from LCO and hydro-conversion of vacuum distillation residue. For the trucks, LCO also leads to a high combustion noise and the hydro-converted vacuum distillation residue seems to increase the specific fuel consumption.

2) Kerosene, as a high contributor to CO and HC emissions (and also to combustion noise and to specific fuel consumption for the trucks), but low contributor to particulate and smoke emissions.

3) Straight-run and hydro-cracked products, for their intermediate contributions. Nevertheless, the hydro-cracked base is a minor contributor to HC, CO and CO₂ emissions from the heavy duty engine.

4) Fischer-Tropsch process fuel, which has a very low level of emissions.

The high density and high aromatic content refinery bases (LCO and HVDR) lead to the highest NOx, particulate and smoke emissions levels. On the other hand, the products of low density and containing no aromatic compound (Fischer-Tropsch and kerosene) lead to the lowest particulate emissions levels. These results can probably be explained by a global physical effect (density) combined with a fine chemical effect (composition in aromatic precursor).

The kerosene, which is the most volatile product, increase the CO and HC emissions.

On the other hand, the Fischer-Tropsch fuel leads to a decrease in the auto-ignition delay because of its chemical composition (95% of linear paraffinic compounds). This is the origin of the improvements of the CO and HC emissions, and also of the smoke/NOx trade-off produced by this base.

Besides, the incorporation of 20% vol. of rapeseed methyl ester (RME) in the centre diesel fuel had no significant impact on regulated engine emissions when the blending of 20% vol. of a naphthenic product in the same center diesel fuel increased, in certain operating conditions on engine or on vehicle, the CO and HC emissions levels.

It may be concluded that the best diesel fuel to reduce significantly present day indirect injection diesel engines emissions and present day heavy-duty diesel trucks emissions is the Fischer-Tropsch base. The very high potential of this very particular base suggests a detailed study to define the optimization of engine with Fischer-Tropsch fuels. This optimization could, for example, focus on lower compression ratios, reduction of the injection timing, different EGR rate, etc.

CONCLUSIONS

The main objective of this study was to determine the impact of fuel refinery bases on engine emissions. The study shows clearly that they have a significant influence on regulated pollutant emissions, unregulated pollutant emissions and on fuel consumption of spark-ignition engines, of indirect injection diesel engines and of heavy-duty diesel engines. These results are valid on engines and on vehicles. The impact of the selected refinery bases (issued from different refinery or synthesis processes) has been mathematically modeled for regulated and unregulated pollutant emissions and for fuel consumption.

Further works are currently under way at IFP with the same fuels blends on new engine technologies (gasoline direct injection and common rail, corresponding to Euro III and Euro IV emissions specifications). It will be interesting to compare the results presented in this paper with those of these last tests.

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