

Effect of Fuel Chemical Structure and Properties on Diesel Engine Performance and Pollutant Emissions: Review of the Results of Four European Research Programs

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ABSTRACT

During recent years, the deterioration of greenhouse phenomenon, in conjunction with the continuous increase of worldwide fleet of vehicles and crude oil prices, raised heightened concerns over both the improvement of vehicle mileage and the reduction of pollutant emissions. Diesel engines have the highest fuel economy and thus, highest CO₂ reduction potential among all other thermal propulsion engines due to their superior thermal efficiency. However, particulate matter (PM) and nitrogen oxides (NO_x) emissions from diesel engines are comparatively higher than those emitted from modern gasoline engines. Therefore, reduction of diesel emitted pollutants and especially, PM and NO_x without increase of specific fuel consumption or let alone improvement of diesel fuel economy is a difficult problem, which requires immediate and drastic actions to be taken. A direct means for reducing diesel engine emitted pollutants, while preserving fuel economy, is the reformulation of conventional diesel fuel. A very promising way to improve diesel fuel behavior is the addition of synthetic or biologically renewable oxygenates. However, as the characteristics of the "parental" conventional diesel oil affect directly the behavior of resulting mixtures it is of utmost importance to first optimize its chemical composition and properties. A vast number of experimental and theoretical studies have been conducted in the past to examine the effect of diesel fuel chemical structure and properties on diesel engine exhaust emissions. The most significant fuel characteristics examined in these studies were aromatic structure and content, sulphur content, hydrocarbon molecular structure, cetane number, fuel heating value, density, viscosity and distillation temperatures. The effects of these fuel characteristics on diesel pollutant emissions have been assessed in various types of diesel engines (direct and indirect) and vehicles under diverse

operating conditions (steady-state and transient). The effects of fuel properties on emissions depend on engine types and operating conditions. Moreover, it turns out that it is quite difficult to separate the effects of various fuel properties on emissions because many of them are statistically interrelated. In addition, the influence of fuel properties such as compressibility factor and surface tension on diesel performance characteristics and pollutant emissions has not been examined thoroughly. For this reason, the purpose of this study is to examine the effect of diesel fuel chemical structure and properties on diesel engine performance characteristics and pollutant emissions. To achieve these, findings of three major research programs funded by the European Commission, in which our team participated during recent years, are utilized in conjunction with pertinent results obtained from the literature. During these programs, the effect of variable aromatic content and structure and the influence of fuel physical properties on diesel engine combustion characteristics and pollutant emissions were investigated both theoretically and experimentally, in various types of diesel engines and under diverse operating conditions. Unlike other studies, emphasis will be given herein on the effects of fuel properties not only on regulated pollutant emissions but also on diesel fuel injection system, combustion evolution and in-cylinder pollutant formation. In addition, the background and the succession of various statistical approaches used in the literature to identify possible correlations between specific diesel fuel properties and exhaust emissions will be discussed. The conclusions of these evaluations will be contrasted with the statistical methods used from our research group to correlate diesel emitted pollutants and fuel characteristics. The ultimate objective of this review is to consolidate existing knowledge and discern the influence of individual conventional diesel fuel characteristics on engine performance and pollutant emissions.

INTRODUCTION

Reduction of engine out emissions and brake specific fuel consumption (bsfc) are major research aspects to engine development in light of increasing concern about environmental protection and preservation of fossil fuel reserves [1-5]. Nowadays, several techniques such as management of injection process, exhaust gas recirculation (EGR) and after-treatment have been used to effect a considerable reduction of diesel-derived pollutants. However, strategies for emission control are often accompanied by fuel consumption or cost penalties [1,2]. To be compliant with future stringent exhaust gas regulations, the development of modern diesel engines requires not only a further improvement of the combustion and injection process but also adequate reformulation of diesel fuels [3-8]. One promising technique for the reduction of gaseous and particulate emissions is the optimization of the chemical composition and the physical properties of conventional diesel fuels [5-7]. Using this technique, significant improvements can be achieved in the environmental behavior not only of new diesel engines but also of existing fleet of diesel vehicles [3-92].

Fundamental studies [93-115] have revealed the profound interconnection between fuel molecular structure and the generating mechanism of soot during diesel combustion. Specifically, studies of soot formation in laminar diffusion flames have shown that the sooting tendency of numerous hydrocarbon compounds varies widely and is strongly affected by the different configurations of carbon atom bonds [94,95,97]. For example, fuels with polycyclic compounds (aromatic rings) and triple-bonded carbon atoms form soot readily, whereas blends with straight chain hydrocarbons containing single-bonded carbon atoms are rather opposed to the formation of soot [93-115].

The most widely discussed aspect of a fuel's molecular structure effects on soot formation is the general ranking of sooting tendencies. Based on data obtained from flames on a Bunsen burner, Street and Thomas in a pioneer investigation [101] reported that the sooting tendencies of hydrocarbons rank; acetylene < alkenes < isoalkanes < n-alkanes < alkylbenzenes < naphthalenes. Takahashi and Glassman [103] concluded that soot emissions in premixed flames arise from a competition between fuel pyrolysis and oxidative attack. They correlated the sooting limits of premixed flames for a wide range of fuels by accounting for C-C bonds and flame temperatures and found that the structure of the fuel molecule was not very important, as all fuels break down to the same essential species, such as acetylene, which build into soot. Thus, fuel pyrolysis controls the sooting tendency. However, in the case of aromatic fuels, an additional fast and direct route may produce soot through condensation of aromatic rings into graphite-like structures, particularly at temperatures below 1800 K [104-106].

The generation of particulate matter in fuel-rich combustion is typically modeled through the formation of small aromatic species, such as benzene, that grow to high molecular mass aromatics including PAH. However, most flame studies of soot formation chemistry have used methane, ethylene or acetylene as the fuel. These C₁-C₂ fuels lack most of the structural features that are characteristic of liquid fuel hydrocarbons: alkyl carbon-carbon bonds, alkyl rings, allylic bonds and benzenoid rings. Thus their flames provide an incomplete picture of fuel decomposition and of the chemistry of the formation of aromatics. A recent, detailed review by McEnally *et al.*, [107] on the combustion chemistry of larger, more complex hydrocarbons investigated the effects of these characteristic structures on the fuel decomposition and aromatic formation chemistry. The general, widely accepted, picture of soot formation in flames has been outlined in another review article by Frenklach [108].

According to Glassman [109], in premixed flames original fuel structures break down to acetylene and soot is formed in the high-temperature post-flame zone. Such a mechanism may comprise elementary reactions involving a sequence of H-atom abstraction and acetylene addition reactions (HACA mechanism [108]) and formation of intermediates, such as vinyl, butadienyl, vinyl acetylene and phenyl acetylene radicals. In recent years, in addition to the HACA mechanism, the importance of resonantly stabilized radicals in soot formation has also been established. These, relatively un-reactive radicals, such as propargyl (C₃H₃-) formed by the combination of vinyl and methyl radicals with subsequent hydrogen abstraction, may be building blocks of aromatic rings particularly in the combustion of aliphatic fuels [93,110]. In the case of aromatic fuels the aromatic benzene ring is already present in the oxidation zone and is mainly oxidized to cyclopentadienyl radicals (c-C₅H₅-) [111]. As a consequence, a large amount of cyclopentadienyl radicals is immediately available for recombination reactions, leading to multi-ring aromatic formation. According to D'Anna and Violi [111] cyclopentadienyl self-combination is the dominant route in the multi-ring aromatic formation process in aromatic fuel flames. McEnally *et al.* [107] suggest two more, important reactions that form two ring aromatic hydrocarbons, i.e. acetylene addition to 2-ethynylphenyl and propargyl addition to benzyl radicals. As the building blocks for large aromatic species formation are the main products of benzene oxidation, PAH are formed in the main oxidation zone of the flame [93,111]. The larger PAH compounds coagulate to form the first soot nuclei (soot inception), which are a few nanometers in size. These particles are initially transparent to visible radiation and exhibit spectroscopic properties typical of PAH with few condensed aromatic rings. These compounds are formed at a high rate in fuel-rich flames just downstream of the flame front and their concentration accounts for the total amount of soot formed in slightly sooting

* Numbers in brackets designate references at the end of the paper

conditions. These nuclei continue to grow via surface reactions with acetylene, PAH and other hydrocarbons present in the flame. Coagulation of growing soot particles leads to a decreasing number density while in total, particle mass remains constant [112].

Over the years, a number of studies have concentrated mainly on the effect of fuel aromatic content on engine exhaust emissions, because commercial diesel fuels contain around 20-30% aromatic compounds, but no definite overall trend has been found [3-7,9-16,26-29,35-37,40,41,43,97]. These studies revealed that it is quite difficult to relate directly certain fuel characteristics with observed experimental findings in terms of engine performance characteristics and pollutant emissions due to the fact that the variation of fuel aromatic fraction is accompanied by changes of fuel physicochemical properties. For example, a decrease of cetane number and a corresponding increase in density and viscosity are normally observed when the aromatic content is increased.

According to the literature [3-92], diesel fuel composition and properties affect in a different way each one of the gaseous and particulate emissions. For example, it has been reported that CO and HC emissions depend on cetane number; NO_x emissions are mainly controlled by fuel density; whereas polyaromatic hydrocarbons (PAHs) and soot are directly related to the fuel aromatic content. Diesel oil composition in single-, double- and triple-bonded hydrocarbons as well as in aromatic rings affects directly its physical and chemical properties and thus formulates its tendency to form gaseous and particulate emissions when burned in diesel engines. In general, there is an interrelation between the molecular structure (paraffins, olefins, naphthenes and aromatic hydrocarbons), the chemical properties (cetane number, ignition point etc.) and the physical properties (density, viscosity, surface tension etc) of a diesel fuel. Consequently, it is quite difficult – if not impossible – to ascribe the variations observed in diesel engine performance and exhaust emissions to the change of a single fuel parameter, when a diesel fuel is replaced with another.

Several theoretical and experimental investigations have been conducted to examine the effect of the physical and chemical properties of conventional fuels on diesel pollutants, which were emitted from various types of diesel engines, in test-cell installation or in vehicles [3-92]. The examination of these studies derived the following general findings concerning the effect of diesel fuel properties on pollutant emissions:

1. Reduction of sulphur content and aromatic content (especially of PAHs) resulted in a noticeable decrease of particulate emissions (PM).
2. NO_x emissions experienced low sensitivity to the variation of diesel fuel properties.

According to the literature [3-92], the effects of diesel fuel effects on engine performance characteristics and exhaust emissions vary significantly with the type of engine used in the experiments, with the experimental procedure followed, and with the method used for the preparation of the test fuels. Furthermore, in previous studies [5-7,9-14,23,24,37,39,44], different methods were employed to statistically correlate diesel emitted pollutants and fuel chemical and physical properties.

For this reason, an extensive review of already published theoretical and experimental data concerning the effects of conventional fuel synthesis and properties on diesel engine performance characteristics and pollutant emissions is conducted herein. The main body of the present study is comprised of theoretical and experimental results, which were produced from our research team under three major European research programs during the last fifteen years. In addition, results obtained from a large research program conducted in Europe, which aimed to identify the effects of diesel fuel composition and properties on engine performance and pollutant emissions are also included in this study. During these research projects, the influence of variable aromatic content and structure and the influence of fuel physical properties on diesel engine combustion characteristics and pollutant emissions were examined both theoretically and experimentally in various types of diesel engines and diesel-powered vehicles under diverse operating conditions. Emphasis is given to comprehend the influence of diesel properties on fuel injection process, combustion characteristics and in-cylinder pollutant formation. In addition, various statistical methods are presented, which were employed to correlate the measured emitted pollutants with fuel properties. The main scope of the present study is to assemble existing knowledge in this field and help clarify the influence of individual conventional diesel fuel characteristics on engine performance and pollutant emissions.

DESCRIPTION OF FUEL PROPERTIES

FUEL PROPERTIES OF THE “EPEFE” PROGRAM - The European Program on Emissions, Fuels and Engine Technologies (“EPEFE”), which was conducted of ACEA (Association des Constructeurs Européens d’Automobiles) and EUROPIA (European Petroleum Industry Association) between 1993 and 1995, provides important information towards the understanding of the effects of diesel fuel properties (i.e. aromatic content, sulphur content, cetane number, density, distillation temperature etc) on diesel engines performance and pollutant emissions [13,23,24]. The objective of the program was to produce a core fuel matrix in which the following fuel parameters were de-correlated; (in order of priority) i) density and poly-aromatics (i.e. di- + tri-aromatics), ii) cetane number and iii) back-end distillation. In Table 1 is shown the original fuel matrix requirements of the “EPEFE” program.

Table 1. Original fuel matrix requirements of “EPEFE” diesel fuels [13,23,24]

Fuel	1	2	3	4	5	6
Density	low	low	high	high	low	low
Poly - aromatics	low	high	low	high	low	low
Cetane number	50±1	50±1	50±1	50±1	55	58

It was agreed that all six fuels would be blended to constant sulphur content (as close as possible to 500 ppm maximum) and should have the same back-end volatility characteristics (as expressed by T95%v/v) as practically possible. Fuels 5 and 6 would be prepared by treating Fuel 1 with increasing levels of ignition improver to allow a change in cetane number without altering any of the other fuel parameters. It was agreed that the densities of the fuels should satisfy the following criteria; minimum 820 kg/m³ and maximum 860 kg/m³ with a spread (low to high) of at least 30 kg/m³. A poly-aromatics (di- + tri-aromatics) spread of at least 6%/m was targeted.

Preliminary assessment by the blending sub-group - In conventional fuels, density and poly-aromatics are highly correlated: a preliminary study confirmed that Fuels 2 and 3 would be difficult to produce and would limit the achievable spreads in density and poly-aromatics to ca. 27 kg/m³ and 5.2 %/m, respectively.

It was believed that a T95 of 345 – 350°C was feasible across the matrix, with a candidate Fuel 7 having an increased T95 of ca. 370°C (EN590 specification maximum). An additional Fuel 8 (decorrelation of di- and tri-aromatics) would be prepared to match Fuel 2 but with the di- to tri-aromatics ratio as high as possible. This fuel proved to be challenging to prepare since it is difficult to selectively increase di-aromatic content without simultaneously increasing tri-aromatic content.

A base cetane number of 50±1 across the matrix appeared to be feasible though it was proposed that Fuel 4 rather than Fuel 1 should be treated with ignition improver at two increasing levels to produce Fuels 5 and 6. This was because of predicted quantity limitations on producing Fuel 1. Meeting the sulphur target of 500 ppm maximum added an increased difficulty to formulating the fuels. Initial studies showed that in order to meet the other target values as closely as possible, the resulting minimum sulphur content achievable across the matrix was typically ca. 650 ppm. Clearly a majority of candidate blending components had to be low sulphur (<500 ppm) materials which would in turn restrict the poly-aromatics spread achievable; low sulphur

components generally have low poly-aromatic contents. It was agreed that modifications were required to make this eight fuel matrix acceptable and that three extra fuels should be added to achieve the following:

- Increase poly-aromatics spread.
- Keep sulphur below 500 ppm.
- Include a fuel with a low T95 (ca. 320-325°C).
- Include a low density/low poly-aromatics fuel with a natural cetane number of ca. 58.
- Include a fuel with low density/low poly-aromatics/low T95 and ignition improved to ca. 58 CN.

Fuel formulation - There were 24 candidate fuel components available at the outset. No individual oil company could have supplied the full range required to blend all 11 fuels. All of these components were typical refinery streams found in commercial use. Since the availability of each of the components varied widely, it was necessary to formulate each fuel not only to meet the target properties, but also to maintain certain quantity constraints in order to be able to produce the required quantity of all 11 fuels. It was agreed that the final blends would not be treated with any additives other than an ignition improver as required in Fuels 8, 9 and 11. The selected formulations required a total of 16 different components to prepare the 11 fuels. These comprised as follows:

- 2 kerosenes
- 1 straight run high sulphur light gas oil
- 5 hydrotreated gas oils
- 4 hydrocracked gas oils
- 3 catalytically cracked gas oils
- 1 highly aromatic, narrow cut refinery stream

The subtle differences necessary between the components were achieved via differences in crudes and individual refining schemes and plant severities. The target requirements of the diesel fuel matrix were successfully met in the 11 fuels which were produced. The actual values vs. the target values are shown in Table 2.

Table 2. Targeted and actual values of main fuel properties of “EPEFE” research program [13,23,24]

EPD-X-94		1	2	3	4	5	6	7	8	9	10	11
Density (kg/m ³)	Target	828	828	855	855	828	855	828	855	855	828	828
	Actual	829.2	828.8	857.0	855.1	828.8	855.5	826.9	855.1	855.4	826.6	827.0
Polyaromatics (%wt.)	Target	1 - 2	7 - 8	1 - 2	7 - 8	4 - 5	7 - 8	7 - 8	7 - 8	7 - 8	1 - 2	1 - 2
	Actual	1.0	7.7	1.1	7.4	7.1*	7.6	1.0	7.3	8.0	1.1	0.9
T95 (°C)	Target	345 - 350	345 - 350	345 - 350	345 - 350	345 - 350	370	320 - 325	345 - 350	345 - 350	345 - 350	320 - 325
	Actual	344	349	348	344	346	371	326	345	344	347	329
CN (± 1)	Target	50	50	50	50	50	50	50	54	58	58	58
	Actual	51	50.2	50	50.3	50.6	50.2	49.5	54.8	59.1	58	57.1
S (± 50) (ppm)	Target	450	450	450	450	450	450	450	450	450	450	450
	Actual	404	416	415	442	402	440	432	420	424	469	447

As mentioned before the main object of that project was to investigate the effects of fuel properties and vehicle technology on the exhaust emissions from European light-duty and heavy-duty diesel vehicles. Thus it was conducted in two separate sub-projects which investigated the effect of diesel fuel properties on exhaust emissions from either light-duty or heavy-duty diesel vehicles.

For each sub-project, emissions measurements had been taken from a set of vehicles or engines over a specially blended fuel matrix. During the project a large number of engines of varying technologies were used for each of the two aforementioned sub-projects (i.e. 19 light-duty diesel vehicles and 5 heavy-duty diesel engines). The diesel matrix (see Table 4) aimed to test the effects of density, cetane number, T95 and polyaromatics on emissions. Because of the many imposed constraints and the interdependencies between these four parameters, it was impossible to build an overall orthogonal design matrix spanning all of the parameter ranges of interest in a collective way. Thus, an 11-fuel matrix was constructed as a series of orthogonal sub-matrices, as depicted in Figure 1.

The 2x2 sub-matrix formed by fuels 1, 2, 3, and 4 allowed the individual and joint effects of poly-aromatics (1% to 8%) and density (0.828 and 0.855 kg/l) to be estimated at fixed levels of cetane number (50) and T95 (345 °C). Fuel 5 was added so that the effect of removing tri-aromatics could be tested by comparing its emissions with those from fuel 2. The 2x2 sub-matrix formed by fuels 1, 7, 10 and 11 allowed the individual and joint effects of T95 (325 to 345 °C) and cetane number (50 to 58) to be estimated at low density (0.828 kg/l) and low poly-aromatics (about 1%). Fuels 4, 8 and 9 form a 3-fuel set which tests the effect of cetane number in high-density (0.855 kg/l) high-polyaromatic (8%) fuels.

Fuels 4 and 6 form a 2-fuel set for testing the effect of T95 (345 to 370 °C), again in high-density and high-polyaromatic fuels. The various sub-matrices possess desirable orthogonality properties and allow the

subsequent data to be analyzed in a very simple way. The results can thus be summarized in the form of simple tables, graphs and local models which are easily understood.

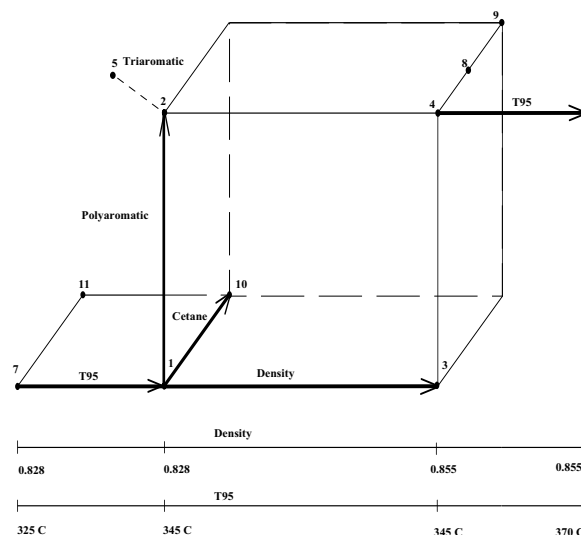


Fig. 1. Schematic view of the methodology used to statistically analyze the fuel properties of “EPEFE” program [13,23,24].

Most fuel effects are estimated by comparing emissions either from a pair of single fuels, or from the means of two pairs of fuels. Comparisons based on such small subsets of the data are much less precise than those based on (say) factorial or D-optimal designs, where all the data is used in each comparison. Moreover, fuel effects estimated from the diesel matrix in Figure 1 are local estimates valid only at the fixed values chosen for the other parameters. In view of these difficulties, it was decided to use a number of modeling approaches to ensure that any conclusions would be robust. Three approaches were used in relating emissions to fuel properties:

1. Fitting a global linear model in density, cetane number, T95 and poly-aromatics to each vehicle/engine individually and to the average emissions across vehicles/engines.
2. Finding the "best" linear model for each vehicle/engine and for the fleet average using stepwise regression. The best linear model was found by backwards stepwise regression. Terms which were not significant at the 5% level, were removed from the model.
3. Fitting local 2-variable linear models to each of the various sub-matrices (the other 2 variables being fixed).

Each emission was analyzed separately and, in each case, the mean of each pair of back-to-back results was taken as the response variable. Again, actual rather than target fuel properties were used. In the light-duty case separate analysis of ECE, EUDC and composite results were conducted. For each statistical model, tables with the statistical parameter estimated according with the standard errors, t- and P-values had been produced.

All the parameters estimated by the aforementioned statistical approaches were generally in good agreement with one another. The light-duty model also gave predictions in good agreement with the emissions actually observed from two additional fuels outside the test matrix. The global heavy-duty diesel emissions models showed significant lack of fit for some emissions, whilst analysis of the first 2x2 sub-matrix (fuels 1-4) revealed interactions between density and poly-aromatics in the light-duty diesel data. When constructing the diesel matrix, the design parameters density, cetane number, T95 and poly-aromatics were assigned target values and other fuel properties, such as sulphur, were kept constant.

However, in order to blend fuels to these predetermined targets, certain other fuel parameters had to be varied, many reflecting the composition of the fuel. These included the fractions of naphthenes, total aromatics, mono-, di- and tri-aromatics and N-paraffins as well as T10 and viscosity. Inevitably the values of these parameters are highly intercorrelated within the fuel matrix by using Partial Least Square (PLS) technique. Furthermore, exploratory analysis (i.e. a combination of PCA and PLS techniques) was used to investigate the effects of both fuel properties and vehicle technology on the emissions for the various combinations of vehicle and fuel types. This allowed an assessment to be made of the relative importance of each of the variables.

FUEL PROPERTIES OF "JOULE -II" PROGRAM – This program aimed to address the following issues relating to the influence of diesel fuel properties on particulate formation and emissions of other pollutants in diesel engines:

- The influence of fuel aromatic content, specifically the bi- and tri-cyclic aromatic components.
- Distinction of the influence of fuel physical properties, notably density, from that of chemical properties which correlate with the physical properties.
- The development and application of chemical and physical models to provide increased understanding of the influence of fuel properties and engine characteristics.

On the base of existing knowledge on fuel effects on emissions, it was decided to investigate the effects on the following fuel properties on particulate formation:

- Density.
- Mono-aromatics.
- Di-aromatics.
- Tri-aromatics.
- Detergent additives.

It was decided to prepare these fuels with the following constraints:

- Keep constant the total aromatic content.
- Keep the sulphur content at a constant level, below 0.05%.
- Keep the cetane number within a narrow range of 52 ± 2 .

In order to satisfy the previous constraints it was decided to produce these fuels synthetically using base components that were mixed at various analogies. The main components were:

- The source of aromatics was a Light Light Cycle Oil (LLCO). This is an aromatic effluent produced in refineries from catalytic cracking. After distillation this was divided into two components C₁ and C₂ the first containing only mono-aromatics and the second containing mono- and di- aromatics.
- Non aromatic components C₃ and C₄ with high cetane numbers from a petrochemical plant.
- Finally other pure components were used to control the other properties of the synthetic fuels and were used in small quantities, phenanthrene was used to adjust the tri-aromatic content, di-benzothiophene to adjust the sulphur level and diglyme to adjust the oxygen content. The properties of these components are shown in Table 3.

Table 3. Properties of fuel components of “JOULE-II” program [9,10]

C ₁	Distillation cut from LLCO (<200 °C) high in mono-aromatic, very low in di-aromatic
C ₂	Distillation cut from LLCO (>200 °C) containing mono- and di-aromatic
C ₃	Petrochemical stream, narrow range in distillation, fully dearomatised, no sulphur, high in cetane (68)
C ₄	Same as C ₃ with lower cetane number (55)
Phenanthrene	Pure phenanthrene, tri-aromatic booster
Benzothiophene	Pure benzothiophene, sulphur booster
α-methylnaphthalene	Pure α-methylnaphthalene, di-aromatic booster

The main properties of the fuels used in the present investigation are given in Table 4. At this point it should be clarified that the cetane number of the fuels was adjusted using a high cetane number component which was a Fisher Tropsch solvent having a cetane number up to 90.

Table 4. Description of physical and chemical properties of the fuels, which were prepared and used in the “JOULE - II” research program [9,10]

Reference Fuel	Base	N1	N2	N3	N4	N5	N7
Monoaromatics (%wt.)	25.3	24.6	21.6	20.9	20.6	17.2	22.1
Diaromatics (%wt.)	0.9	2.9	4.2	3.6	4.6	9.5	4.4
Triaromatics (%wt.)	0.1	0.2	0.1	1.0	0.1	0.1	0.1
Total Aromatics (%wt.)	26.3	27.7	25.9	25.5	25.3	26.8	26.6
Paraffins (%wt.)	41.6	37.6	43.8	40.5	55.3	52.7	41.9
Napthenics (%wt.)	27	29.5	33.4	34.2	22.8	22.2	33.4
Carbon (%wt.)	86.3	86.2	86.3	85.9	85.8	86.6	86.4
Hydrogen (%wt.)	13.6	13.6	13.6	13.6	13.7	13.4	13.5
C/H mass ratio	6.35	6.35	6.35	6.32	6.26	6.46	6.4
Cetane number	53.0	52.1	51.8	52.7	49.4	51.4	52.4
Density at 15°C (kg/m ³)	0.8161	0.8261	0.8287	0.8301	0.8129	0.8292	0.8290
Viscosity at 40°C (mm ² /s)	1.719	2.011	2.148	2.123	1.680	2.110	2.138
Surface tension at 20°C (mN/m)	27.7	28.4	28.5	28.4	26.6	27.6	28.5
Net heating value (MJ/kg)	42.52	42.77	42.77	42.72	43.01	42.87	42.94
IBP (°C) ASTM D86	98	152	196	189	194	205	193
T50 (°C) ASTM D86	252	252	253	251	219	248	251
FBP (°C) ASTM D86	309	304	309	307	305	305	307

FUEL PROPERTIES OF “JOULE-III” PROGRAM - Thirteen test fuels having different aromatic content were prepared in an oil refinery in Finland under a EU-funded research program [5,6,11,40]. The objective of this program was the examination of the effect of fuel aromatic content on diesel emitted pollutants aiming ultimately to the determination of a low aromatic content (“aromatic threshold”) in the fuel sooting tendency. A detail description of the test fuels is given in Table 5. Fuel preparation was conducted according to the following constraints:

- to keep the sulphur content as low as possible (<50 ppm).
- to preserve distillation the curve within narrowed boundaries.
- to allow no significant variations in the physical properties of the fuel.

Fuel D1 is a synthetic fuel, high in paraffins (95%wt.) with an aromatic content near zero (<1%wt.) whereas ‘reference’ fuel D0 is a low-sulphur European diesel fuel

for road vehicles used as a reference for the engine tests. Various amounts of diesel fuel, toluene (a single-aromatic compound) and methylnaphthalene (a two-ring aromatic compound) were added to fuel D1 to derive fuels D2 to D12. Having in mind the salient features of Table 5, test fuels are classified as follows:

- The test fuels D1, D3, D5, D4, D8, D9, D10 and reference fuel D0 indicate a progressively increasing aromatic fraction. As a result, the effect of total aromatics on engine performance characteristics and pollutant emissions can be examined. According to Table 5, the aromatic content of test fuels increases progressively from below 1% for D1 up to 26.8% for reference fuel D0.
- Test fuels D1, D3, D5, D6, D8, D9 and D10 comprise a series of increasing monoaromatic content from <1% up to 12.2%wt. Considering this, the effect of monoaromatic content on engine pollutants is investigated.
- According to Table 5, fuels D4 and D5 have the same aromatic content and almost negligible

triaromatics, while the diaromatics of fuel D4 are substituted by monoaromatics in fuel D5. Thus, the effect of the type of aromatic structure on

measured emissions can be examined by comparing the results obtained for test fuels D4 and D5.

Table 5. Chemical composition and properties of conventional diesel fuels of "JOULE-III" program [5,11,40]

Reference Fuel	D0	D1	D3	D4	D5	D6	D8	D9	D10	D12
Blending Information	Road vehicle diesel	Base Fuel	Base+ diesel	Base+ napthenics	Base+ diesel	Base+ diesel	Base+ diesel	Base+ diesel	Base+ diesel	Base+ diesel+ napthenics
Monoaromatics (%wt.)	22.2	<1.0	2.3	<1.0	4.4	6.1	7.5	9.4	12.2	10.1
Diaromatics (%wt.)	4.2	<0.1	0.4	5.4	0.6	1.0	1.3	1.6	1.8	4.2
Triaromatics (%wt.)	0.34	<0.02	0.03	<0.02	0.06	0.09	1.1	0.13	0.14	0.13
Total aromatics (%wt.)	26.8	<1.0	2.6	5.7	5.0	7.1	8.8	11.0	14.0	14.3
Paraffinics (%wt.)	47.1	95.0	89.1	89.9	82.9	77.2	71.7	58.9	60.6	58.5
Napthenics (%wt.)	24.5	4.5	8.1	5	11.7	14.9	17.9	28.4	24.5	26.4
Carbon (%wt.)	86.3	84.7	84.7	84.7	84.2	83.6	84.4	85.3	85.6	84.6
Hydrogen (%wt.)	13.8	15.7	15.5	15.2	15.2	14.9	14.9	14.8	14.7	14.5
C/H mass ratio	6.25	5.39	5.47	5.57	5.54	5.61	5.67	5.76	5.82	5.84
Cetane number	52.5	64.05	64.5	60.8	62.25	62.05	61.1	60.25	59.95	57.95
Density, 15 °C (kg/m ³)	833.7	779.6	785.8	789.1	792	798.2	804.4	810.5	816.4	815.2
Viscosity, 40 °C, (mm ² /s)	2.72	2.49	2.58	2.44	2.63	2.72	2.81	2.92	2.99	2.85
Specific Energy (net) (MJ/kg)	42.74	43.88	43.695	43.61	43.565	43.5	44.075	43.405	43.855	43.13
IBP (°C)	176	191.1	190.1	194.4	192.9	190.8	193.8	193.2	194	191.6
T50 (°C)	268	254.8	258.6	251.9	262.6	266.2	269.1	272.1	276.3	270.1
FBP (°C)	361	354.2	353.7	353.6	355.8	352.7	356.4	354.5	355.3	357

Multivariable statistical analysis of fuel properties of "JOULE-II" program - As evidenced, strong interrelations exist between some fuel properties. Hence, it is quite difficult to ascribe the differences observed in diesel engine performance characteristics and emitted pollutants to one or more fuel characteristics. This is attributed to the fact that the variation of one fuel characteristic results in the variation of one or more fuel properties, which are directly or indirectly dependent from it. Hence, a multivariable statistical analysis is conducted to determine the correlation coefficients between fuel composition characteristics and its physicochemical properties. The results of this multivariable analysis are presented in Table 6, where the Pearson product moment correlation for each pair of

fuel properties is given. Pearson coefficients, P, reflect the statistical significance of the estimated correlations whereas correlation coefficients R^2 vary between -1 and +1 and they correspond to the degree of linear correlation between fuel characteristics. Pearson coefficient P values, which are lower than 5%, indicate statistical significant non zero correlations at 95% degree of confidence. All the pairs of independent fuel variables (identified as those with P values higher than 0.05) are given in Table 7. Pearson moment correlation value P is used as criterion of statistical independence between fuel properties instead of using a predefined minimum value for the correlation coefficient.

Table 6. Correlation coefficients of fuel characteristics of “JOULE III” research program [5]

	Cetane number	C/H mass ratio	Density (kg/m ³)	Diaromatics (%wt.)	T50 (°C)	FBP (°C)	Net heating value (kJ/kg)	IBP (°C)	Monoaromatics (%wt.)	Napthenics (%wt.)	Paraffinics (%wt.)	Total aromatics (%wt.)	Triaromatics (%wt.)	Viscosity (mm ² /s)
Cetane number	1													
C/H mass ratio	*-0.92 **0.00	1												
Density (kg/m ³)	-0.86 0.00	0.99 0.00	1											
Diaromatics (%wt.)	-0.70 0.04	0.46 0.21	0.32 0.39	1										
T50 (°C)	-0.62 0.08	0.85 0.01	0.92 0.00	-0.07 0.87	1									
FBP (°C)	-0.57 0.11	0.51 0.16	0.54 0.13	0.16 0.67	0.48 0.19	1								
Net heating value (MJ/kg)	0.62 0.07	-0.47 0.20	-0.40 0.29	-0.49 0.18	-0.21 0.60	0.14 0.72	1							
IBP (°C)	-0.52 0.15	0.44 0.24	0.39 0.30	0.48 0.19	0.24 0.54	0.33 0.39	0.06 0.88	1						
Monoaromatics (%wt.)	-0.75 0.02	0.93 0.00	0.97 0.00	0.12 0.76	0.98 0.00	0.53 0.14	-0.31 0.42	0.30 0.44	1					
Napthenics (%wt.)	-0.77 0.02	0.92 0.00	0.96 0.00	0.16 0.69	0.94 0.00	0.51 0.16	-0.45 0.22	0.25 0.52	0.96 0.00	1				
Paraffinics (%wt.)	0.83 0.01	-0.96 0.00	-0.98 0.00	-0.24 0.53	-0.93 0.00	0.53 0.14	0.45 0.23	0.31 0.41	-0.97 0.00	-0.99 0.00	1			
Total aromatics (%wt.)	-0.92 0.00	0.99 0.00	0.99 0.00	0.45 0.22	0.86 0.00	0.54 0.14	-0.45 0.23	0.43 0.25	0.94 0.00	0.92 0.00	-0.96 0.00	1		
Triaromatics (%wt.)	-0.17 0.67	0.21 0.58	0.29 0.46	-0.09 0.81	0.34 0.38	0.48 0.19	0.44 0.24	0.36 0.35	0.28 0.48	0.23 0.56	-0.25 0.52	0.21 0.58	1	
Viscosity (mm ² /s)	-0.65 0.06	0.88 0.00	0.94 0.00	-0.01 0.98	0.99 0.00	0.48 0.20	-0.22 0.58	0.26 0.50	0.99 0.00	0.96 0.00	-0.95 0.00	0.88 0.02	0.32 0.40	1

*Values in bold indicate correlation coefficients R^2 .

**Values with normal characters indicate Pearson moment coefficients.

Table 7. Statistically independent fuel property pairs of “JOULE-III” research program [5]

Property 1	Property 2	Correlation coefficient	P value	Property 1	Property 2	Correlation coefficient	P value
Cetane number	T50	-0.62	0.08	>>	IBP	0.24	0.54
>>	FBP	-0.57	0.11	>>	Triaromatics	0.34	0.38
>>	Net heating value	0.62	0.07	FBP	Net heating value	-0.14	0.71
>>	IBP	-0.52	0.15	>>	IBP	0.33	0.39
>>	Triaromatics	-0.17	0.67	>>	Monoaromatics	0.53	0.14
>>	Viscosity	-0.65	0.06	>>	Napthenics	0.51	0.16
C/H mass ratio	Diaromatics	0.46	0.21	>>	Paraffinics	-0.53	0.14
>>	FBP	0.51	0.16	>>	Total aromatics	0.54	0.14
>>	Net heating value	-0.47	0.20	>>	Triaromatics	0.48	0.19
>>	IBP	0.44	0.24	>>	Viscosity	0.48	0.19
>>	Triaromatics	0.22	0.58	Net heating value	IBP	0.06	0.88
Density	Diaromatics	0.32	0.40	>>	Monoaromatics	-0.31	0.42
>>	FBP	0.54	0.13	>>	Napthenics	-0.45	0.22
>>	Net heating value	-0.40	0.29	>>	Paraffinics	0.45	0.23
>>	IBP	0.39	0.30	>>	Total aromatics	-0.45	0.23
>>	Triaromatics	0.29	0.46	>>	Triaromatics	0.44	0.24
Diaromatics	T50	-0.07	0.87	>>	Viscosity	-0.21	0.58
>>	FBP	0.16	0.67	IBP	Monoaromatics	0.30	0.44
>>	Net heating value	-0.49	0.18	>>	Napthenics	0.25	0.52
>>	IBP	0.48	0.19	>>	Paraffinics	-0.32	0.41
>>	Monoaromatics	0.12	0.76	>>	Total aromatics	0.43	0.25
>>	Napthenics	0.16	0.69	>>	Triaromatics	0.36	0.35
>>	Paraffinics	-0.24	0.53	>>	Viscosity	0.26	0.50
>>	Total aromatics	0.45	0.22	Triaromatics	Monoaromatics	0.28	0.47
>>	Triaromatics	-0.09	0.81	>>	Napthenics	0.23	0.56
>>	Viscosity	-0.01	0.98	>>	Paraffinics	-0.25	0.52
T50	FBP	0.48	0.19	>>	Total aromatics	0.21	0.58
>>	Net heating value	-0.21	0.60	>>	Viscosity	0.32	0.40

Independent fuel property pairs facilitate the examination of the statistical interrelation between measured diesel emitted pollutants and fuel characteristics.

FUEL PROPERTIES OF THE “NEDENEF” PROGRAM - The fuels of this program were developed to identify diesel fuel formulations to be used in future diesel engines. The main objective of this program was to specify the “optimum” fuel physical properties for further decreasing diesel exhaust emissions without affecting negatively or if possible, decreasing further bsfc in modern diesel engines [7,12].

Hence, seven test fuels with different molecular type were prepared to study the effect of fuel density, viscosity and compressibility factor on DI diesel engine performance and pollutant emissions. Initially, the specifications of a reference fuel named as “base” DS1 were selected. This fuel mixture would be used for the preparation of the other test fuels. The characteristics of the “base” fuel, which was selected to be a Finnish summer - grade city diesel oil, were the following:

Table 8. Design specifications of “base” fuel DI1 from “NEDENEF” research program [7,12]

Density	820 – 840 kg/m ³
Viscosity	2 – 4 mm ² /s
Cetane number	around 55
Total aromatic content	around 20%wt
Polyaromatic content	less than 5%wt
Sulfur content	around 20 ppm
T50	around 265 °C
T95	around 360 °C

Then, a series of six conventional diesel fuels was prepared with values of density ranging from 800 to 850 kg/m³, viscosity varying between 1.5 and 5 mm²/s and compressibility factor ranging between 6.6 and 7.05 x 10⁻⁵ bar⁻¹. The composition, the chemical and physical properties of the test fuels are shown in Table 9. At this point it is necessary to address the basic differences in chemical synthesis and physical properties between fuels DS2 – DS3 and DS4 – DS5:

1. According to the initial planning of the research program, fuels DS2 and DS3 are called “Density Fuels” because they were prepared in order to have different densities while all other fuel parameters were to be kept to be constant. However, as evidenced from Table 9, the increase of density is accompanied by a significant increase of fuel viscosity (almost 75%), increase of cetane number and decrease of compressibility factor. This is

attributed mainly to the partial replacement of fuel paraffinic content of fuel DS2 by naphthenics and secondarily, to the increase of distillation temperature due to the addition of a high distillation temperature additive.

2. Fuels DS4 and DS5 were initially named "Viscosity Fuels" because they were prepared to have different viscosities with all other properties were to be kept constant. However, in this case also, the drastic increase of viscosity (almost 170%) was accompanied by increase of density, increase of cetane number and decrease of compressibility factor. In this case, such changes can be ascribed mainly to the increase of distillation temperature and to the partial replacement of paraffines by naphthenics.

Hence, both fuel pairs DS2 – DS3 and DS4 – DS5 can be used to examine the combined effect of fuel density, viscosity and compressibility factor mainly due to the increase of distillation temperature on diesel engine performance characteristics and pollutant emissions utilizing pertinent measurements from Lister LV1 engine. According to research program planning, fuels DS6 and DS7 were prepared to examine the effect of variable compressibility factor on diesel engine performance and exhaust emissions. For this reason, they were initially named "Compressibility Fuels". However their compressibility and density values are almost the same. The transition from fuel DS6 to DS7 is accompanied by reduction of fuel viscosity due to small decrease of distillation temperatures. Thus, the examination of experimental findings for fuel pair DS6 – DS7 will assist to the comprehension of the effect of fuel viscosity on diesel engine performance and exhaust emissions.

Table 9. Salient features of test fuels DS1 – DS7 of the "NEDENEF" program [7,12]

Fuel	DS1 "Base"	DS2	DS3	DS4	DS5	DS6	DS7
Recipe	Finnish City diesel summer grade	Paraffinics + Low distillation temperature additive	Napthenics + High distillation temperature additive	Base fuel + Low distillation temperature additive	High distillation temperature fuel	Base fuel + Paraffinic compound	Base fuel + Napthenic compound
Monoaromatics (%wt.)	19.9	15.3	14.6	15.7	14.4	14.8	14.4
Diaromatics (%wt.)	2.2	1.1	1.3	0.7	1.3	1.7	1.7
Polyaromatics (%wt.)	2.4	1.2	1.5	0.8	1.7	1.8	1.9
Total Aromatics (%wt.)	22.3	16.5	16.0	16.5	16.1	16.6	16.3
Paraffines (%wt.)	40.1	53.0	33.5	40.7	37.5	46.2	40.8
Napthenics (%wt.)	40.1	32.2	52.7	45.3	48.6	39.1	44.6
Aromatics (%wt.)	19.8	14.8	13.8	14.0	13.9	14.7	14.6
Density, 15°C, (kg/m ³)	833.7	817.2	839.3	818.8	837.7	827.7	830.0
T5 (°C)	208.0	208.7	219.9	194.1	227.2	210.8	210.5
T50 (°C)	270.2	246.0	299.1	223.2	319.4	273.4	261.3
T95 (°C)	347.9	311.8	347.2	301.1	380.2	340.5	344.1
Cetane Number	53.3	53.3	56.1	50.9	57.5	54.8	54.7
Viscosity, 40°C, (mm ² /s)	2.94	2.22	3.88	1.80	4.81	2.97	2.74
Surface Tension, 20°C, (mN/m)	28.0	28.1	29.4	28.1	29.7	28.8	28.9
Net Heating Value (MJ/kg)	43.03	43.41	43.00	42.92	43.22	43.31	43.22
Compressibility, 60 bar, 20°C (x10 ⁻⁵ bar ⁻¹)	6.81	7.04	6.62	7.04	6.60	6.81	6.80
C/H Ratio	6.1	6.0	6.14	6.14	6.14	6.04	6.07