

FUEL FORMULATIONS

Field of the Invention

This invention relates to diesel fuel formulations, their preparation and their use, and to the use of certain materials in diesel fuel formulations for new purposes.

Background to the Invention

In the interests of the environment, and to comply with increasingly stringent regulatory demands, it is necessary to increase the amount of biofuels used in automotive fuels.

Biofuels are combustible fuels, typically derived from biological sources, which result in a reduction in "well-to-wheels" (ie from source to combustion) greenhouse gas emissions. In diesel fuels for use in compression ignition engines, the most common biofuels are fatty acid alkyl esters (FAAEs), in particular fatty acid methyl esters (FAMES) such as rapeseed methyl ester and palm oil methyl ester; these are used in blends with conventional diesel fuel components.

Lower dialkyl carbonates, in particular dimethyl carbonate (DMC) and diethyl carbonate (DEC), are also biofuels which have in the past been added to both gasoline and diesel fuels. They have been used for instance as oxygenates, as combustion improvers and to reduce pollution levels. However, there are a number of practical constraints on the concentrations at which DMC and DEC can be included in automotive diesel fuels. In particular, their low flash points - and the consequently reduced flash points of blends containing them - tend to limit DMC concentrations to less than 2% v/v and DEC concentrations to around 3% v/v. As a result, dialkyl

carbonates have received little attention as fuel components other than at relatively low levels.

FAMES have much higher flash points than both DMC and DEC, and as a result could potentially be blended with the dialkyl carbonates in order to increase their suitability for use as diesel fuel components. However, there can be a number of drawbacks associated with the use of FAMES in diesel fuels, in particular at higher concentrations. The addition of a FAME to a diesel fuel formulation raises its cloud point, to an extent dependent on the FAME concentration. It also raises the cold filter plugging point (CFPP) of the formulation. Moreover, due to the incomplete esterification of oils (triglycerides) during their manufacture, FAMES can contain trace amounts of glycerides, in particular monoglycerides. These glycerides tend, on cooling, to crystallise out before the FAMES themselves, and can cause fuel filter blockages. These three effects can compromise the cold weather performance of a FAME-containing diesel fuel. It can therefore be difficult to formulate diesel fuel/FAME blends within the relevant regulatory specifications, particularly in colder climates.

FAMES and their oxidation products also tend to accumulate in engine oil; this too has limited their use in modern FAME/diesel blends. At higher concentrations they can also cause fouling of fuel injectors. FAMES are also more expensive to produce than ethanol (the biofuel most commonly included in gasoline formulations), and their world production levels much lower.

It would be desirable to provide new biofuel-containing diesel fuel formulations which could overcome or at least mitigate the above problems.

Statements of the Invention

According to a first aspect of the present invention there is provided a diesel fuel formulation containing (i) a lower molecular weight dialkyl carbonate (DAC) selected from dimethyl carbonate (DMC), diethyl carbonate (DEC) and mixtures thereof; and (ii) di-n-butyl carbonate (DBC).

The formulation may also contain (iii) an additional diesel fuel component.

It has surprisingly been found that DBC can raise the flash points of diesel fuel formulations containing DMC or DEC, to a greater extent than might have been predicted based on its own flash point of 89°C. In particular, its flash point raising effect appears to be significantly greater, at any given concentration, than that of the same concentration of the common biodiesel component rapeseed methyl ester (RME), despite the fact that the flash point of neat RME (170°C) is far higher than that of DBC.

This surprising discovery allows DBC to be used as a component of DMC- or DEC-containing diesel fuel formulations, for the purpose of raising their flash points, but without the drawbacks potentially associated with the inclusion of a FAME for the same purpose. In turn, diesel fuels can be formulated with higher concentrations of DMC and DEC, without or without undue impact on their overall flash points. The inclusion of the DBC can help to bring a DMC- or DEC-containing diesel fuel within a desired flash point specification; this can be of particular value where the fuel is for use in a warmer climate. Thus the present invention is able to provide more optimised methods for formulating biofuel-containing diesel fuel formulations, in

particular summer grade diesel fuels, more particularly to achieve target flash points.

There can be a number of advantages to increasing the concentration of DACs in a diesel fuel formulation. Not only does DBC have a lower cloud point (-60°C) and CFPP (-36°C) than FAMES, and thus the ability to lower the cloud point and CFPP of a fuel formulation to which it is added; it also has low toxicity and is biodegradable. Its inclusion in a diesel fuel formulation can increase the total bioenergy content of the formulation, so long as the DBC is derived from a biological source, and in turn reduce the greenhouse gas emissions associated with the production and use of the fuel, yet with fewer of the drawbacks associated with higher FAME concentrations. DBC can also be produced from renewable ingredients (carbon dioxide and bio-butanol). When used in diesel fuels, it can be a cheaper alternative to the more traditionally used FAME biofuel components such as RME.

In an embodiment of the invention, the lower molecular weight DAC used in the formulation is DMC. In an embodiment, it is DEC.

The dialkyl carbonates used in a fuel formulation according to the invention (DMC and/or DEC, and DBC) may be obtained from any known source, of which many are available. They can for example be synthesised from the corresponding alcohol(s): methanol may be used as a starting material for the production of DMC, ethanol for the production of DEC, and butanol for the production of DBC. Such alcohols may themselves be derived from biological sources.

DACs can also be prepared by oxidative carbonylation of alcohols, or by transesterification of dimethyl

carbonate with alcohols, or they may be generated as co-products in the synthesis of monoethylene glycol from ethylene oxide and carbon dioxide via ethylene carbonate.

In an embodiment, it may be preferred for the DACs not to have been synthesised using phosgene (COCl_2), as this may introduce undesirable impurities such as chlorides or carbonochloridic acid derivatives. Such impurities may contribute to deposit, stability and corrosion problems in a fuel formulation.

The concentration of the DMC, DEC or mixture thereof, in a diesel fuel formulation according to the invention, may be 0.5% v/v or greater, or 1 or 2 or 3% v/v or greater, or in cases 3.5 or 4 or 4.5 or 5% v/v or greater. Its concentration may be up to 20% v/v, or up to 15 or 12 or 10% v/v.

The concentration of the DBC in the formulation may be 0.5% v/v or greater, or 1 or 2 or 3% v/v or greater, or in cases 3.5 or 4 or 4.5 or 5% v/v or greater. Its concentration may be up to 99.5 or 99 or 98% v/v, or up to 95 or 90% v/v, or up to 80 or 70 or 60 or 50 or 30 or 25 or 20% v/v, or up to 15 or 12 or 10% v/v.

The volume ratio of the lower molecular weight DAC (i) to the DBC (ii) in the formulation may for instance be up to 25:1, or up to 10:1 or 5:1 or 2:1. The ratio may be 1:199 or greater, or 1:99 or greater, or 1:90 or greater, or 1:75 or greater, or 1:50 or greater. It may be 1:25 or greater, or 1:10 or 1:5 or 1:2 or greater. It may be 1:1 or approximately 1:1.

The additional diesel fuel component (iii), if present, may be any fuel component suitable for use in a diesel fuel formulation and therefore for combustion within a compression ignition (diesel) engine. It will typically be a liquid hydrocarbon middle distillate fuel,

more typically a gas oil. It may be petroleum derived. It may be or contain a kerosene fuel component.

Alternatively it may be synthetic: for instance it may be the product of a Fischer-Tropsch condensation. It may be derived from a biological source. It may be or include an oxygenate such as an alcohol (in particular a C1 to C4 or C1 to C3 aliphatic alcohol, more particularly ethanol).

An additional fuel component (iii) will typically boil in the range from 150 or 180 to 360°C (ASTM D86 or EN ISO 3405). It will suitably have a measured cetane number (ASTM D613) of from 40 to 70 or from 40 to 65 or from 51 to 65 or 70.

A formulation according to the invention may contain a mixture of two or more additional diesel fuel components (iii).

The concentration of the component(s) (iii) in the formulation, if present, may be 2 or 5 or 10% v/v or greater, or 20 or 30 or 40% v/v or greater. In embodiments of the invention, it may be 50 or 60 or 70% v/v or greater, or 75 or 80 or 85% v/v or greater, or 90 or 92 or 95% v/v or greater. It may be up to 98% v/v, or up to 95 or 92 or 90 or 85 or 80% v/v. In cases it may be up to 70 or 60 or 50% v/v. The component(s) (iii) may represent the major part of the fuel formulation: after inclusion of the lower molecular weight DAC (i), the DBC (ii) and any optional fuel additives, the component(s) (iii) may therefore represent the balance to 100%. Alternatively, the fuel formulation may comprise the lower molecular weight DAC and the DBC, optionally with one or more diesel fuel additives, but without any additional diesel fuel components.

A fuel formulation according to the invention suitably has a flash point (ASTM D92 or D93, or IP 34) of

38°C or higher, or of 40 or 45°C or higher, or of 50 or 55 or in cases 60 or 65 or 70 or 75°C or higher.

The formulation of the invention should be suitable for use in a compression ignition (diesel) internal combustion engine. Such an engine may be either heavy or light duty. The formulation may in particular be suitable for use as an automotive diesel fuel.

In an embodiment, the formulation is suitable and/or adapted for use as a "summer grade" automotive diesel fuel, for use in warmer climates such as Australasia and/or in warmer seasons. In an embodiment, it is suitable and/or adapted for high temperature use such as at 30°C or higher.

In further embodiments, the formulation may be suitable and/or adapted for use as an industrial gas oil, or as a domestic heating oil.

The formulation will suitably comply with applicable current standard diesel fuel specification(s) such as for example EN 590 (for Europe) or ASTM D975 (for the USA).

By way of example, the overall formulation may have a density from 820 to 845 kg/m³ at 15°C (ASTM D4052 or EN ISO 3675); a T95 boiling point (ASTM D86 or EN ISO 3405) of 360°C or less; a measured cetane number (ASTM D613) of 51 or greater; a kinematic viscosity at 40°C (ASTM D445 or EN ISO 3104) from 2 to 4.5 centistokes; a sulphur content (ASTM D2622 or EN ISO 20846) of 50 mg/kg or less; and/or a polycyclic aromatic hydrocarbons (PAH) content (IP 391(mod)) of less than 11% w/w. Relevant specifications may however differ from country to country and from year to year, and may depend on the intended use of the formulation. Moreover a formulation according to the invention may contain fuel components with properties outside of these ranges, since

the properties of an overall blend may differ, often significantly, from those of its individual constituents.

The relative concentrations of the components (i) to (iii) may be chosen to achieve desired properties for the formulation as a whole, for example a minimum desired flash point. Thus the relative concentrations will also depend on the physicochemical properties of the individual components. Suitable concentrations may be calculated by applying appropriate blending rules to the properties (in particular the flash points, but also potentially other properties such as cloud points and/or cetane numbers) of the individual components, and may be visualised using a two- or three-way composition plot.

A fuel formulation according to the invention may contain standard fuel or refinery additives which are suitable for use in diesel fuels. Many such additives are known and commercially available.

According to a second aspect of the present invention, there is provided a process for the preparation of a diesel fuel formulation, which process involves blending together (i) a lower molecular weight DAC selected from DMC, DEC and mixtures thereof and (ii) DBC, optionally with (iii) one or more additional diesel fuel components, and optionally with one or more fuel additives. The process may be used to produce at least 1,000 litres of the fuel formulation, or at least 5,000 or 10,000 or 25,000 litres, or at least 50,000 or 75,000 or 100,000 litres.

In an embodiment of the second aspect of the invention, the lower molecular weight DAC (i) and the DBC are premixed in an appropriate volume ratio, and if necessary the mixture then blended with one or more additional fuel components (iii). The DAC mixture may for

instance be blended with the component(s) (iii) at a concentration of up to 30% v/v based on the product fuel formulation, or at a concentration of up to 25 or 20% v/v, or up to 15 or 10% v/v. It may be blended at a concentration of 1% v/v or greater based on the product formulation, or of 2 or 3 or 4 or 5% v/v or greater, or in cases of 6 or 7 or 8 or 9 or 10% v/v or greater. Mixing the DBC with the lower molecular weight DAC can, by raising its flash point, help to improve its handling and storage properties.

A third aspect of the invention provides a method of operating an internal combustion engine, and/or a vehicle which is driven by an internal combustion engine, which method involves introducing into a combustion chamber of the engine a diesel fuel formulation according to the first aspect of the invention. The engine is suitably a compression ignition (diesel) engine. Such a diesel engine may be of the direct injection type, for example of the rotary pump, in-line pump, unit pump, electronic unit injector or common rail type, or of the indirect injection type. It may be a heavy or a light duty diesel engine.

The third aspect of the invention also embraces introducing DBC into a reservoir which contains a DMC- and/or DEC-containing diesel fuel formulation, prior to introduction of the resultant mixture into a combustion chamber of the engine. In other words, the diesel fuel formulation of the invention may be prepared in situ in a reservoir from which fuel is fed into an internal combustion engine.

According to a fourth aspect of the invention there is provided the use of DBC, in a diesel fuel formulation containing a lower molecular weight DAC selected from

DMC, DEC and mixtures thereof, for the purpose of increasing the flash point of the formulation.

5 The flash point of a fuel formulation is the lowest temperature at which, under a predetermined set of test conditions, the application of an ignition source causes the vapour above a sample of the formulation to ignite and the flame to propagate across the surface of the liquid. It can be measured using a standard test method such as ASTM D92 or D93, IP 34, or an analogous method: a
10 suitable procedure is described in Example 1 below.

The invention may be used to achieve any degree of increase in the flash point of the formulation. It may be used for the purpose of achieving a flash point at or above a desired target value.

15 By way of example, the invention may be used to increase the flash point of the formulation by at least 0.2% of its value (expressed in Kelvin) prior to addition of the DBC, or by at least 0.5 or 0.6%, or by at least 0.8 or 1% or in cases even by 2 or 5 or 8 or 10% or more.

20 In the context of the fourth aspect of the invention, the diesel fuel formulation may contain one or more additional diesel fuel components (iii) in addition to the lower molecular weight DAC. It may in particular be a summer grade diesel fuel formulation. It will
25 typically have a flash point, prior to addition of the DBC, which is lower than that of the DBC alone (i.e. which is lower than 89°C).

30 It has been found that DBC can "boost" the flash point of a diesel fuel formulation containing DMC and/or DEC, above the level that would be expected if conventional blending rules applied, that is to say if the level of flash point is calculated by proportionating the flash point index of the individual components

according to the proportion of each component in the blend. This phenomenon has a number of potential uses. Firstly, it can allow the achievement of a higher flash point than was previously thought possible, for any given concentration of DBC, in a DMC- and/or DEC-containing diesel fuel formulation. Secondly, it can allow the achievement of a target flash point using a lower than predicted concentration of DBC. This in turn can reduce the costs which might be associated with the addition of DBC to the formulation. Thirdly, it can allow the use of a higher DMC and/or DEC concentration than would have been predicted to be feasible, whilst still maintaining the flash point of the overall formulation at or above a desired target value; this in turn can boost the bioenergy content of the formulation, as well as increasing the advantages associated with the DMC and/or DEC, for example reductions in cloud point and CFPP. Fourthly, the DBC may be used to replace, at least partially, a FAAE which would otherwise have been included in the formulation in order to increase its flash point.

Thus according to a fifth aspect of the invention, there is provided a method for increasing the flash point of a diesel fuel formulation which contains a lower molecular weight DAC selected from DMC, DEC and mixtures thereof, in order to achieve a target minimum flash point X, which method comprises adding to the formulation a concentration c of DBC, wherein c is lower than the minimum concentration c' of DBC which theory would predict needed to be added to the formulation in order to achieve flash point X.

The theoretical DBC concentration, c' , may be calculated using any suitable flash point blending rule.

It may for instance be calculated as follows, making use of the Wickey-Chittenden flash point model.

The flash point index of a blend of fuel components (in this case of the lower molecular weight DAC, the DBC and any additional diesel fuel components present) is calculated by combining the flash point indices of the blend components as a function of their volume fractions in the blend:

$$Index_{blend} = \sum_i V_i Index_i$$

where V_i is the volume fraction of component i and $Index_i$ is the flash point index for component i .

The flash point index for each component can be calculated using the Wickey-Chittenden model (Wickey R.O. and Chittenden D.H., *Hydrocarbon Processing*, **42**(6), 1963: 157-158):

$$\text{Log}_{10} (Index_i) = -6.1188 + \frac{2414}{FP + 230.5556} \quad (\text{equation 1})$$

where FP is the flash point of the component.

When using equation (1), the blending flash point of DMC is taken to be 0°C, and that of DEC 17.7°C. These figures take account of potential mismatches in Hansen solubility parameters between the DAC and any hydrocarbon fuel components present.

Having calculated the flash point index for the overall blend, the Wickey-Chittenden equation (1) may be used to calculate back the flash point for the blend. By inserting suitable values into these equations, it is possible to work back from a target flash point X to determine the volume fraction or concentration c' (of DBC) which would be required to achieve X .

In embodiments of the fifth aspect of the invention, the actual DBC concentration c may be at least 0.5% v/v lower than the predicted concentration c' , or at least 1 or 2 or 5% v/v lower, or in cases at least 10 or 25 or 50 or 75% v/v lower.

A sixth aspect of the invention provides the use of DBC, at a concentration c , in a diesel fuel formulation which contains a lower molecular weight DAC selected from DMC, DEC and mixtures thereof, for the purpose of increasing the flash point of the formulation by an amount x , wherein x is greater than the flash point increase x' which theory would predict would result from adding DBC to the formulation at concentration c .

The theoretical (predicted) flash point increase x' may be calculated using the equations above. The actual flash point increase x may for instance be at least 0.5°C higher than the predicted increase x' , or at least 1 or 1.5 or 2°C higher, or in cases at least 5 or 8 or 10°C higher.

According to a seventh aspect of the invention, there is provided the use of DBC, at a concentration c , in a diesel fuel formulation which contains a lower molecular weight DAC selected from DMC, DEC and mixtures thereof, for the dual purposes of:

- a) achieving a target minimum flash point X for the formulation; and
- b) allowing an increase in the concentration of the lower molecular weight DAC to a level above the maximum concentration d' which theory would predict could be included in the formulation, after addition of the DBC at concentration c , without reducing the flash point of the formulation below the target minimum X .

Again, the theoretical maximum concentration d' , for the lower molecular weight DAC, may be calculated using the above rules.

5 It may be desirable to include DMC and/or DEC in a diesel fuel formulation for a number of reasons, for example to improve the cold flow properties of the formulation (in particular to reduce its cloud point and/or CFPP), and/or to reduce emissions from a fuel-consuming system (typically an engine) running on
10 the formulation, and/or to reduce greenhouse gas emissions associated with the production and use of the formulation, and/or to increase the bioenergy content of the formulation, and/or as a combustion improver. However it has been necessary, in the past, to balance such
15 benefits against the generally undesirable reduction in flash point which results from increasing the concentration of the DMC and/or DEC. The ability to increase their concentration without undue detriment to the flash point of the formulation can therefore provide
20 significant advantages. Generally speaking the present invention can provide greater flexibility in fuel formulation, allowing a target flash point to be achieved more readily by altering the concentration of the added DBC.

25 An eighth aspect of the invention provides the use of DBC in a diesel fuel formulation containing a lower molecular weight DAC selected from DMC, DEC and mixtures thereof, for the purpose of replacing, at least partially, a fatty acid alkyl ester (FAAE) which is or
30 would otherwise have been included in the formulation.

The FAAE may in particular be a fatty acid methyl ester (FAME). It may for instance be RME. It may have been included, or intended to be included, at least

partly for the purpose of increasing the flash point of the DMC- and/or DEC-containing formulation. According to the eighth aspect of the invention, the DBC may again be used at a lower concentration than theory would predict to be necessary in order to achieve a target flash point after reduction of the amount of the FAAE in the formulation. Thus, the DBC may be used to achieve a greater reduction in the FAAE concentration (including in cases reduction to zero) than theory would predict to be possible whilst still achieving the target flash point.

In the context of the present invention, "use" of DBC in a diesel fuel formulation means incorporating the DBC into the formulation, typically as a blend (ie a physical mixture) with one or more other diesel fuel components. The DBC will conveniently be incorporated before the formulation is introduced into an engine or other system which is to be run on the formulation. Instead or in addition the use of DBC may involve running a fuel-consuming system, typically an internal combustion engine, on a diesel fuel formulation containing the DBC, typically by introducing the formulation into a combustion chamber of an engine.

"Use" of DBC in the ways described above may also embrace supplying the DBC together with instructions for its use in a diesel fuel formulation to achieve the purpose(s) of any of the fifth to the eighth aspects of the invention, for instance to increase the flash point of the formulation. The DBC may itself be supplied as part of a composition which is suitable for and/or intended for use as a fuel additive, in which case the DBC may be included in such a composition for the purpose of influencing its effect on the flash point of a fuel formulation.

In the context of the invention, "achieving" a desired target property also embraces - and in an embodiment involves - improving on the relevant target. Thus for instance the DBC may be used to produce a fuel
5 formulation which has a flash point above a desired target value.

Throughout the description and claims of this specification, the words "comprise" and "contain" and variations of the words, for example "comprising" and
10 "comprises", mean "including but not limited to", and do not exclude other moieties, additives, components, integers or steps. Moreover the singular encompasses the plural unless the context otherwise requires: in particular, where the indefinite article is used, the
15 specification is to be understood as contemplating plurality as well as singularity, unless the context requires otherwise.

Preferred features of each aspect of the invention may be as described in connection with any of the other
20 aspects. Other features of the invention will become apparent from the following examples. Generally speaking the invention extends to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims and
25 drawings). Thus features, integers, characteristics, compounds, chemical moieties or groups described in conjunction with a particular aspect, embodiment or example of the invention are to be understood to be applicable to any other aspect, embodiment or example
30 described herein unless incompatible therewith. Moreover unless stated otherwise, any feature disclosed herein may be replaced by an alternative feature serving the same or a similar purpose.

The present invention will now be further described with reference to the following non-limiting examples.

Example 1

Diesel fuel formulations were prepared by blending one or more of diethyl carbonate (DEC), di-n-butyl carbonate (DBC) and rapeseed methyl ester (RME) with a diesel base fuel DBF1. The DEC, DBC and RME were each added to the formulations at a concentration of 5% v/v.

The base fuel was a commercially available zero sulphur automotive diesel base fuel, ex. Shell. It had a flash point (IP 34) of 72.5°C. It had a density at 15°C (ASTM D4052) of 840.9 kg/m³, an initial boiling point (ASTM D86) of 177.5°C, a T95 boiling point (ASTM D86) of 357°C, a final boiling point (ASTM D86) of 363°C, a measured cetane number (ASTM D613) of 55.4, an E250 (IP 123) of 22.4°C and an E350 (IP 123) of 89.7°C.

The DEC and DBC were sourced from Sigma Aldrich, UK and the RME from ADM.

The flash points of the prepared formulations were measured by the Pensky-Martens Closed Cup method (IP 34), as follows. A sample of the formulation under test was placed in the test cup of a Pensky-Martens apparatus and heated to give a constant rate of temperature increase with continuous stirring. An ignition source was directed through an opening in the test cup lid at regular temperature intervals, with simultaneous interruption of stirring. The lowest temperature at which the application of the ignition source caused the vapour of the sample to ignite and the flame to propagate over the surface of the liquid was recorded as the flash point at the ambient barometric pressure. This value was corrected to standard atmospheric pressure as per IP 34.

Three readings were taken for each formulation, in order to calculate an average (mean) flash point. The results are shown in Table 1 below, together with the flash points for the neat DEC, DBC and RME, which were obtained using the standard test method IP 34.

Table 1 also shows theoretical flash points for the formulations, calculated using the Wickey-Chittenden equation above using a blending flash point of 17.7°C for the DEC.

Table 1

% v/v DEC	% v/v RME	% v/v DBC	Average flash point (°C)	Predicted flash point (°C) by W-C	Measured improvement relative to 5% v/v DEC (°C)	Measured improvement relative to that predicted by W-C (°C)
0	0	0	72.5	-	-	-
5	0	0	51	51.9	-	-0.9
5	5	0	53	52.0	+2	+1.0
5	0	5	54.5	52.0	+3.5	+2.5
100	0	0	25	-	-	-
0	100	0	170	-	-	-
0	0	100	89	-	-	-

It can be seen from Table 1 that the base fuel alone, with no dialkyl carbonate or FAME present, has an average flash point of 72.5°C. The addition of 5% v/v DEC (neat flash point only 25°C) reduces this considerably, to 51°C.

RME has a neat flash point of 170°C, far higher than that of the base fuel. Yet the addition of 5% v/v RME to the base fuel/DEC blend raises its flash point by only 2°C. In contrast, the addition of 5% v/v DBC to the base fuel/DEC blend, in accordance with the invention, raises the average flash point by 3.5°C, to 54.5°C. This increase is particularly surprising since the flash point for neat DBC is 89°C, much lower than that of neat RME. It would therefore have been expected that RME would have

a greater effect on the flash point of a DEC/base fuel blend than would the same volume of DBC. As can be seen from the fifth column of Table 1, the increase in flash point caused by the addition of 5% v/v DBC to the DEC/base fuel blend is in fact greater than the Wickey-Chittenden model would have predicted.

These results suggest that there is a synergistic interaction between the DEC and the DBC, which is not present between DEC and RME.

Example 2

Example 1 was repeated, but adding the DEC, DBC and RME to a second diesel base fuel, DBF2, at 10% v/v. DBF2 was a commercially available zero sulphur automotive diesel base fuel, ex. Shell. It had a flash point (IP 34) of 65°C. It had a density at 15°C (ASTM D4052) of 833 kg/m³, an initial boiling point (ASTM D86) of 165°C, a T95 boiling point (ASTM D86) of 340°C, a final boiling point (ASTM D86) of 352°C, a measured cetane number (ASTM D613) of 54.1, an E250 (IP 123) of 28.2°C and an E350 (IP 123) of 96.8°C

The flash point results are shown in Table 2 below. Again, the table shows predicted flash points as calculated using the Wickey-Chittenden equation, using a DEC blending flash point of 17.7°C.

Table 2

% v/v DEC	% v/v RME	% v/v DBC	Average flash point (°C)	Predicted flash point (°C) by W-C	Measured improvement relative to 10% v/v DEC (°C)	Measured improvement relative to that predicted by W-C (°C)
0	0	0	65		-	-
10	0	0	44	44.2	-	-0.2
10	10	0	45	44.4	+1	0.6
10	0	10	46	44.3	+2	+1.7

Here the addition of 10% v/v DEC reduces the flash point of the base fuel from 65 to 44°C. Adding 10% v/v RME to the DEC/base fuel blend increases its flash point by only 1°C, whereas adding 10% v/v DBC to the blend increases the flash point by 2°C. Again, the DBC unexpectedly has a greater impact on the blend flash point than does the RME, despite the fact that neat DBC has a much lower flash point than neat RME. The DBC also increases the blend flash point by more than would have been predicted using the Wickey-Chittenden model.

Example 3

Example 1 was repeated, but using dimethyl carbonate (DMC) instead of DEC, and the base fuel DBF2 as in Example 2. The DMC was sourced from Sigma Aldrich, UK.

The flash point results are shown in Table 3 below. The fifth column shows predicted flash points as calculated using the Wickey-Chittenden equation, using a blending flash point of 0°C for the DMC.

Table 3

% v/v DMC	% v/v RME	% v/v DBC	Average flash point (°C)	Predicted flash point (°C) by W-C	Measured improvement relative to 5% v/v DMC (°C)	Measured improvement relative to that predicted by W-C (°C)
0	0	0	65	-	-	-
5	0	0	30	31.5	-	-1.5
5	5	0	31	31.6	+1	-0.6
5	0	5	66	31.6	+36	+34.4
100	0	0	16.5	-	-	-

DBC can be seen to have an even greater effect on the flash point of a DMC/base fuel blend than on a DEC/base fuel blend. Again, the addition of 5% v/v of DBC to a blend of 5% v/v DMC in the diesel base fuel causes a far greater increase in the blend flash point than does

the addition of 5% v/v RME, despite the higher flash point of neat RME. This increase is also significantly greater than the Wickey-Chittenden model would have predicted. Again there appears to be a synergistic interaction between the DMC and the DBC as regards their combined flash points.

Example 4

Example 1 was repeated, but using dimethyl carbonate (DMC) instead of DEC, and the base fuel DBF3. DBF3 was a commercially available zero sulphur automotive diesel base fuel, ex. Shell. It had a flash point (IP 34) of 65°C. It had a density at 15°C (ASTM D4052) of 825 kg/m³, an initial boiling point (ASTM D86) of 172°C, a T95 boiling point (ASTM D86) of 329°C, a final boiling point (ASTM D86) of 342°C, a measured cetane number (ASTM D613) of 53.8, an E250 (IP 123) of 57.5°C and no E350 (IP 123). The DMC was sourced from Sigma Aldrich, UK.

The flash point results are shown in Table 4 below. The fifth column shows predicted flash points as calculated using the Wickey-Chittenden equation, using a blending flash point of 0°C for the DMC and 89°C for the DBC.

Table 4

% v/v DMC	% v/v DBC	Average flash point (°C)	Predicted flash point (°C) by W-C	Measured improvement relative to that predicted by W-C (°C)
0	0	65		
10	0	19	23.8	-4.8
10	10	26	23.8	2.2
15	0	17.5	19.4	-1.9
15	10	25.5	19.4	6.1
20	0	18.5	16.3	2.2
20	10	23.5	16.3	7.2
20	20	25.5	16.3	9.2

DBC can be seen to have an even greater effect on the flash point of a DMC/base fuel blend than on a DEC/base fuel blend. This increase is also significantly greater than the Wickey-Chittenden model would have predicted. Again there appears to be a synergistic interaction between the DMC and the DBC as regards their combined flash points.

Example 5

Example 1 was repeated, but using diethyl carbonate (DEC) instead of DMC, and the base fuel DBF3 from Example 4. The DMC was sourced from Sigma Aldrich, UK.

The flash point results are shown in Table 5 below. The fifth column shows predicted flash points as calculated using the Wickey-Chittenden equation, using a blending flash point of 17.7°C for the DEC and 89°C for the DBC.

Table 5

% v/v DEC	% v/v DBC	Average flash point (°C)	Predicted flash point (°C) by W-C	Measured improvement relative to that predicted by W-C (°C)
0	0	65		
10	0	42	43.1	-1.1
10	10	49.5	43.4	6.1
15	0	38.5	38.8	-0.3
15	10	45.5	39.0	6.5
20	0	36	35.6	0.4
20	10	43.5	35.7	7.8
20	20	45.5	35.9	9.6

This increase is also significantly greater than the Wickey-Chittenden model would have predicted. Again there appears to be a synergistic interaction between the DEC and the DBC as regards their combined flash points.

C L A I M S

1. A diesel fuel formulation containing (i) a lower molecular weight dialkyl carbonate (DAC) selected from dimethyl carbonate (DMC), diethyl carbonate (DEC) and mixtures thereof; and (ii) di-n-butyl carbonate (DBC).

5 2. A fuel formulation according to claim 1, which also contains (iii) an additional diesel fuel component.

3. A fuel formulation according to claim 1 or claim 2, wherein the lower molecular weight DAC is DEC.

10 4. A fuel formulation according to claim 1 or claim 2, wherein the concentration of the lower molecular weight DAC is from 0.5 to 20% v/v.

5. A fuel formulation according to any one of the preceding claims, wherein the concentration of the DBC is from 0.5 to 99.5% v/v.

15 6. A fuel formulation according to any one of the preceding claims, wherein the volume ratio of the lower molecular weight DAC to the DBC is 1:1.

20 7. A fuel formulation according to any one of the preceding claims, wherein the flash point of the formulation (ASTM D92 or D93) is 50°C or higher.

25 8. A process for the preparation of a diesel fuel formulation, which process involves blending together (i) a lower molecular weight DAC selected from DMC, DEC and mixtures thereof; (ii) DBC; and optionally (iii) one or more additional diesel fuel components.

30 9. A method of operating an internal combustion engine, and/or a vehicle which is driven by an internal combustion engine, which method involves introducing into a combustion chamber of the engine a diesel fuel formulation according to any one of claims 1 to 7.

10. Use of DBC, in a diesel fuel formulation containing a lower molecular weight DAC selected from DMC, DEC and mixtures thereof, for the purpose of increasing the flash point of the formulation.

5 11. A method for increasing the flash point of a diesel fuel formulation which contains a lower molecular weight DAC selected from DMC, DEC and mixtures thereof, in order to achieve a target minimum flash point X, which method involves adding to the formulation a concentration c of
10 DBC, wherein c is lower than the minimum concentration c' of DBC which theory would predict needed to be added to the formulation in order to achieve flash point X.

12. Use of DBC, at a concentration c, in a diesel fuel formulation which contains a lower molecular weight DAC
15 selected from DMC, DEC and mixtures thereof, for the purpose of increasing the flash point of the formulation by an amount x, wherein x is greater than the flash point increase x' which theory would predict would result from adding DBC to the formulation at concentration c.

20 13. Use of DBC, at a concentration c, in a diesel fuel formulation which contains a lower molecular weight DAC selected from DMC, DEC and mixtures thereof, for the dual purposes of:

- 25 a) achieving a target minimum flash point X for the formulation; and
b) allowing an increase in the concentration of the lower molecular weight DAC to a level above the maximum concentration d' which theory would predict could be included in the formulation, after addition
30 of the DBC at concentration c, without reducing the flash point of the formulation below the target minimum X.

14. Use of DBC, in a diesel fuel formulation containing a lower molecular weight DAC selected from DMC, DEC and mixtures thereof, for the purpose of replacing, at least partially, a fatty acid alkyl ester (FAAE) which is or would otherwise have been included in the formulation.

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