



IGNITION QUALITY OF RESIDUAL FUEL OILS

Francisco Arvelo Valencia¹, Isidro Padrón Armas²

ABSTRACT

The relevance of residual fuel oil aromaticity for its ignition performance in diesel engines has been demonstrated previously and led to the concept of calculating aromaticity from known specification properties. Thus the Calculated Carbon Aromaticity Index (CCAI) can be calculated from density and viscosity, and provides a useful tool to rank the ignition quality of different residual fuel oils: the lower the number, the better the ignition characteristics.

Potential improvements to the CCAI concept have been investigated. The CCAI represents the aromaticity of the entire fuel. However, at low load engine operations ignition occurs at relatively low temperatures, when only part of the injected fuel may have evaporated. Under these conditions the high molecular weight, highly aromatic (asphaltene) components in all probability are not all vaporised. Thus the aromaticity of the (lighter) part of the fuel might be different from the bulk and possibly more relevant to ignition quality. A programme to investigate the relationship between ignition delay and the aromaticity of the fuel vapour under certain engine conditions has been carried out.

The relationship between ignition delay and CCAI was demonstrated to be valid at all engine conditions employed and comparable to the one found previously. No improvement could be realised by taking into account the micro carbon residue (MCR) content as a measure for the heavy fraction of the fuel, nor any other of the available fuel parameters. The results of Pyrolysis Combustion Mass Spectrometric Element (PCME) analysis of the fuels, providing detailed compositional information of the vapour at different temperatures, indeed confirm that the aromaticity of the lighter fuel fractions does not dominate the aro-

¹ Dr. en Marina Civil, ETS de Náutica y maquinas y Radiotelegrafia Naval (parva@telefonica.net).

² Profesor ETS de Náutica y Maquinas y radiotelegrafia Naval (ipadron@ull.es).



maticity of the fuel vapour and therewith does not dominate the ignition performance of the fuel. However, in view of the still rather limited predictive power of the CCAI, other, not yet identified fuel parameters must play a role.

Key word: Carbon Aromaticity index, ignition, residual fuel oil

INTRODUCTION

In the absence of an indicator for ignition quality of residual fuels, like the Cetane Index for distillate fuels, extensive research by Zeelenberg et al.^{1,2} resulted in the concept of the Calculated Carbon Aromaticity Index (CCAI). Since its introduction in the early eighties an increase in the use of CCAI has been observed in the industry. Experience with the concept learns that it is a useful tool for ranking fuels roughly on ignition quality, but also that the CCAI is not a very accurate measure. Apparently fuel parameters other than carbon aromaticity play a role. Possible improvements of the CCAI have been sought in the quality of the light end components of fuels, assumed to ignite first.

THE SHELL CCAI CONCEPT

Ignition difficulties when using distillate fuels are almost unheard of. For many years the ignition quality of these fuels, such as gas oil, has been characterised primarily by a parameter known as Cetane Number, although to a lesser extent other methods such as Cetane Index or Diesel Index have been used also. Current international specifications for marine distillate fuels, such as the ISO 8217: 1996 and BS MA100: 1996, include a minimum limit for Cetane Number. Regrettably there is no similar widely recognised procedure for characterising the ignition quality of residual fuel oil. For a number of reasons the methods used for determining ignition quality of distillate fuels cannot be applied to residual fuel oils. Therefore in the early eighties Shell Research embarked upon a programme with the objective of gaining an understanding of the factors controlling the ignition performance of residual fuel oils, and to identify means of quantifying ignition quality.

Both the physical and chemical properties of residual fuel oil were found to have an influence on ignition performance. Physical properties are viscosity and temperature. Atomisation quality is greatly affected by fuel viscosity. Too high a viscosity at injection increases fuel droplet size, which hinders fuel/air mixing in the cylinder and extends ignition delay and combustion. Many engine designs now incorporate fuel management systems capable of operating at temperatures which allow a wide range of residual fuels to be burned without difficulty.

The relevance of the chemical composition of residual fuel oil on ignition was also demonstrated. This led to the recognition that ignition performance relates to fuel aromaticity. Since aromaticity is a difficult parameter to measure in the absence



of specialist laboratory equipment, Shell developed the concept of calculating residual fuel aromaticity. The resulting Calculated Carbon Aromaticity Index (CCAI) can be calculated on the basis of specification properties viscosity and density. It is this parameter which has gained favour as the most practical and meaningful method for characterising ignition quality of residual fuel oils.

CCAI can be calculated from the following formula:

$$CCAI = D - 81 - 141 \text{Log}[\text{Log}(V_k + 0.85)] - 483 \text{Log}\left[\frac{T + 273}{323}\right]$$

Where: D = density at 15°C, kg/m³

V_k = kinematic viscosity (mm²/s) at temperature T°C

It must be stressed that CCAI is a unit-less number allowing ranking the ignition qualities of different residual fuel oils: the lower the number, the better the ignition characteristics. CCAI does not give an absolute measure of ignition performance since this is much more dependent upon engine design and operating conditions. For this reason no attempt has been made to include limiting values in international standards, since a value which may be problematical to one engine operated under adverse conditions may perform quite satisfactory in many other instances. Modern medium speed engines will tolerate CCAI values up to 870 to 875, and even values up to 890 and beyond are acceptable to some engine types. Medium speed diesel engines are sensitive to fuels having poor ignition characteristics, while low speed cross head engines may be more tolerant of higher CCAI values. The limits for viscosity and density in international marine fuel specifications in themselves provide a control of

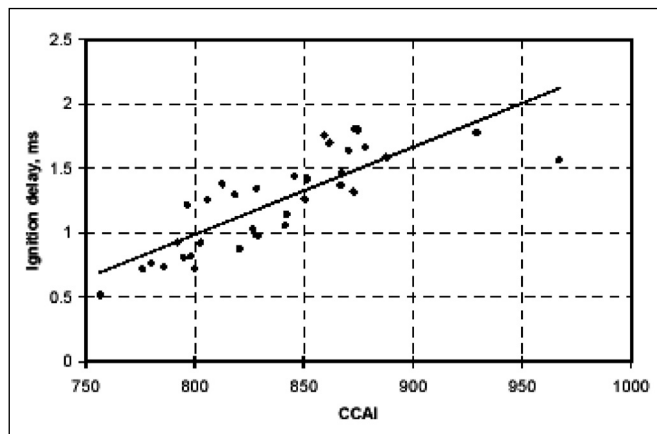


Figure 1: Correlation Ignition delay - CCAI

ignition quality for the main residual fuel oil grades. For example, a 380 mm²/s (@ 50°C) fuel oil at maximum specification density of 991 kg/m³ has a CCAI of 852, whilst a 180 mm²/s (@ 50°C) fuel oil with the same density has a CCAI of 861. Ignition characteristics improve with increasing viscosity and decreasing densi-



ty. Ignition difficulties can become more acute at lower fuel viscosity (e.g. $< 100 \text{ mm}^2/\text{s}$ @ 50°C) if there is not a significant corresponding reduction in density. This is one of the reasons for the lower density limits applying to the low viscosity grades in the international specifications.

The correlation between ignition delay and CCAI is not ideal (see Figure 1 for typical results obtained in a research engine). The scatter of data points around the regression line is rather large. At lower engine outputs this scatter is even larger. This is not necessarily due to experimental errors since cases have been reported where from two fuels with similar analyses one gave ignition problems at low engine output, but the second ran as normal. It is recognised that fuels may appear on the market whose poor ignition performance is not predicted by their CCAI value, but also that fuels which perform satisfactorily should not be rejected on basis of their too high CCAI value.

Thus the CCAI is based on bulk fuel properties only and does not require detailed chemical information of the fuel. The use of CCAI has been evaluated^{3,4} and it has been concluded that this parameter gives a rough estimate of the ignition performance of heavy fuels at best. In contrast, CCAI has been found to correlate very well with the ignition performance of distillate fuels. The latter could suggest that the ignition quality of residual fuels is more closely related to the quality of the distillate part of the fuel rather than to the bulk properties. This has lead to further research attempting to improve the CCAI correlation by including vapour composition.

INFLUENCE OF VAPOUR AROMATICITY

A critical element of the CCAI concept is the assumption that at the moment of ignition of the vapour, almost all of the injected fuel has vaporised, i.e. that the aromaticity of the vapour is identical to that of the bulk. Particularly at low temperatures, at engine start-up conditions and low load operation, this is not necessarily the case. The high molecular weight fraction of the fuel will not vaporise at all or only with great difficulty. Therefore the aromaticity of the bulk as indicated by the CCAI is not representative for the aromaticity of the igniting vapour^{4,5}. Theoretically the following situations could exist:

- At low ignition temperatures, the vapour composition may be primarily that of the distillate diluents and contains hardly any heavy residue of the fuel. If the diluent has a paraffinnic character the ignition performance will be better than predicted by the CCAI and worse for an highly aromatic diluent.
- At somewhat higher temperatures, the residue will also begin to vaporise and take part in the ignition process. Because the aromaticity is mainly contained in the high molecular weight part of the residue, the contribution to the nature of vapour is mainly paraffinnic. The ignition performance will therefore be more or less the same for a fuel with a paraffinnic diluent or might even improve in case of an aromatic diluent.



- At high temperatures almost all of the residue evaporates and contributes to the nature of the vapour phase. In this case the aromaticity of the vapour will be similar to that of the bulk and the ignition performance may be as predicted by the CCAI.

The Calculated Vapour Aromaticity Index (CVAI)

Work to better predict ignition quality by taking the aromaticity of the vapour phase into account was initiated by J.C. van der Werff, J.S.E.A.M. Naber and F.M. Wortel (unpublished work). A crucial element in the estimate of the vapour aromaticity, is the selection of a parameter for the amount of non-vaporisable aromatic carbon of the fuel. For pragmatic reasons the micro carbon residue (MCR) content has been chosen for this purpose. MCR is determined at 500°C close to the experimental conditions in the engine. Also MCR (or Conradson carbon residue, CCR) is an existing fuel specification. To obtain a measure for vapour aromaticity, the CCAI was corrected for MCR for which the following equation was derived (Appendix I):

$$CVAI = \frac{CCAI - 10.5c(MCR)}{1 - c\left(\frac{MCR}{100}\right)}$$

Correlation with ignition delay in test rig

The validity of this CVAI has been evaluated on a series of test fuels blended from short residues or thermally cracked residues with either kerosene or light catalytically cracked cycle oil (LCCCO). The choice of these components was to create so-called gap-fuels with a distinct difference between the aromaticity of the distillate and residual fraction. The ignition tests were performed in a fuel ignition test rig, consisting of an electrically heated, cylindrical combustion chamber of approximately 4 litre in which compressed air at a pressure of maximum 50 bar is heated to a temperature of maximum 600°C.

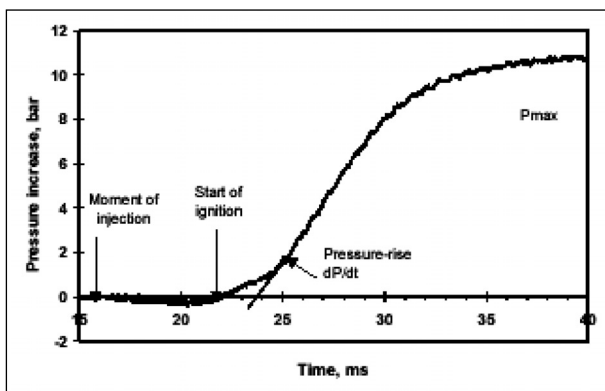


Figure 2: Pressure increase in the combustion chamber after injection of fuel.

At the test conditions one single amount of fuel is injected with a volume of maximum 0.15 ml. The moments of injection and ignition are derived from the fuel pressure or needle lift and cylinder pressure or light emission signal, respectively. A typical curve of the pressure development in the combustion chamber is shown in Figure 2.

The ignition delay of the test fuels was measured at three different temperature and air pressure conditions: 450°C and 45 bar, 490°C and 50 bar, and 525°C and 50 bar. Each fuel was measured 10 times at each condition.

The results show that the high CCAI (>850) fuels with LCCCO as cutter, give considerable variation in results. On the other hand, the low CCAI fuels with kerosene as cutter give much less variation. This was particularly valid at 450 °C. This may be interpreted to be the result of incomplete residue vaporisation at this relatively low temperature, although it is not at all clear why this is not observed similarly with the high CCAI fuels.

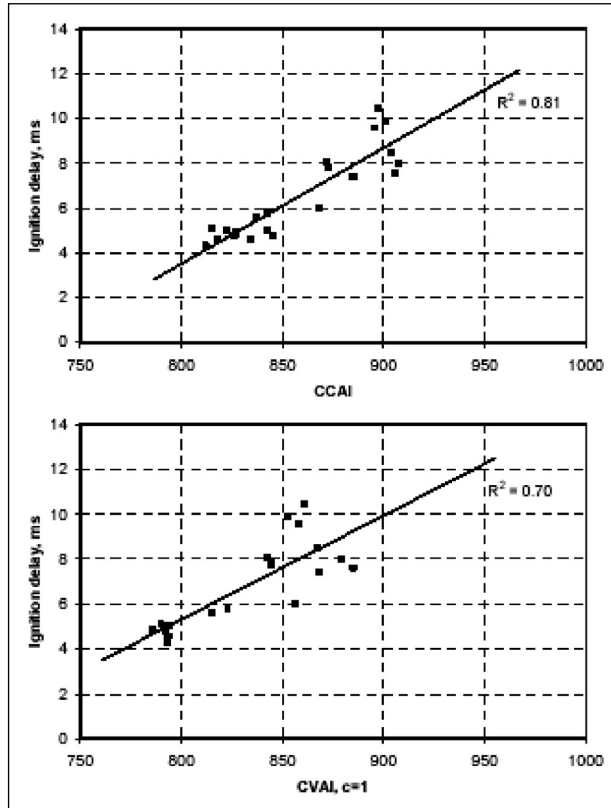


Figure 3: Relation between test-rig ignition delay and CCAI and CVAIc = 1. Temperature 490°C / Pressure 50 Bar

		525 °C	490 °C	450 °C
CCAI	c = 0	0.92	0.81	0.85
CCAI	c = 0.5	0.93	0.79	0.90
CCAI	c = 1.0	0.88	0.70	0.93
CCAI	c = 1.2	0.84	0.64	0.92

Table 1: R2-values for linear regression of test-rig ignition delays versus CCAI and CVAI (Fuel 1-21).



Bore, mm	137
Stroke, mm	168
Volume at TDC, ltr	0.19
Compression ratio	13.8
Speed, min ⁻¹	1000
Load, Nm	100 - 300
Power output, kW	10.5 - 31.5
Charge air pressure, bar	0.9 - 2.2
Charge air temperature, °C	30 - 60
Static injection timing, °CA BTDC	31

Table 2: Technical details and operating conditions of the AVL-Caterpillar 1Y540 engine used for ignition delay measurements.

The CVAI does not give a better correlation with ignition delay than CCAI. The regression coefficients decrease with increasing c-value (Table 1), i.e. increasing effect of correction for MCR, for the tests at 525°C and 490°C. Only for the tests at 450°C the regression coefficient tends to improve a little.

Correlation with ignition delay in test engine

To investigate the correlation of CVAI under realistic conditions an extended series of fuels was tested in an AVL-Caterpillar 1Y540 single cylinder 4-stroke high speed diesel engine.

The engine is fully instrumented for ignition parameter measurements, i.e. with pressure transducers in both combustion chamber and high-pressure fuel line approximately 10cm in front of the injector housing, injector needle lift sensor and shaft encoder for main axis angular position (degrees crank angle, °CA). The engine was run at well controlled conditions with respect to speed, load, air inlet temperature and pressure, cooling water and lubricating oil temperatures and pressures.

The fuel was supplied from a heated 60 litre container placed on a balance, allowing continuous monitoring of fuel consumption at the desired fuel temperature for a 12-15 mm²/s injection viscosity. For each ignition measurement, combustion pressure, fuel line pressure and needle lift data were recorded by an AVL Indiskop 647 instrument, transferred to an IBM compatible PC and analysed with dedicated software for ignition delay and combustion hardness.

Test Mode	At moment of injection		At Top Dead Centre	
	°C	Bar	°C	Bar
I	411	21.0	487	31.2
II	423	27.8	499	41.6
III	456	39.3	537	58.9
IV	479	50.9	562	76.2

Table 3: Typical adiabatic compressed air temperatures and pressures calculated for the AVL Caterpillar 1Y540 engine.

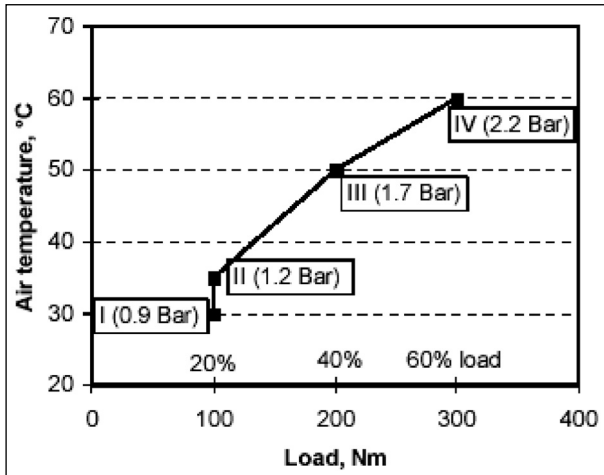


Figure 4: AVL-Cat engine test conditions. Variation of load and air temperature/pressure

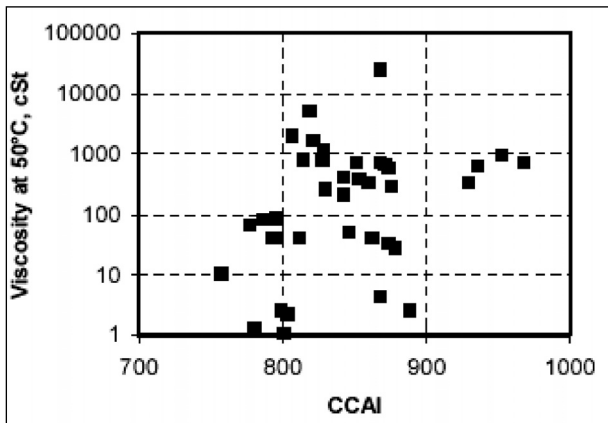


Figure 5: Viscosity/CCAI of ignition test fuels.

rated (0.9 bar) inlet air at a temperature of 30°C. Then the gasoil was quickly switched for the test fuel to start Mode I. For Mode II the air compressor and in line heater were activated giving inlet air with temperature of 35°C and pressure of 1.2 bar. For Mode III these parameters were raised to 50°C and 1.7 bar, respectively, allowing the power output to be raised to 40% with a load of 200 Nm. For Mode IV the inlet air temperature and pressure were raised further to 60°C and 2.2 bar, respectively, at engine load of 300Nm representing 60% power output. After Mode IV the engine was turned off and allowed to cool. Mode IV closely resembles the conditions on the MaK engine used previously by Zeelenberg¹

Test modes

The test sequence was designed to have in a single engine test both low and high ignition temperatures, thus allowing demonstration of both the CVAI and CCAI ignition prediction concepts. This was attempted with a sequence of 4 modes (I,II,III and IV) by stepwise raising engine load (100 to 300 Nm) and inlet air temperature (30 to 60°C) and pressure (0.9 to 2.2 bar), while maintaining engine speed (1000 rpm) and cooling water and lubricating oil temperatures (80°C) and pressures constant.

The cold engine was started on gasoil and then operated in approximately 5 minutes towards 20% power output with 1000 rpm speed (1400 rpm nominal) and 100 Nm load (360 Nm nominal) using naturally aspirated



Ignition parameters

Start of injection was set to occur at 31°CA BTDC (static). Injector opening was derived from both the needle lift signal and the fuel line pressure reaching 260 bar, as for every test the spring tension of the cleaned injector was adjusted to open at this pressure. This injector opening generally occurred at approximately 19°CA BTDC (dynamic). Start of ignition/combustion was derived from the combustion pressure trace, obtained from the cylinder pressure by mathematical correction for the compression pressure. The °CA scale was converted into a time scale assuming the speed of rotation to be constant. This was independently verified to be the case within the accuracy of the measurement. Ignition delay is defined as the time period in milliseconds (ms) between start of injection and onset of ignition and combustion.

The combustion hardness, or the rate of pressure rise at incipient combustion (dP/dt in kbar/s), is much less often quoted as ignition parameter. This is because it is not as well defined and easily determined as the ignition delay, and, maybe more importantly, previously a satisfactory correlation was established with CCAI. Thus, high combustion hardness was associated with high ignition delays and CCAI ($R^2 = 0.4 - 0.6$). In this investigation the combustion hardness was computed from the smoothed combustion pressure/time trace in two ways (a and b), viz. from the slope of the straight lines created by the 0 and 5 Bar (dP/dt -a) and the 5 and 10 Bar (dP/dt -b) combustion pressure points, respectively.

Test variability

Ignition parameters were recorded after 5 min (test-1) and after 25 min (test-2) into every test mode, and each measurement was repeated 10 times.

One of the commercial fuels (RFO-Tank 11) was tested throughout the investigation as a reference fuel to assess test variability. The resulting 13 separate tests showed satisfactory overall repeatability of ignition delay ($SD \approx 8\%$), although single results (max., min) can deviate quite substantially. Much greater variation exists in the combustion hardness data, however, particularly when defined over 5-10 kbar/s combustion pressure rise ($SD \approx 19\%$).

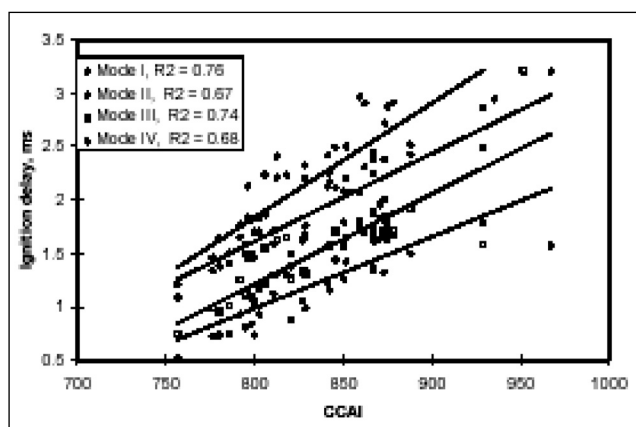


Figure 6: Relation between ignition delay and CCAI

Test Mode	Parameter	R ²
I	CCAI	0.76
	CCAI, MCR	0.76
	CCAI, S	0.78
	CCAI, MCR, S	0.79
	CCAI, MCR, FP	0.76
	CCAI, MCR, S, FP	0.80
II	CCAI	0.67
	CCAI, MCR	0.70
	CCAI, MCR, S	0.71
	CCAI, MCR, FP	0.75
	CCAI, MCR, S, FP	0.75
III	CCAI	0.74
	CCAI, MCR	0.74
	CCAI, MCR, S	0.74
	CCAI, MCR, FP	0.75
	CCAI, MCR, S, FP	0.75
IV	CCAI	0.68
	CCAI, MCR	0.72
	CCAI, S	0.76
	CCAI, MCR, S	0.76
	CCAI, MCR, FP	0.72
	CCAI, MCR, S, FP	0.76

Table 4: Summary of linear regression analysis attempts between ignition delay and several fuel parameters.

Test Mode	dP/dt-a	dP/dt-b
I	0.65	0.02
II	0.66	0.29
III	0.21	0.10
IV	0.04	0.38

Table 5: Linear Regression analysis between combustion hardness and CCAI. (R²-value).

temperature 60°C) and 0.71 (at inlet air temperature 45°C) found previously by Zeelenberg in the MaK engine (1).

With the present results no improvement of the correlation between ignition delay and CCAI could be realised by taking into account the MCR content nor other bulk fuel parameters sulphur (S) and flash point (FP) as is summarised in Table 4.

The results from the first (test-1) and second series (test-2) of measurements in every test mode were always closely identical. This clearly suggests that following a change in engine operating conditions (thermal) equilibrium is quickly re-established.

Test fuels

In the test program a total of 39 different fuels were used. They are 22 heavy fuels specially blended from a selection of residue and diluent components, four commercial RFO's and 2 special high density fuels, and 8 light and 3 heavy fuel blending components. In Figure 5 the total variation in CCAI and viscosity (Vk50) values is illustrated, highlighting the wide CCAI range of 757 - 959 at viscosities between 1.1 and 26000 mm²/s.

Ignition delay results

From the plots between ignition delay and CCAI for all test modes in Figure 6 it is clear that the relationships and also their slopes are very similar. Only the ignition delays become smaller upon going from Mode I to IV.

Correlation coefficients (R²-value) for linear regression are between 0.68 (Mode IV) and 0.76 (Mode I) as is shown in Table 4. These values are closely identical to the 0.77 (at inlet air



Clearly the ignition delays correlate best with CCAI alone and because this correlation is also hardly affected by the engine output, it must be concluded that the CCAI best represents the ignition performance of the fuel vapour. This may be either because all of the injected fuel is vaporised and contributes to the vapour aromaticity (i.e. $CCAI = CVAI$), or, alternatively, if not all of the fuel is vaporised the vapour aromaticity is proportional to the aromaticity of the bulk (i.e. $CCAI = CVAI$). This appears irrespective of the engine conditions employed.

Combustion hardness

The rate of pressure rise or combustion hardness data for the first ($dP/dt-a$) and second parts ($dP/dt-b$) of the combustion pressure show poor correlations with CCAI (Table 5).

In fact, only for $dP/dt-a$ in Modes I and II and for $dP/dt-b$ in Mode IV linear correlation coefficients are observed that may be comparable to the 0.61 (at inlet air temperature 60°C) and 0.45 (at inlet air temperature 45°C) found by Zeelenberg. Strangely enough, in these modes $dP/dt-a$ decreases with CCAI, while $dP/dt-b$ increases with CCAI. The latter result may well be in agreement with the positive correlation found by Zeelenberg.

Vapour composition analysis

To obtain further insight in the volatility of heavy fuels and their vapour composition, the fuels were analysed with Pyrolysis Combustion Mass Spectrometric Elemental analysis (PCME), which gives the volatility of the fuel by means of a True Boiling Point (TBP-PCME) temperature and also the elemental composition of the emitted vapour (Appendix II). From these data both the vapour carbon aromaticity index (VCAI, not to be confused with the CVAI which is calculated from CCAI and

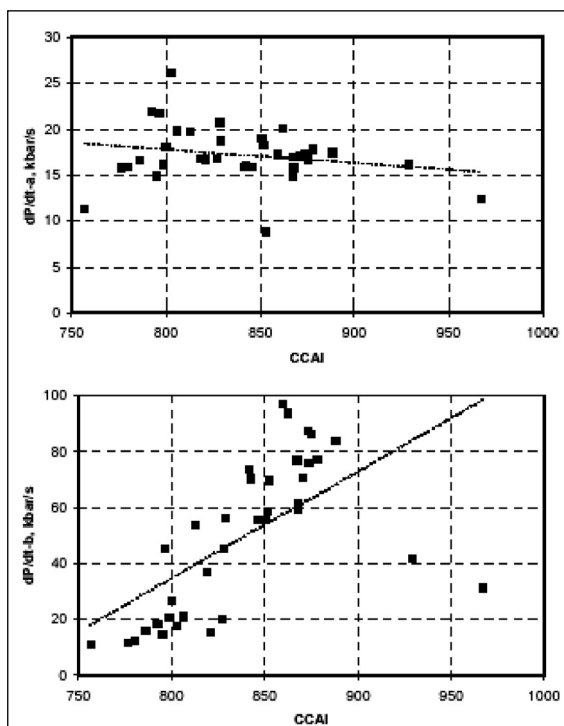


Figure 7: Relation between combustion hardness and CCAI as observed in Mode IV

MCR) and the aliphatic and aromatic carbon yields of the vapour were calculated for various arbitrary TBP-PCME temperature limits.

From the results it is concluded that strong correlations exist between CCAI values and the calculated vapour parameters VCAI, aliphatic carbon yield and aromatic carbon yield for TBP-PCME temperatures above 500°C. Not surprisingly, therefore, that also in plots of ignition delay against these parameters for the different TBP-PCME temperature limits the best linear correlations exist with data from temperatures above this arbitrary limit of 500°C. However, correlation coefficients are found less good (Figure 8) than for ignition delay/CCAI relationships. This may have been caused by errors in the determination of VCAI.

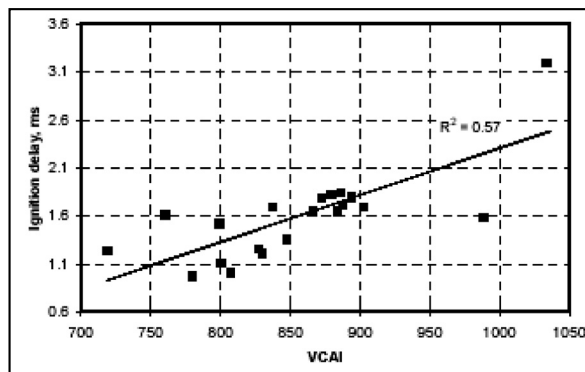


Figure 8: Relation between ignition delay and VCAI for Mode III (TBP-PCME up to 650°C)

CONCLUSIONS

Previous work on the ignition performance of heavy fuels in diesel engines has shown that at medium load (MaK) engine operation the CCAI best describes ignition performance. The CCAI is based upon fuel density and viscosity, and accurately represents the aromaticity of the bulk of the fuel. It can be used to rank fuels on ignition performance but does not offer a direct measure of ignition quality.

In the assumption that the aromaticity of the vapour from a fuel is not the same as that of the bulk of the fuel, the CVAI was derived by correction of the CCAI with the MCR content, assumed to represent the aromatic carbon of the bulk which cannot be evaporated.

Results presented in this paper show that ignition delay still correlates best with CCAI at all engine conditions employed, and these correlations were comparable to that found previously by Zeelenberg (R^2 -value ≈ 0.7). No improvement could be realised by either CVAI, taking into account the MCR content or the other available fuel parameters: sulphur content and flash point.

This conclusion is also supported by PCME studies. Thus, both ignition delay and CCAI correlate best with the aromaticity and also with the aliphatic carbon yield of the cumulated vapour formed up to (and above) a temperature of 500°C in this analysis.



Although bulk aromaticity may be the paramount fuel parameter determining its ignition performance, also other fuel parameters must play a role to explain the non-ideal correlation between CCAI and ignition delay. At this point it is worth mentioning that results from further tests indicate that one of these additional parameters may be contained in the processing nature of the blend components in the fuel.

The introduction of CCAI in the early 1980's made available a tool by which engine manufacturers could specify an acceptable range of ignition values for fuels to be used in their engines. The current work confirms CCAI as still the best available parameter to indicate ignition quality. But it cannot be used as an absolute measure of quality because of its limited accuracy.

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APPENDIX

Calculation of the aromatic carbon content of fuel vapour (CVAI)

In order to correct the CCAI for the aromatic carbon in the residue which cannot be vaporised the following procedure was defined:

- Calculation of the aromatic carbon content from the CCAI of the bulk of the fuel from the empirically established equation:

$$\%C_{ar} = -255 + 0.339CCAI$$

Calculation of the vaporisable aromatic carbon content by correction for the amount of non-vaporisable aromatic carbon with MCR:

A gram of residue contains on average 0.85 g carbon. Consequently, the mass of aromatic carbon per gram residue is given by:

$$mC_{ar} = \left[\frac{0.85x\%C_{ar}}{100} \right]$$

Per gram of residue, the mass of vaporisable aromatic carbon is given by:

$$mC_{ar}(vap) = mC_{ar} - MCR'$$

Where MCR' is the MCR content in g/g residue (%MCR/100), where it is assumed that Micro Carbon Residue consists of pure aromatic carbon.

Per gram of residue, the total mass of carbon in the vapour can be expressed as:

$$mC_1(vap) = 0.85 - MCR'$$

The mass percentage of aromatic carbon in the vapour is then given by:

$$\%C_{ar}(vap) = \frac{mC_{ar}(vap)}{mC_1(vap)} \cdot 100, \text{ or}$$

$$\%C_{ar}(vap) = \frac{\frac{0.85x\%C_{ar}}{100} - MCR'}{0.85 - MCR'} \cdot 100, \text{ or}$$

$$\%C_{ar}(vap) = \frac{\%C_{ar} - 1.18MCR}{100 - 1.18MCR} \cdot 100$$



However, depending on the test temperature, the full MCR correction may be over or under estimating the crackability of the larger aromatic structures into smaller components which will end up in the vapour phase. Therefore a correction factor c instead of 1.18 is used which can be optimised to obtain the best correlation, which results the equation.

$$\%C_{ar}(vap) = \frac{\%C_{ar} - c(MCR)}{1 - \frac{c(MCR)}{100}}$$

For $c=0$ all the MCR is evaporated and CVAI and CCAI are identical.

- Calculation of CVAI from the inverse equation in the first step:

$$CVAI = 752 + 2.95x\%C_{ar}(vap)$$

This sequence of calculations can be reformulated into the following overall formula:

$$CVAI = \frac{CCAI - 10.5c(MCR)}{1 - c\left(\frac{MCR}{100}\right)}$$

CALIDAD DE IGNICIÓN DE LOS ACEITES COMBUSTIBLES RESIDUALES

RESUMEN

Con anterioridad ya se ha demostrado la importancia de la aromaticidad del aceite combustible residual con respecto a su actuación y ha dado lugar al concepto de cálculo de aromaticidad a partir de propiedades conocidas de las especificaciones. De este modo, el Índice de Aromaticidad Carbónica Calculada (Calculated Carbon Aromaticity Index, CCAI) se puede calcular a partir de la densidad y viscosidad, y proporciona una herramienta útil para clasificar la calidad de ignición de diferentes aceites combustibles residuales: cuanto más bajo sea el número, mejor serán las características de ignición.

Se han investigado las mejoras potenciales al concepto de CCAI. El CCAI representa la aromaticidad de todo el combustible. Sin embargo, en operaciones de baja carga del motor se da la ignición con temperaturas relativamente bajas, cuando sólo parte del combustible inyectado se puede haber evaporado. Bajo estas condiciones el alto peso molecular, los componentes altamente aromáticos (asfaltenos) con toda probabilidad no se han evaporado del todo. Así, la aromaticidad de la parte del combustible (más ligera) podría ser diferente del grueso y posiblemente más relevante para la calidad de la ignición. Se ha llevado a cabo un programa para investigar la relación entre el retraso en la ignición y la aromaticidad del vapor del combustible bajo ciertas condiciones.

Se ha demostrado la validez de la relación entre el retraso de la ignición y el CCAI en todas las condiciones de motor empleadas y comparables a la ya descubierta. Ninguna mejora se podría realizar teniendo en cuenta el contenido del residuo micro-carbónico (micro carbon residue, MCR) como medida para la fracción pesada del combustible, ni para cualquier otro de los parámetros de combustible disponibles. Los resultados del análisis de los combustibles mediante Elementos Espectrométricos de Combustión de Masa por Pirólisis (Pyrolysis Combustion Mass Spectrometric Element, PCME), proporcionando información detallada de la composición del vapor a diferentes temperaturas, confirma de hecho que la aromaticidad de las fracciones de combustible más ligeros no domina la aromaticidad del vapor del combustible y por consiguiente no domina el resultado de la ignición del combustible. Sin embargo, a la vista del potencial predictivo todavía limitado del CCAI, otros parámetros de combustible, aún no identificados podrían desempeñar un papel.

Palabras Clave: Índice de Aromaticidad Carbónica, ignición, aceite combustible residual



CONCLUSIONES:

Los trabajos precedentes sobre el resultado de la ignición de combustibles pesados en motores diesel han mostrado que el CCAI describe mejor el resultado de la ignición con el motor funcionando a media carga (MaK). El CCAI se basa en la densidad y viscosidad del combustible, y representa adecuadamente la aromaticidad del grueso del combustible. Se puede utilizar para clasificar los combustibles según su ignición pero no ofrece una medida de la calidad de ignición.

Asumiendo que la aromaticidad del vapor de un combustible no es la misma que la del grueso del combustible, el CVAI se derivó por corrección del CCAI con el contenido del MCR, que se supone representa el carbono aromático del grueso que no se puede evaporar.

Los resultados que se presentan en este artículo muestran que el retraso de la ignición se corresponde todavía mejor con CCAI en todas las condiciones del motor empleadas, y estas correlaciones fueron comparables a las descubiertas anteriormente por Zeelenberg (R^2 -valor ≈ 0.7). No se pudo apreciar ninguna mejora CVAI, teniendo en cuenta el contenido de MCR ni con los demás parámetros de combustibles disponibles: contenido de azufre y punto de combustión.

Esta conclusión también está apoyada por los estudios de PCME. Así, tanto el retraso en la ignición como la CCAI se corresponden mejor con la aromaticidad y también con el residuo del carbono alifático del vapor acumulado que se forma a temperaturas de (y por encima de) 500°C en este análisis.

Si bien el grueso de la aromaticidad puede ser el principal parámetro que determine el resultado de la ignición, también otros parámetros del combustible pueden desempeñar un papel para explicar la correlación no-ideal entre el CCAI y el retraso de ignición. En este punto vale la pena mencionar que los resultados de pruebas posteriores indican que uno de estos parámetros adicionales puede estar contenido en la naturaleza del tratamiento de la mezcla de componentes del combustible.

La introducción del CCAI a principios de la década de 1980 hizo posible una herramienta con la que los fabricantes de motores podían especificar una tasa de valores de ignición aceptables para los combustibles a utilizar en sus motores. El presente trabajo confirma CCAI como todavía el mejor parámetro disponible para indicar la calidad de ignición. Pero no se puede utilizar como una medida de calidad absoluta debido a su limitada exactitud.

Calidad de encendido

Los parámetros experimentales relacionado con la calidad de encendido de CCAI de CII desarrollados, proporcionan un método experimental para la clasificación de combustibles residuales

La calidad del combustible suministrado a la embarcación puede afectar a la navegabilidad, así como el subsiguiente tratamiento del combustible a bordo. En un mundo dónde es común la inconstante calidad del combustible, hay una necesidad

por establecer medidas más adecuadas que regulen la efectividad del tratamiento del combustible a bordo.

Metodología:

La metodología utilizada en el presente artículo ha consistido en la consulta de diversas bibliografía, para poder entender correctamente la evolución y estado actual del tema tratado, se ha utilizado además de la bibliografía ordinaria la información disponible en la red, en portales de organismo internacionales solvente. La bibliografía ha sido tanto nacional como internacional.

Finalmente complementamos el artículo con la información más reciente en cuanto a la legislación correspondiente a dicho tema por parte del organismo correspondiente, la OMI.

Después de esta elección metodológica, se efectuó la revisión de los textos, figuras y tablas. Para entender esta tarea, utilizando como herramienta fundamental los textos ya seleccionados y a nuestra disposición.

La calidad de los productos comienza a forjarse en la etapa de diseño, siguiendo los máximos estándares de calidad a nivel internacional y teniendo en cuenta las mayores exigencias a las que serán sometidos al momento de ser utilizados.

Posteriormente, se elaboran a través de tecnología de última generación presente en cada una de las refinerías que posee la Compañía. Por último, en la etapa de distribución, almacenaje y comercialización, se lleva a cabo un estricto seguimiento que comprende monitoreos continuos de calidad y certificación.

Este sistema de gestión integral de la calidad asegura al cliente la utilización del productos con calidad de origen, permitiendo su trazabilidad desde el mercado a la refinería a través del número de Certificado de Calidad.

Fuel Testing

Residual Fuel, Fuel Oil Testing Analysis	Fuel Oil Test Methods
API Gravity / Density / Relative Density (Elevated temp)	D287 / D1298 / D4052
Ash Content Test	D482
Flash Point Test (PMCC)	D 93B
Pour Point Test	D 97
Sediment Content	D473
Sulfur Content Analysis	D4294
Viscosity - Kinematic at 40 & 100C (100 & 210F if necessary).	D445
Water Content	D95
S & W (Centrifuge)	D1796
Number 2 Fuel Oil Basic Testing Analysis	
API Gravity / Density / Relative Density	D287 / D1298 / D 4052
Appearance or Haze	D4176 / Colonial
Cetane Index (Calculation Only)	D976
Cetane Index (Calculation Only)	D4737A or B
Cloud Point	D2500/D5771/D5773
Color	D1500
Copper Corrosion	D130



Distillation	D86
Flash Point	D93A
Pour Point	D97/D5950/D5949
Sulfur Content	D4294
Sulfur Content (WDXRF)	D2622
Sulfur Content by Oxidative Microcoulometry	D3120
Sulfur Content by UV Fluorescence	D5453
S & W (Centrifuge) if required	D1796 / D2709
Metals Analysis- Al, Si Ashing & Fusion	D5184 / IP377, AAS/AES
Metals Analysis- Al, Si, V, Ni, Fe, Na Ashing & Fusion	IP470, AAS/AES
Metals Analysis- Ni, V, Na Solvent Dilution	D5863B, AAS/AES
Metals Analysis - Ni, V, Fe Digestion & Ashing	D5863A, AAS/AES
Metals, (Graphite furnace for three elements) AAS/AES	—
Metals Testing- Ni, V, Fe Solvent Dilution ICP	D5708A
Metals Testing- Ni, V, Fe Digestion & Ashing ICP	D5708B
Metals Testing, Each additional outside scope of procedure	Various
Microscopic Characterization of Particulates (wear debris)	—
Molecular Weight (Includes necessary tests)	D2502
NACE Corrosion Test	TM0172
Nitrogen Content Kjeldahl	D3228
Nitrogen Content, Nitrogen Speciation	D4629, D5762 Chemiluminescence
Nitrogen - Bases	UOP269 / UOP313
Oxidation Stability (Accelerated)	D2274, D6468 (Octel F21)
Oxidation Stability (Oxygen Overpressure)	D5304.
Particulate Contamination	D6217/IP 415
pH Value	D1293
Polypropylene in Fuels, Qualitative.	BPMarine A.
Polypropylene in Fuels, Quantitative by FTIR	BPMarine B
Pour Point (Amsterdam Procedure)	Shell Method
Refractive Index	D1218
Salt Content	D3230 / D6470 / IP77
Sediment in Lube Oils	D2273
Sediment by Hot Filtration	D4870 / IP375
Sediment - Potential (Accelerated)	IP390 + IP375
Simulated Distillation	D2887 Sim Dis
Simulated Distillation	High Temperature Sim Dis
Storage Stability of Diesel	D4625
Stability Testing, Fuel Oil Peptization Value	P-value and P0/Frmax
Sulfur / Sulphur (Bomb Method)	D129
Sulfur Dioxide Emissions (Calculation Only)	—
Sulfur / Sulphur Speciation	—
Toluene or Xylene Equivalence	—
Ultimate Analysis (C.H.N. with O by difference.)	D5291
Unulfonated Residue in Diesel	D483
Viscosity (Saybolt) in Diesel	D445 & D2161
Viscosity - Kinematic at 40 & 100C (100 & 210F if necessary)	D445
Viscosity - Kinematic at other temps	D445
Viscosity Index (Including tests)	D445 & D2270
Water Content (Volumetric Karl Fischer)	E203
Water Content (Coulometric Karl Fischer)	D6304
Wax Appearance in Distillates	D3117
Wax Content	UOP46
Water Separability (Demulsification)	D1401 / FTM3201



ETAPAS DE CONTROL DE CALIDAD

Elaboración

Cada refinería cuenta con un laboratorio altamente equipado donde se evalúa la calidad de todos los productos intermedios que salen de cada planta de proceso y fundamentalmente se efectúa la evaluación de la calidad de los productos finales.

Los laboratorios fijos y móviles de Servicio Técnico de Productos controlan la calidad de los combustibles y asisten técnicamente al cliente.

Distribución, almacenaje y comercialización

En esta segunda etapa, el combustible es transportado a través del sistema de distribución de la Compañía y almacenado en las distintas Terminales de Despacho. En esta instancia, el Departamento de Servicio Técnico de Productos efectúa una nueva evaluación de calidad dando lugar a la certificación del combustible y habilitando su despacho.

Inspecciones periódicas

La última etapa la constituyen las inspecciones periódicas que realiza Servicio Técnico en las distintas Terminales y demás puntos de distribución. Las mismas comprenden la evaluación de la calidad del combustible y la verificación de las condiciones de almacenaje, de modo de asegurar en el tiempo la ausencia de ciertos elementos que podrían alterar las propiedades del combustible (agua, partículas, etc.)

La estructura de Servicio Técnico consta una serie de laboratorios distribuidos geográficamente a lo largo y ancho del país con cobertura sobre todo el territorio nacional. Están equipados con tecnología de última generación y operados por personal altamente calificado, que además de realizar los controles de calidad mencionados anteriormente cumplen la función de asistir técnicamente al Cliente.