

**Engine Use of Biodiesel in the Marine Sector**  
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**John McCrystal and Associates**

**30 September 2011**

## **1. Executive Summary**

This report considers the use of biodiesel in the marine sector. For this report “biodiesel” refers to the methyl esters made from vegetable oils and animal fats (the most common, commercially available form of biodiesel currently available).

Numerous potential advantages arise with the use of biodiesel, including lower toxicity, the faster rate at which it degrades when spilt, its lower greenhouse gas footprint, and some engine-compatible combustion properties. However, biodiesel is chemically different to mineral diesel and there is potential for compromise in some aspects of its performance unless these factors are adequately managed. The relevant differences are its solvent properties (and related to this, its compatibility with different materials); its stability; its different volatility; and its different cold temperature performance.

While this list may appear daunting, it must be put into perspective. These differences are *potential* issues, which can generally be managed with a range of techniques. These techniques include:

- Ensuring that the quality of the fuel is appropriate and is maintained right through to use in the end-use application (one of the most important things to get right for any fuel, and no less so for biodiesel and fuel containing it).
- Diluting the chemical difference between biodiesel and mineral diesel by blending the fuels.
- Ensuring that at-risk components are compatible with the use of biodiesel (including through parts replacement).
- Choosing applications where the duty and other characteristics are well matched to the use of fuels containing biodiesel.

Taking the second, for example, many engine manufacturers accept the use of B7 (a blend containing 7% biodiesel in mineral diesel), which is provided for by EN590 (the specification of diesel in Europe, and the one most often referenced by the engine manufacturers). At this level, the chemical and physical properties of the fuel are little different to those of straight mineral diesel and no significant difference in the fuel’s performance is expected, either.

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The solutions applied as biodiesel content increases (and differences in the performance of the fuel are more likely to exhibit themselves) are many and varied, as different engine manufacturers accept different levels of biodiesel (and their acceptance may even vary between engine models), some applications are more suited to the use of fuel containing higher proportions of biodiesel than others) some consequences of the differences are more acceptable than others, and different users will have varying levels of understanding of the subject in general. One aim of this report is to equip potential users of biofuel with the science they need to make decisions regarding the suitability of biodiesel to their application and the solutions they might apply to any issues that may arise.

A list of the compatibility of different engines makes, as provided by various engine manufacturers, is also supplied. Engine manufacturers' attitudes range from acceptance of the use of fuel containing no more than 5% biodiesel only, through to the acceptance of the use of straight biodiesel. Experience in New Zealand also shows that engine manufacturers, or their agents, are sometimes willing to accept the use of fuel containing higher biodiesel content than their advertised limits for specific applications. Hence, the engine manufacturer compatibility results are to be considered a guide only, to be followed up with direct discussions between the engine owner and the manufacturer's the local agent.

The marine sector environment places different demands on fuels than on-road and other land-based applications do, and this should also be taken into consideration when looking to switch to the use of biodiesel fuels in the marine sector:

- Main engines (on commercial vessels, at least) tend to be operated under moderate to high load for much of their running time, which is well-suited to the use of biodiesel.
- Generator engines, however, tend to be lightly loaded, which is not well-suited to the use of fuel containing biodiesel. This may require changes in how the generator is operated, in how electrical power is managed, or some other solution.
- Sophisticated exhaust after-treatment devices are not normally used in the marine sector, which eliminates concerns over the performance or consequences of using such devices with biodiesel.
- Tank vents and filling ports can be exposed to the elements and may require modification in order to better avoid the ingress of water.

One of the benefits often cited for the use of biodiesel in the marine sector is its lower toxicity upon marine ecosystems and higher rate of degradation. A literature review indicated that the biodiesel component is indeed less toxic than mineral diesel, and not only does biodiesel degrade more quickly than mineral diesel, but its presence also accelerates the degradation of mineral diesel.

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## 2. Introduction

Concern in recent years about the threat from climate change has prompted the development of transport fuels from ‘renewable’ sources – among them fuels derived from biomass rather than from fossil sources. One of these is “biodiesel”, a mixture of compounds formed by the chemical reaction “transesterification” on animal fats and vegetable oils that results in a liquid fuel that can be used in compression-ignition engines either as a replacement for, or a supplement to, conventional, mineral diesel. The common forms in which biodiesel is currently used in the New Zealand market are “B5” (for blends comprising up to 5% biodiesel in mineral diesel), “B20” (comprising 20% biodiesel and 80% mineral diesel), and straight biodiesel (B100).

If you’re the owner of a vessel powered by a diesel engine or engines who is considering switching to a biodiesel blend, however, you’ll likely have found that there’s conflicting information swirling around about its suitability for marine applications. On the one hand, there’s the reassuring evidence from those who have already switched to biodiesel and who through controlling the quality of the fuel have experienced no difficulties. On the other hand, the manufacturers of most commonly available diesel engines and their local representatives have tended to take a more precautionary stance in their advice, and most won’t let you use blends containing more than a certain (usually low) proportion of biodiesel before they’ll withdraw their warranty.

One of the prototypes of the very first compression-ignition engine actually ran on neat peanut oil. But for over a century since Rudolf Diesel developed it, the engine that bears his name has run on mineral diesel, and as the technology and demands of the diesel engine itself have evolved, so too has the precise formulation of the fuel. These days, trying to run many modern diesel engines on peanut oil would result in disaster, which is why such oils require a chemical change in order to render them suitable for this purpose.

While in many respects biodiesel is an excellent substitute for mineral diesel, it does differ chemically from mineral diesel. Some of these differences are advantageous: besides the obvious benefit of its derivation from the recent living rather than from the fossil carbon cycle, it has other things going for it. Its toxicity is very low both to its handler and (in the event of a spill) to the environment. The emissions produced when it is burned are, on the whole, less harmful than those yielded by mineral diesel combustion. As could be expected, given that it’s derived from recently living plant or animal tissue, biodiesel is readily biodegradable; and better yet, studies seem to suggest that when it is used in blends with mineral diesel, it accelerates the biodegradation of the mineral portion of the blend, too.

But some of the differences in the chemical properties of biodiesel present potential problems for its use in modern diesel engines. Some of these have actually been encountered by biodiesel users. Others can be inferred from scientific principles. In each case, they represent a risk that the performance (including the durability) of an engine may be compromised. It is these risks that have encouraged engine manufacturers to adopt a careful approach to the introduction of biodiesel to their engines’ fuelling diet.

And it is also vital that everyone proposing to switch to fuelling their diesel engine on biodiesel or biodiesel blends acquaints themselves with these risks, and the ways in which they can be managed.

This report is intended to inform the marine diesel engine operator of the risks associated with switching to biodiesel and biodiesel blends, and the steps that a prudent operator will take to manage them. After all, until engine manufacturers fully approve the use of biodiesel in their engines, it is the operator who must assess the risk and who must (in the absence of warranty coverage) ultimately shoulder it.

This subject can be discussed in considerable technical detail. In order to make this report widely accessible, the heavy technological discussion has been relegated to the appendices. Those with the stomach for it are invited to revel in the greater technical depth contained in these latter pages.

### **3. Mineral Diesel and Biodiesel: an Introduction to Fuel Technology**

Modern diesel engines are expected to last a long time (a heavy road vehicle can serve for more than 800,000 km between engine rebuilds), and to go for extended periods between services. They are also expected to emit very low levels of emission species of concern (and to maintain this performance over the useful life of the engine). These demands have meant that fuels, engines and their combinations have become vastly more sophisticated in recent decades, and both fuel and engine specifications have been tightened accordingly.

Any alternative to mineral diesel must be capable of delivering similar performance to mineral diesel or, where performance is in any way compromised, that compromise must be offset by the benefits of using it. It must, in other words, have ‘auto-ignition’ and combustion properties that match those of mineral diesel. The engine must not be adversely affected by any action of or reaction with the fuel or its combustion products. You would expect to be able to store the fuel, as you can mineral diesel – for many months without any significant degradation – and its storage and handling shouldn’t require anything beyond the usual precautions. Donning a space suit every time you refuel shouldn’t be necessary.

Because biodiesel is chemically different to mineral diesel (and is also physically different in some aspects because of this), it will sometimes perform differently. Whether these differences significantly compromise performance depends upon a number of factors, some of which may be specific to a particular application. Here, we’ll consider the differences, with particular regard to their implications for marine applications. The best place to start is with an understanding of the base chemistry of mineral and biodiesel alike.

### 3.1. What is Mineral Diesel?

Like petrol (and other familiar liquid fuels, such as kerosene and aviation fuel), mineral diesel is a mixture of hundreds of different “hydrocarbons” – molecules made up of predominantly carbon and hydrogen arranged in various configurations (such as simple chains of carbon atoms, chains with branches, rings, or any combination of these). Hydrocarbons with longer carbon chain lengths are generally more viscous, and are more suited for use in “heavy fuel” applications (those with still longer chain length are so viscous as to be tar-like, and are used for the likes of bitumen). Petrol, on the other hand, is typically made up of hydrocarbons that are of shorter chain length and are thus more volatile (that is, vaporise more readily). Their volatility is one of the characteristics that make them suitable for use in spark-ignition engines.

Like petrol, diesel is normally the product of refining and treating crude petroleum (literally, “rock oil”: petroleum is the sludgy hydrocarbon residue formed when ancient biomass buried deep beneath the ocean floor was subjected over aeons to precisely the right combination of geological pressure and temperature). In the case of diesel, the cracking and distillation processes involved in refining tend to select those hydrocarbons with carbon chain lengths in the approximate range of C<sub>9</sub> (i.e., containing 9 carbon atoms in the fuel molecule) to C<sub>20</sub><sup>1</sup>.

The basic fuel-related characteristics of mineral diesel to which our engines have become accustomed include:

1. Relative stability: no significant degradation is expected if the fuel is stored for a time in (what the industry considers to be) “normal” conditions. Diesel is stable because it has relatively few weak molecular bonds that can be attacked under normal storage conditions.
2. Good ignition and combustion properties: the longer hydrocarbon chains in the mixture produce good “auto-ignition” properties (that is, they will ignite at the temperatures and pressure reached when the fuel-air charge in the combustion chamber is compressed by the motion of the piston), while the shorter chains reduce the fuel’s overall viscosity and permit good atomisation of the fuel, which in turn enables more complete combustion to occur.
3. Relatively benign to handle: from a personal safety point of view and in terms of compatibility with the materials used, diesel can be readily handled.

These are the basic characteristics of mineral diesel. In practice, the quality of diesel is assured by specifications that stipulate a multitude of performance requirements that the fuel is normally expected to meet. Engine manufacturers rely on the fuel meeting these specifications in order to warrant the minimum performance (including durability) expected from an engine.

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<sup>1</sup> Or, more precisely, it is a fraction boiling at an initial distillation temperature of 160° (90% range of 290-360°C) - Encyclopedia of Chemical Technology; Third Ed.; John Wiley & Sons: New York, NY, 1980, Vol. 11; pp. 682-689.

### 3.2. What is biodiesel?

For the purposes of this report, “biodiesel” is a mixture of organic compounds named esters that are produced by the “transesterification”<sup>2</sup> of vegetable oils or animal fats. And more specifically, biodiesel is the mixture of esters produced when using methanol as the alcohol reagent (the most commonly used alcohol when making biodiesel). The ester products are sometimes referred to as “methyl esters” as a result. There are a number of other naming conventions used for biodiesel, some of which refer to their chemical origins (e.g., “monoalkylesters”), or to the feedstock from which the biodiesel was derived (e.g., soy methyl ester, tallow methyl ester, and so on).

When you buy a commercial-grade biodiesel, around 98% of what you’ll get is a mixture of the methyl ester compounds. The remainder comprises partially converted oils and fats, a range of non-ester hydrocarbons (that transfer through from the base feedstock), and any performance modifiers that may have been added. These alternatives to methyl esters, in small and varying proportions, are provided for by the specifications that govern the quality of biodiesel.

The precise composition of the different methyl esters in any given biodiesel can differ quite markedly, and is usually a reflection of the feedstock from which it was derived. The different temperatures at which biodiesel derived from different feedstocks begins to gel is one of the most striking physical differences that transpires: biodiesel derived from tallow (animal fat), for example, begins to gel at around 14°C, compared with rapeseed oil and some used cooking oil-derived biodiesels that won’t do the same until temperatures fall below 0°C. This difference is due to the level of “saturation” of the biodiesel molecules (a molecule is said to be “saturated” when the available bonds around the carbon are fully occupied). Tallow-derived biodiesel comprises a far greater proportion of saturated methyl esters than biodiesel derived from rapeseed oil and many of the used cooking oils used for biodiesel manufacture. Needless to say, a fuel that begins waxing up at relatively balmy temperatures is going to be pretty limited in its practical applications.

The differences in saturation also lead to performance differences in stability and combustion, but these differences are generally either relatively insignificant or can be otherwise managed (for example, through the use of anti-oxidation additives, in the case of biodiesels that are more unstable because they contain higher proportions of “unsaturated” esters).

And more generally, the base chemical structure of methyl esters differs from the mineral diesel on which the vast majority of engines and related systems have been tried, tested and proven. These differences mean that there is the potential for engines to perform differently when asked to run on fuels containing methyl esters, and this *may* lead to some degree of compromise in performance, compared with the use of mineral diesel.

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<sup>2</sup> In this particular case, a reaction that essentially breaks the three main hydrocarbon chains off an oil or fat molecule (which are a type of ester) into three separate chains (which are also esters, and hence the term “trans-esterification”).



A well documented example of this is that due to its chemical composition, biodiesel exhibits greater solvent properties than mineral diesel. Switching to biodiesel fuels can therefore result in the loosening of dirt and other deposits in the fuel system, with this material then carried through to, and sometimes blocking, the fuel filter.

Despite all this, biodiesel has come a long way from the days of the backyard brew-ups of the 1970s fuel crises (although there are still diehard home-brewers around, just as there are other fuel options that are unlikely to be fit for use in modern engines). Biodiesel is produced commercially in New Zealand these days, and it is also subject to a range of specifications, many of which are designed to mitigate the risk that arises from the differences between mineral diesel and biodiesel.

In short, these regulations demand that the feedstock is of appropriate quality and that the processing and product finishing is such that non-desirable species are kept within limits where they should not pose a concern. Take, for example, the specification for triglycerides (the chemical name for the original unreacted oil and fat molecules) which limits their content to a maximum of 0.2% (requiring good production processing), to avoid injector tip fouling and other similar issues due to the propensity of this molecule to detrimentally degrade at certain conditions found in an engine. These regulated specifications and what they mean for biodiesel are further detailed in Appendix A.

The next section looks at the key differences between quality biodiesel (not the backyard stuff) and diesel.

#### **4. Key Differences between Biodiesel and Mineral Diesel**

In general terms, the differences between biodiesel and mineral diesel that *may* affect the performance of biodiesel as a fuel in modern diesel engines are: energy density; solvent properties; hydroscopicity; saturation point; fuel stability; volatility; combustion characteristics; and cold temperature operability.

Each of these differences has implications for the use of biodiesel in diesel engines in general, and some in marine applications in particular. This section considers each of these differences in turn, in order to identify where the risks arise, then describes potential management methods, including any that might be specific to the marine sector. It attempts to provide the various arguments in an unbiased manner by taking them back to the science from which they are derived.

But there may still be gaps in our knowledge when appraising the use of biodiesel fuels in a specific application: the exact materials used in a specific engine's fuel system may not be known, for example, which will give rise to differences in opinion on how compatible the fuel is with that particular application. And different end users may find the level or risk more or less acceptable when confronted with the same assessment results. This difference of opinion is further discussed in Appendix B.

It's important to note from the outset, though, that the effect of any chemical and physical differences between mineral and biodiesel is diluted (and so too are any performance differences) when the two fuels are blended (and this is a common management method where biodiesel is used). There's no hard or fast rule regarding the point at which the properties of biodiesel suddenly assert themselves as the biodiesel proportion of a blend increases, but it's safe to say that the lower the biodiesel proportion of a blend, the less significant any differences in fuel specification will become. That's why the New Zealand regulations currently allow fuel retailers to sell blends up to B5 (containing 5% biodiesel) without disclosing that there is any biodiesel in the mix at all. And that's why many engine manufacturers will tolerate the use of low-proportion blends (up to around B7<sup>3</sup>, but sometimes as high as B20) without withdrawing their warranty.

#### 4.1. Energy Density

Biodiesel is less 'energy dense' than mineral diesel. Energy density is best considered as the 'bang for your buck' that a fuel delivers — the amount of energy that a given quantity of fuel will yield. Considered on a unit volume basis, straight biodiesel contains around 6% less energy than the equivalent volume of mineral diesel.<sup>4</sup>

Most diesel engines meter fuel volumetrically, and the comparatively lower energy density of biodiesel might be expected to yield correspondingly less power than mineral diesel, all else being equal. In general, the results of engine dynamometer tests (i.e., where the engine is tested by itself, and without the influence of driver and drivetrain dynamics) tend to reflect this. However, an effective advance in the combustion timing<sup>5</sup> and small improvement in combustion under high load operation,<sup>6</sup> for some engines, can bring about small improvements in the engine's "brake thermal efficiency", returning volumetric fuel consumptions not too dissimilar to those of ordinary diesel (despite the lower energy content). There is, of course, also the potential for a deterioration in fuel consumption performance.

Care is required in this regard to understand that the changes found can be quite engine-specific due to different fuel injection and control-related system arrangements.

For similar reasons the peak power of the "average" engine is expected to decrease to the order of 6% when operating on straight biodiesel, but some engines may experience a lower decrease in peak power, or even a power increase, while others may see a

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<sup>3</sup> The small increase in allowance from B5 to B7 is due to many engine manufacturers making reference to EN590, the specification for diesel in Europe, which allows the use of up to B7. B5 was the allowance provided by EN590 at the time of drafting New Zealand's regulated specifications for biodiesel, and is also that accepted by the Japanese engine manufacturers.

<sup>4</sup> For hydrocarbon fuels such as petrol, diesel and biodiesel, the "fuel energy" comes from the chemical reaction of the hydrogen and carbon in the fuel with oxygen from the air. The methyl esters that comprise biodiesel contain oxygen molecules besides carbon and hydrogen, and this "dilutes" the hydrogen-carbon density of biodiesel – and thus the energy density of the molecules. The 6% results from the use of a calculated net heating value for diesel of 42.6 MJ/kg and a density of 0.825 kg/l (typical figures for New Zealand diesel), and heating value for biodiesel of 37.2 MJ/kg and density of 0.884 kg/l.

<sup>5</sup> For example, that brought about by the higher modulus of elasticity for biodiesel for some injection systems, or higher viscosity for some types of injection pump, timing advance coupling arrangements.

<sup>6</sup> Through improved oxygen availability under higher loads – discussed in Section 4.6.

deterioration of greater than 6%. This tends to be inconsequential in the marine sector, as the engine power curve is qualified by the propeller specification, and the engine and propeller are matched so that peak engine load is not sustained.

In many cases, the use of biodiesel changes the “note” of the engine by eliminating some of the harsh knocking sounds. In on-road applications, this can provide the (seat-of-the-pants) impression that the engine is “working better” on biodiesel, and may result in the operator changing driving styles and sometimes attaining noticeable improvements in fuel economy as a consequence. This is less likely to happen in marine applications, due to the manner in which main engines tend to be operated.

And finally, the difference in energy density between mineral diesel and a B20 blend is around 1%: similar differences in energy density can be found between different batches of mineral diesel<sup>7</sup>.

#### **4.2. Solvent Properties**

The esters of biodiesel have a greater solvent effect than the mixture of hydrocarbons that comprise mineral diesel. This means that they may loosen deposits and contaminants in the fuel tank and fuel lines, and these may become lodged in the fuel filter. A blocked fuel filter will interfere with engine performance, and may even starve it of fuel altogether.

In not too dissimilar manner, biodiesel esters have also been shown to be more readily absorbed than mineral diesel by some kinds of elastomers (flexible compounds), such as are used in many of the flexible components in engines and engine systems — o-rings, flexible fuel hoses, diaphragms and so on. This absorption and solvent action can, for some materials, result in a range of responses from swelling and softening to hardening and cracking.

Let’s look at these two problems in turn:

The risk of contaminants being dislodged in fuel tanks and lines by the more highly solvent qualities of biodiesel is neither greater nor less in marine applications than in others, and the precautions to be taken are therefore the same – even if the unforgiving nature of the sea makes them more important. The risk, needless to say, is greatest just after biodiesel is first used, so it’s prudent to change your fuel filter shortly after you’ve switched to fuel containing biodiesel. For on-road applications, some diesel engine users even fit a filter before the factory-fitted filter for added protection. The high quality of the filtration systems used in marine applications, however, suggests that it is preferable to replace the filter rather than to fit another.<sup>8</sup>

Experience from on-road applications suggests that filter changes are not necessary for the use of blends containing up to 20% biodiesel where the fuel systems are in good, clean condition.

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<sup>7</sup> Based on calculated energy content using typical specifications for summer and winter grade diesel fuels.

<sup>8</sup> Recommendation, Shaw Diesels.

The vulnerability of elastomers – flexible materials – is a trickier issue (and, incidentally, one of the key reasons for the engine manufacturers’ reluctance to approve their engines for use with higher blend ratios of biodiesel). While modern mineral diesel is also more aggressive to a range of elastomers than its older counterparts, meaning some particularly vulnerable materials (such as natural rubber and their early synthetic replacements) have been phased out, a small number of materials that remain in common use are more likely to suffer detrimental effects from biodiesel than from mineral diesel.<sup>9</sup>

And complicating the problem is the fact that knowing which materials have been used in your engine may not be as simple as checking your engine’s model number with the manufacturer. In many cases, the engine manufacturer is an assembler, the last member of a long supply chain and (particularly for older engine models) it may be impractical or even impossible to identify the exact materials that were used by this method.

As has been mentioned, some elastomers used to make o-rings, seals, gaskets and the like may swell, shrink, soften or harden to a greater extent in the presence of biodiesel than they would when mineral diesel is used, and these effects may prove problematic. The general experience from the on-road sector has found (but noting that these may not necessarily hold true for a specific engine application):

- It is difficult for someone in the trade to say at a glance whether at-risk materials have been used in a particular engine, but if it can be established that they have, then consideration should be given to replacing them with compatible components before switching to biodiesel.
- An alternative is to monitor an engine’s at-risk components for signs of swelling or fuel leakage. Failures are unlikely, and tend in any case not to be catastrophic, which means that there is time for repair. It’s prudent, if adverse effects are anticipated or feared, to begin with the use of lower blend ratios of biodiesel.
- It is very unlikely that problems will be found at a B20 blend level.
- It can be extremely difficult to view at-risk components (although the open engine rooms typical of many marine applications are a bonus in this regard).
- And from the science: those components most at risk are those that are old, worn or in otherwise poor condition, as these tend to have little capacity to absorb any change. It is therefore recommended to identify these components in a pre-switch check, and replace them.

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<sup>9</sup> Using the guide provided in Biodiesel Handling and Use Guideline (Fourth Edition), NREL/TP-540-43672, December 2009, those elastomer materials that show reasonable to good compatibility with biodiesel include butyls, Chemraz, fluoro-compounds, Hifluour, Nylon, Teflon, and most Vitons. Those elastomer materials that can exhibit poor compatibility with biodiesel fuels include Buna-N, Butadiene, Hypalon, natural rubbers, neoprene, most nitriles, polypropylene and styrene-butadiene. In short, Teflon, Viton, and Nylon react very little to biodiesel and are among the materials that can be used to update incompatible equipment.

Most tanks designed to store diesel fuel are expected to be adequate for storing B100: the (US) National Biodiesel Board reports that acceptable storage tank materials include aluminum, steel, fluorinated polyethylene, fluorinated polypropylene, Teflon, and most fibreglasses.

Design and improved manufacture tracking systems have meant that many engine manufacturers have begun to supply engines for marine and industrial applications that are known to be compatible with the use of blends containing high proportions of biodiesel (or even straight biodiesel). This is so even for some engines intended for on-road applications (although this tends not to be so straightforward due to the typically more stringent exhaust emissions performance requirements, and related equipment used).

Note again, the biodiesel component in low-proportion blends (5-7%) is not expected to have any significant effect, even on materials considered vulnerable.

### **4.3. Hydroscopicity and Saturation Point**

Biodiesel can (and does) absorb water from the atmosphere at a greater rate than mineral diesel, risking the presence of free water occurring. The presence of free water is of concern as it can cause mechanical damage to fuel injection components and provides the necessary conditions for corrosion, hydrolysis and microbial degradation (discussed in the next section). The risk is greatest where large variations in fuel temperature occur, as the fuel tank “breathes” more under these conditions. This breathing tends to be moderated in marine applications where the fuel tank is only exposed to the surrounding water temperatures. It’s recommended that the up take of water through tank breathing is carefully considered and that desiccant-type filters are used on tank breathers where there is risk of high water up take<sup>10</sup> (for example, where high biodiesel content blends are used and/or there is a slow turnover of fuel<sup>11</sup>).

Meanwhile, biodiesel can also absorb around three times as much water as diesel before it reaches “saturation point” (where any additional water added forms free water). This means that biodiesel has a greater ability to absorb any free water that enters a tank, and there is anecdotal evidence to show that switching to the use of biodiesel blends has seen free water absorbed and so “dried out” at least two land-based storage tanks<sup>12</sup>.

### **4.4. Fuel Stability**

In general, biodiesel is less stable than mineral diesel, and this instability is heightened because many of the esters are unsaturated. It is the degree and configuration of this unsaturation that determines the liability of any given biodiesel to degradation (and also to gelling, which will be discussed further in section 4.7).

Degradation itself may take the form of: hydrolysis (the tendency of esters to form acids when exposed to free water); oxidation (the tendency of esters to form peroxides and other corrosive species in the presence of oxygen: the presence of these in turn catalyses the formation of gums and polymers); microbial activity (which can also cause the formation of acid by-products and, in due course, gums and deposits); thermal

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<sup>10</sup> Tyson, Shaine. 2004 Biodiesel Handling and Use Guidelines. Department of Energy/NREL. DOE/GO 102004. September 2004

<sup>11</sup> For example, where it takes more than three months to completely turn over the fuel tank contents, turn over introducing fresh, low water content fuel.

<sup>12</sup> Field experience, Biodiesel New Zealand, personal communication.

degradation (where the fuel forms polymers that are highly viscous compared with the base fuel).

Marine applications will test the stability of biodiesel: hydrolysis and microbial degradation rely on the presence of free water, and there is obviously an elevated risk in the very watery marine environment unless suitable precautions and practices are adopted. Less obviously, there is also an increased risk due to the presence in many marine fuel systems of corrosion-resistant, non-ferrous metals such as copper, brass, bronze, lead, tin and zinc, each of which can catalyse fuel oxidation reactions.

As usual, the lower the proportion of a blend that biodiesel comprises, the lower the susceptibility of the blend to these problems. But in any event, most can be addressed by observing good fuel “housekeeping” practices. After its delivery, it’s good practice to avoid storing fuel (especially biodiesel and biodiesel blends) for long periods, and in containers (such as tote tanks and intermediate bulk containers or IBCs) that expose it to sunlight. Similarly, the best method of safeguarding against hydrolysis, microbial degradation and other processes that depend upon the presence of free water is to limit as far as possible the exposure of the fuel to water and water vapour (as has been discussed in the previous section). This can often mean taking care over the design of tank breathers – in this regard the simple, U-bend tank breather commonly mounted on a vessel’s deck is likely to be inadequate to prevent the absorption of water.

The use of high-quality particulate and water-separating fuel filtration in the fuel lines supplying the engines is also recommended as general good practice. Such filtration will protect the engine’s fuel system components from the presence of free water and much of the foreign matter that may find its way into the fuel. However, such filtration will not protect the engine from many of the products of fuel degradation that may occur upstream of this point, regardless of what fuel is used. These degradation products include acids and some sludges that will pass through even the best filtration.

As well, anti-oxidation additives may be used where fuel must be stored for extended periods, and the fuel monitored for the presence of acids – indicating that not insignificant degradation has occurred. Metal chelating additives (sometimes known as “metal inhibitors”) may be used to reduce the catalytic effects of any reactive metals present (i.e., the corrosion-resistant metals mentioned earlier). In some circumstances, biocides could be used as a precaution against microbes (although this would tend to stabilise the biodiesel in the event of a spill, and might not be an acceptable consequence to some users because of this).

Thermal degradation is most unlikely to occur in normal engine operation where quality biodiesels are used, as the high temperatures required for these polymerisation degradation reactions are not normally reached. But prolonged storage at elevated temperatures will, in the absence of precautions, promote other forms of degradation, such as oxidation or the growth of microbes.

It should be noted, before we move on, that it's not only biodiesel that degrades. Mineral diesel can do it too, albeit, normally, at far lower rates. One particular concern for mineral diesel is microbial degradation, or "diesel bug" which is becoming more of an issue in New Zealand because of the intolerance of newer engine technology to the products of such fuel-eating bacteria. Diesel bug is further discussed in Appendix C.

#### **4.5. Volatility**

As mentioned in Section 3.1, mineral diesel is a mixture of hydrocarbons with the vast majority ranging in boiling point from around 160°C up to around 390°C. The esters comprising biodiesel have boiling points that are all around 340°C. A small proportion of any fuel will find its way into the engine's lubricating oil in typical operation of the engine and the wider and lower boiling point range for mineral diesel means that a higher proportion of mineral diesel will vaporise from the lubricating oil compared with biodiesel. This means that biodiesel is expected to survive for longer, to dilute the lubricating oil more than mineral diesel does. This effect is compounded by:

- Certain other physical attributes for biodiesel<sup>13</sup> which mean that a greater proportion of biodiesel is expected to survive combustion and find its way into the engine oil in the first place;
- Mineral diesel is more like the lubricating oil after vaporisation than biodiesel is.

Because biodiesel's greater tendency to dilute lubricating oil, many engine manufacturers recommend more frequent oil changes where fuels with higher biodiesel content are used. But the typical, high-load engine duty of main engines in marine applications is well-suited to the use of biodiesel (and fuel loss to the lubrication oil is far lower in this type of operation) and thus longer periods between oil changes could be contemplated for this type of operation). Caterpillar recommends using oil analysis to determine the best oil service intervals, but this is difficult where fuels containing biodiesel are used, as the results from such oil analysis programmes are less reliable.

Simple, regular checking of the oil level (checking after the engine has been run for a time under load<sup>14</sup>) can provide a reasonable indication of lubricating oil dilution. Increasing oil levels on the dipstick indicate increased uptake of fuel by the lubricating oil, and the oil should be changed without delay. The engine will run well with B5 in the fuel tank, but it should not be run with B5 in the sump.

Engines in marine and industrial applications seldom feature the more advanced exhaust after-treatment devices often found in on-road applications, which is a distinct advantage, as the late and supplementary injection of fuel sometimes used with such devices can greatly exacerbate the dilution of lubricating oil by fuel.

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<sup>13</sup> Including higher surface tension, higher viscosity and higher density, when compared with mineral diesel.

<sup>14</sup> Running the lubrication oil for a time under normal engine operating temperatures will release much of the water bound in the oil, which may otherwise give a false, or at least inconsistent dipstick reading.

#### 4.6. Combustion and Emission Characteristics

In compression ignition engines, fuel is “atomised” (sprayed so that it forms minute droplets) upon injection into the combustion chamber. The fuel droplets then progress through vaporisation and different types of ignition and combustion reactions depending upon conditions and what other reactions are occurring around them at the time. There are a multitude of factors that influence what happens during these phases, including (but far from limited to): fuel injection system temperatures and pressures; in-cylinder temperatures and pressures; fuel physical parameters such as density, viscosity, surface tension and modulus of elasticity; fuel droplet size; fuel volatility; fuel auto-ignition and other combustion properties; local oxygen availability, etc. And these operating parameters may change radically depending on how the engine is operating at the time — whether it is no-fuelling (when decelerating, for a marine application, or when used to brake, in an on-road application) or going “full noise”.

Due to its various characteristics, biodiesel is well suited to medium- to high-load operation. Compared with mineral diesel, its higher viscosity, higher surface tension and higher density result in larger droplets that are “thrown” further, providing for good fuel-air mixing; its lower volatility and the risk of droplets reaching the cylinder walls are offset by higher in-cylinder temperatures found at these higher loads; and biodiesel’s good combustion qualities – as indicated by its high cetane value (the cetane number of a fuel is a measure of the rate at which it ignites and is expected to be representative of how it combusts, also: see Appendix A.7) – are further accentuated by the higher in-cylinder temperatures. This favourable matching of biodiesel with higher loads generally<sup>15</sup> produces a good exhaust emission signature (lower emission of products of partial fuel combustion carbon monoxide, hydrocarbons and particulate) and can yield improved engine brake thermal efficiency<sup>16</sup> (i.e., a greater proportion of the fuel’s energy is transferred through to the engine’s output shaft which, has been mentioned, is one reason for why the use of fuels containing biodiesel may provide better fuel economy than expected).

Biodiesel is not so well suited to use under very light loads: the lower volatility of biodiesel combined with lower in-cylinder temperatures leads to higher amounts of unburnt fuel; some fuel injection systems would have a greater propensity to fail to atomise the fuel adequately, which will heighten the risk of dilution of the lubricating oil; and cooler in-cylinder temperatures can delay the ignition and combustion of biodiesel more than would be indicated by its cetane value. This is why fuels containing higher proportions of biodiesel are not recommended for use in engines that are operated for reasonable time at light load or at idle.

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<sup>15</sup> Care is required in deriving and interpreting such generalisations due to the number of factors involved. For example, biodiesel’s higher modulus of elasticity is also expected to bring about an advance in effective injection timing for certain fuel injection arrangements, which would be expected to return higher engine brake thermal efficiencies and other changes.

<sup>16</sup> Mittelbach et al. Biodiesel, The Comprehensive Handbook, Publisher: Martin Mittelbach, 2006 ISBN: 3-200-00249-2.



This has consequences for the marine sector, as many vessels have separate engine generators that are specified to meet occasional significant loads, but may run at low load or even at idle at governed high speed for the majority of time. Such operation risks significant dilution of the lubricating oil, among other issues. Alternatives should be considered if this situation exists, including better managing the loads on the generator (including through managed use of batteries and other), use of supplementary main engine powered generation, and the use of fuel containing lower biodiesel content.

### ***Exhaust Emissions***

Exhaust emissions are directly related to combustion properties – any change in the combustion-related factors mentioned earlier (plus any change brought about by any exhaust after-treatment device fitted) will also change the exhaust emission signature.

The emissions of concern from internal combustion engines are:

- Hydrocarbons (HC); the product of the partial combustion of fuel. They include toxins (including a group of hydrocarbons containing a ring of carbon atoms and known as “aromatics”) and are a major contributor to smog.
- Carbon monoxide (CO); from the incomplete combustion of carbon in the fuel. Low concentrations are dangerous, high concentrations can be fatal.
- Particulate matter (PM, a component of which is smoke and soot) also from the incomplete combustion of fuel or entrained lubrication oil. They are known toxins and carcinogens. Their small size permits aspiration deep into the lungs.
- Oxides of nitrogen (NO<sub>x</sub>): formed from the reaction of nitrogen and oxygen in the combustion air at higher temperatures. NO<sub>x</sub> is harmful to humans and is a contributor to smog.

Studies have found that, in general, the PM component of diesel exhaust is the most concerning.<sup>17</sup> Also, in general, total PM emission is expected to decrease with increasing content of biodiesel in the fuel. One exception to this is under lighter load operation, where the “soluble organic fraction” component of the PM emitted can increase significantly for the use of biodiesel (a function of biodiesel’s low volatility, among others) and result in an increase in total PM emission (a trend that is not normally exhibited in published emissions data due to the higher-load load profiles used in emissions testing). The typical load profile for main engines means that they would tend to emit less PM where biodiesel was used. The load profile of generator set engines may put them into the higher PM emission category.

Visible smoke emission (only one component of total PM emission) is expected to decrease across all loads.

Whether the exhaust emission from fuels containing biodiesel is more harmful overall is further complicated by differences in mutagenic (that is, causing cellular change) and toxic effect and the size distribution of the PM component. On the one hand, biodiesel-

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<sup>17</sup> PM exhaust emission from vehicles are responsible for the vast majority of the exhaust emission-related health costs in New Zealand Fisher et. al., *Health Effects due to Motor Vehicle Air Pollution in New Zealand*, Report to the Ministry of Transport, January 2002.

derived PM is often reported to possess lower mutagenic and toxic effect<sup>18</sup>. On the other hand, a number of studies have found that the use of biodiesel causes an increase in the concentration of small PM compared with the use of mineral diesel<sup>19</sup> which is of greater concern from a health perspective due to the greater efficacy with which particles of smaller size can be drawn deep within the lungs and even absorbed into the bloodstream. Ultimately, since there doesn't appear to be any analysis that takes all of these factors into account, there are no grounds on which to claim that one emissions signature is more beneficial – or less harmful – than the other.

By comparison, the emission of CO, HC and NOx is relatively inconsequential, particularly considering the minute contribution of the light marine sector to global emissions, and the outdoors nature of marine vessel operation when considering (immediately) local emissions. Nevertheless, CO and HC emissions are expected to trend slightly downwards and NOx emission is expected to trend slightly upwards with increasing content of biodiesel in the fuel.

Note the use of the term “trend” in this discussion. Engines are fickle, and one engine may respond quite differently from another to a change in fuel diet or other parameters. Individual engines may respond differently to the trend shown by the average.

And finally, the complete combustion of carbon in the fuel results in the emission of carbon dioxide (CO<sub>2</sub>), a greenhouse gas. However, in the main, the CO<sub>2</sub> derived from the combustion of biodiesel derived from the feedstocks most commonly used in New Zealand is from carbon that has recently been taken out of the atmosphere (for example, from CO<sub>2</sub> absorbed from the air when the rapeseed plant grows). Unlike the combustion of fossil fuels, which release CO<sub>2</sub> derived from carbon that was sequestered from the atmosphere many of millions of years ago, burning biodiesel doesn't add to the total stock of atmospheric carbon. Hence the use of biodiesel offers a far lower global warming potential.

#### **4.7. Cold Temperature Operability**

Straight biodiesel derived from tallow, and otherwise unmodified, begins to cloud at around 14°C (its “cloud point”) and fuel filters will begin to plug if the temperature of the fuel falls much below this. Straight biodiesel derived from palm oil will exhibit similar performance. Biodiesel derived from rapeseed oil will begin to show similar tendencies at around -10°C for virgin oil and -6°C for used cooking oil<sup>20</sup>. The temperatures at which biodiesel derived from various blends of these feedstocks begin to exhibit filter blocking tendencies lie somewhere in between.

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<sup>18</sup> As determined by the results of salmonella typhimurium/mammalian microsome plate-incorporation assays. Bünger, J., et al *Mutagenic and Cytotoxic Effects of Exhaust Particulate Matter of Biodiesel Compared to Fossil Diesel Fuel*. Mutation Research/Genetic Toxicology and Environmental Mutagenesis Volume 415, Issues 1-2, 8 July 1998, Pages 13-23

<sup>19</sup> Tsolakis, A., *Effects on Particle Size Distribution from the Diesel Engine Operating on RME-Biodiesel with EGR*. School of Engineering, Mechanical and Manufacturing Engineering, University of Birmingham, Birmingham B15 2TT, U.K. *Energy Fuels*, 2006, 20 (4), pp 1418–1424.

<sup>20</sup> From BDNZ test results, published with permission.

A blend with mineral diesel tends to take on a cold temperature performance close to the weighed average of its constituents (although a blend left to settle in a stationary tank for a time at or below its cloud point may begin to stratify, and the lower, more biodiesel rich layer may exhibit filter blocking tendencies earlier than expected. Recommendations from the US industry are to maintain temperatures at 3°C above the blend's cloud point to prevent this).

It's important to check that the performance of the blend supplied matches the application. The more moderate temperatures found in the marine sector within New Zealand's coastal waters provides opportunity to use biodiesel possessing higher cloud point, to say nothing of the moderate fuel tank temperatures frequently maintained due to their proximity to the warm engine room or due to heating from the returned fuel.

## **5. Risk Management When Switching To and Using Biodiesel**

As we have seen, biodiesel does differ from mineral diesel and switching to and using it in marine diesel engines requires the user to be aware of, and to take prudent steps to address, certain issues that may arise. These steps should include:

- Quality, quality, quality! Ensure biodiesel and biodiesel blends meet relevant standards (i.e., is sourced from a reputable provider who can assure the quality of the biodiesel that they supply). While fuel available for retail sale (i.e., on a public forecourt) must be guaranteed "fit for purpose", there is no obligation on commercial supplier entering a supply contract to offer the same protection. Such assurance ought to be sought as one of the terms of the contract. Ask the supplier for evidence that their product makes the grade.
- Acquaint yourself with the terms of your engine manufacturer's warranty, and in particular, the maximum biodiesel blend proportion that they will approve. Any decision to disregard the manufacturer's recommendations will make the remaining precautions all the more important.
- Do a pre-switch engine inspection, to identify any elastomers that may be vulnerable (i.e., any components that have deteriorated or that are old and/or are made from incompatible materials).
- Observe good fuel "housekeeping" practice: take precautions to prevent water ingress (including from the atmosphere), and avoid long-term storage of fuel. Where fuel must be stored for long periods, consider taking steps to prevent degradation (i.e., depending upon the circumstances, consider fitting desiccant filtration on air breathers, and adding metal inhibitors, biocides and anti-oxidising agents) and instituting a quality testing régime.
- Change the fuel filter soon after the switch to fuel containing higher proportions of biodiesel and where the fuel system is not in new condition.
- Acquaint yourself with your engine manufacturer's recommended servicing and oil change régime, and ensure that you are not putting the equipment at risk if you deviate from it (e.g., extended oil change periods may be possible for extended,

near-continuous engine operation under moderate load, but do not do this blindly).

- Avoid using biodiesel in applications that do not suit it, especially where engines are run for prolonged periods under idle or at light loads (such as where generator sets are run continuously to provide only for the house load).

And in any assessment made, it is useful to consider the industry knowledge that has evolved, including:

- There have been no reports of problems associated with the use of B20 blends in Western Australia (from Gull stations) after over one million refuellings carried out at public fuel stations, suggesting that B20 can provide acceptable performance and compatibility for many applications.
- There are many reports of the need to replace fuel filters soon after switching to fuels containing more than 50% biodiesel, suggesting that this could be a normal course of preemptive action when switching to the use of such fuels.
- Engine problems have been found with the use of poorly processed biodiesel, even when used in blends with diesel (i.e., even when the compromise in quality has been diluted by mineral diesel). The problems found are similar to those encountered when using raw vegetable oil (the use of which is also not recommended).
- Fuel storage and handling standards are sometimes substandard, which can lead to a loss in fuel quality and put the engine at risk also.
- The risk of encountering changes in fuel properties increases as the proportion of biodiesel increases.
- The use of biodiesel better suits higher-load engine operation and users who tend to run their engines at high loads can thus afford a higher blend ratio of biodiesel.

Hence, instead of one solution, there can be many, with the final selection depending upon many factors, including: the user's understanding of the problem; the perceived risks involved; the user's ability to manage the risks; whether the user accepts the (managed) risks; the perceived benefits to be gained; and the cost involved. The specifics of the engine involved also need to be considered, and the application (duty of engine, quality of fuel, quality of servicing and support, etc.).

## **6. Advantages of Biodiesel**

Given that we've been giving the potential downside of biodiesel airtime, it's perhaps desirable to remind ourselves of the reasons for switching to biodiesel in the first place. These include:

- Because of the feedstocks and methods used, the vast majority of biodiesel available in New Zealand is a fuel option that offers a very low carbon footprint compared with mineral diesel.
- Biodiesel is less toxic to its handler and to the marine environment than mineral diesel.

- Biodiesel biodegrades more readily than mineral diesel (and may even accelerate the biodegradation of the mineral diesel component of a blend) in the event of a spill.
- In general, biodiesel emits less of the exhaust species of concern than mineral diesel.

## 7. The Position of the Engine Manufacturer

### 7.1. Advertised Compatibility

It is emphasised that this report focuses on the use of biodiesel in high-speed diesel engines only – those engines that generally run at engine speeds above 1000 rpm, and would be expected to be found in the vast majority of marine vessels of less than 50 tonnes displacement (including most coastal fishing and tourist craft). Larger vessels are more likely to be powered by medium-speed engines, which can be fitted to operate on a range of fuels including raw vegetable oil (i.e., without conversion to biodiesel). This ability is largely irrelevant when it comes to high-speed engines of the same make.

There are a number of sources of information from engine manufacturers on the compatibility of their engines with fuels containing biodiesel, including: engine manufacturer-sourced technical bulletins; engine manufacturers' websites; New Zealand representatives' websites; and various biofuel information resource sites (such as [www.biodiesel.org](http://www.biodiesel.org), the United States National Biodiesel Board).

Data on engine compatibility tends to be specific to the engine model, making that information from overseas relevant (unlike the information on some types of vehicles which can be irrelevant to New Zealand models, which may be fitted with different engines). Regardless of source, however, there can be inconsistencies. For example:

- For the most part, New Zealand representatives appear to follow the recommendations of their parent (overseas) engine manufacturer. But this is not always the case. The New Zealand agent for MAN trucks and buses, for example, states that only fuels containing up to 7% biodiesel will be accepted for its engine range designed for on-road applications – even though selected engines and applications are approved for use with B100 overseas.<sup>21</sup> Hitachi and MTU have locally accepted the use of B20 in selected engines and applications, even though their technical bulletins state that they do not accept the use of fuels containing more than 5% and 7% biodiesel respectively.
- Engine manufacturer websites may indicate acceptance of low-blend proportions of biodiesel only (i.e., up to 5% or 7%), but technical bulletins only accessible through their representatives may accept the use of B20 or higher blend proportions (e.g., Yanmar).

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<sup>21</sup> It is noted that the stance taken by the New Zealand agent for MAN arose from their reluctance to make generalised statements about the suitability of specific engines for use with B100, on the grounds that such acceptance might be misleading without sufficient qualification (with regard to fuel quality, special maintenance, etc).

- Website or technical bulletin information may refer to accepting the use of fuel meeting EN590, the European specification for diesel, which from 2009 allowed the use of fuels containing up to 7% biodiesel (up from 5%, as provided in EN590:2004). Yet many manufacturer sites that refer to EN590 still refer to a maximum of 5% biodiesel.

And hence a range exists as to what proportion of biodiesel contained in the fuel is accepted by the engine supplier for any specific application. The answer to the question: can my engine run on biodiesel? will rely on many factors, including the application, the fuel quality and local agent awareness and attitude. As a consequence, website and technical bulletin information ought to be treated more as guides on the expected local agent response rather than the definitive statement of a manufacturer's position (should engine manufacturer acceptance be required).

Table 1 (at the end of this section) is provided on this basis. It has been developed using website and technical bulletin information supplied by either the New Zealand agent or parent engine manufacturer, and is intended as a guideline only to the expected response of the local (informed) agent for the engine manufacturer. Further detail provided by various engine manufacturers or agents is listed in Appendix D.

## **7.2. Engine Warranty**

For many of those who consider switching to fuels containing biodiesel, the implications for their engine's warranty are a significant factor.

An engine manufacturer's warranty is normally limited to making good "defects in material or factory workmanship". Fuel-related engine damage, should this occur, would not ordinarily be considered the result of defects in material or workmanship, and wouldn't be covered in the ordinary run of things. This is the case for any fuel used, including the use of straight mineral diesel.

An exception to this rule of thumb can be made where although the fuel used can be proven to meet the engine manufacturer's recommended specification, a fault nevertheless occurs in normal engine service – suggesting that the engine build or design was at fault. Otherwise, the risk associated with the use of poorly performing fuels falls upon either the fuel supplier or the end user.

The risk falls on the fuel supplier if they are contracted to provide a fuel that is fit for purpose (noting that the Consumer Guarantees Act doesn't always apply for business-to-business transactions: this relieves the fuel supplier of any fit-for-purpose requirement unless it is explicitly stipulated in the fuel supply contract) or they do not meet their quality-related obligations.<sup>22</sup>

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<sup>22</sup> Ministry of Economic Development, personal communication.

The risk falls on the end-user if they decide to go ahead and use a fuel in the absence of supplier quality or fit-for-purpose assurances, or where the fuel has altered in quality since receiving it from the fuel provider.

As a rough guide to the protection that exists for the end-user in this regard:

- Engine manufacturers will provide fuel quality specification guidelines and recommendations on how an engine should be operated;
- Regulations stipulate the minimum quality specifications that a fuel must meet (currently the Engine Fuel Specification Regulations 2008, in the case of New Zealand), and these have been developed with input from the engine manufacturers (among others);
- The fuel supplier may provide information on or assistance with the correct handling and storage of fuel. They may also use additives or take other steps to reduce the risk of fuel degradation in the field (i.e., measures over and above those required to solely meet the regulated specifications at the time of sale).

The comfort factor to an end-user who stays within the engine warranty requirements where there are also robust fuel supplier obligations is that the responsibility to make good in the event of engine damage should ordinarily fall on one of these two providers (although, as anyone who has sought reparation for a “diesel bug”<sup>23</sup> failure will attest, this does not necessarily mean a fast resolution).

Some engine manufacturers claim that their warranty is totally void if the fuel used does not meet their recommendations. However, it appears debatable whether an engine manufacturer can write themselves out of their non-fuel related warranty obligations where the fuel is not at fault. So the combined assurance of a fuel supplier’s obligation to provide a fuel that is fit-for-intended-purpose (whether it meets the engine manufacturer’s recommendations, or not) and the normal engine manufacturer’s warranty may provide a similar protection for the end-user (i.e., with the obligation for a fault to be made good by either the fuel supplier or the engine manufacturer).

Of course, an engine manufacturer’s obligations expire after the designated warranty period, whereas a fuel supplier’s obligation to provide fit-for-intended-purpose fuel continues. Whether a fuel supply company has the expertise and capacity to provide and back up such obligations (in terms of sufficient technical understanding through to the means to write-down liabilities incurred) is another subject altogether.

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<sup>23</sup> See Appendix C for further information on diesel bug.

<b>Engine Make</b>	<b>New Zealand Contact</b>	<b>Biodiesel Acceptance and Comments</b>
Caterpillar	Goughs.	Accept up to B5 across engine range, up to B30 in specific engine models. Recognises some may use higher proportion of biodiesel again. Recommends use of S-O-S Service Oil Analysis.
Cummins	Cummins New Zealand Ltd.	Accept up to B7 across engine range, up to B20 in specific, later engine models.
Detroit	Transdiesel, Christchurch.	Accept up to B5 across engine range (but may accept B7 due to reference to EN590).
Deutz	Deutz Australia Pty Ltd.	Accept up to B20 for specific engine models if biodiesel meets ATSM specification. Up to B100 for specific engine models if biodiesel meets EN14214.
Hitachi	CablePrice (NZ) Limited.	Acceptance of up to B5 advertised but the use of B20 has been accepted in a specific industrial application in New Zealand.
Isuzu	Isuzu NZ.	Accept up to 5% biodiesel. Will accept up to B10 for specific model 2012 engines. Recently accepted the use of B20 in specific on-road engines in the US (and may be engines specific to US).
JCB Dieselmax	Whiting Power Systems, Auckland.	Accept the use of up to B5 across engine range and accept the use of up to B20 in engines supplied from January 2007.
John Deere	John Deere Limited, Australia.	Prefers the use of up to B5, but up to B100 can be used in all engines if fuel meets EN14214.
Kubota	C B Norwood Distributors Limited.	Accepts the use of up to B5 across engine range. Up to B20 can also be used.
Lister-Petter	Lister-Petter Oceania.	Accept the use of up to B20 across engine range.
Lombardini Marine	Transdiesel, Christchurch.	Accept the use of up to B30 for specific engine models.
MAN	Whiting Power Systems, Auckland.	The use of B5 or B7 accepted across the engine range. Information from overseas suggests some models can operate on B100.
Mitsubishi	Mitsubishi New Zealand.	Accept the use of up to B5.
MTU	Transdiesel, Christchurch.	Accept the use of up to B7 across engine range. The use of up to B20 accepted in some specific engine models.
Niigata	Niigata, Japan.	The use of biodiesel is not accepted.
Northern Lights/Lugger	Whiting Power Systems, Auckland.	The use of biodiesel is not recommended for marine applications. If using, up to B5 is preferred and engine will tolerate up to B20.
Perkins Marine	Transdiesel, Christchurch.	The use of up to B5 accepted across the engine range. The use of up to B20 accepted for specific engines. Recommend same oil service period but shortened fuel filter service period. Recommend the use of B5 if engine used infrequently.
Scania	South Pacific Diesel Systems.	Accept the use of up to B8 across engine range. Accept the use of up to B100 in specific engine models. Recommend changing fuel filter frequently during first use after previous use on mineral diesel.
Volvo Penta	Volpower NZ Ltd, Auckland.	Accepts the use of up to B5 in compliance with EN590 (which now allows the use of up to B7). Realise that some customers may use greater proportion of biodiesel.
Wartsila	Wartsila Australia Pty Ltd (NZ Branch).	Can provide engines that are compatible with the use of B100.
Yanmar Marine	Whiting Power Systems Ltd, Auckland.	Accept the use of up to B5 across engine range. Accept the use of up to B20 in specific engines.

**Table 1: Summary Position of the Engine Manufacturers on Compatibility with Biodiesel.**



## 8. The Fate of Biodiesel in Spills in the Marine Environment.

### 8.1. Toxicity

The authoritative work on the relative toxicities to laboratory mammals and freshwater aquatic species of neat biodiesel feedstocks, uncombusted biodiesel, biodiesel blends and mineral diesel was done at the University of Idaho in the 1990s. Peterson et al<sup>24</sup> administered topical doses of test substances to rabbits, oral doses to rats, and dissolved doses in aquaria containing juvenile rainbow trout and a freshwater crustacean, *daphnia magna*. The test substances used were ‘number 2 diesel’ (Phillips 2D low-sulphur diesel), neat rape and soybean oils, methyl ester biodiesels derived from these oils, ethyl ester of rape and a range of blends of the esters with the mineral diesel. For the aquatic assays, a reference toxicant was used: for daphnia, table salt, and for rainbow trout, cadmium chloride. Concentrations were progressively increased in an attempt to produce 50% mortality (LC50), although in the event, many of the assays failed to produce 50% mortality even at very high concentrations.

In general, the skin and oral applications in mammals found both biodiesels and mineral diesel to be relatively harmless (mineral diesel was more harmful than biodiesel, but neither was without adverse effects). In the aquatic tests, mineral diesel was found to be 2.6 times more toxic than table salt to daphnia; the most toxic of the biodiesels, rapeseed methyl ester, was 6.2 times less toxic than salt, rapeseed ethyl ester was 26 times less and soybean methyl ester was 89 times less toxic. Thus, even the most toxic of the biodiesels (rapeseed methyl ester) was 16 times less toxic than mineral diesel. Soybean methyl ester was 237 times less toxic. The assays involving rainbow trout could not produce conclusions regarding toxicity as even the highest sample concentrations failed to produce sufficient mortality.

One of the most significant findings of this work was that the relative insolubility of esters had a deleterious biological effect, forming a ‘sheen’ or surface film that trapped and suffocated daphnia, and potentially produced a barrier to the dissolution of oxygen in the water beneath. Further studies<sup>25</sup> using marine rather than freshwater species arrived at broadly similar conclusions: the mortality of aquatic organisms due to biodiesels seems to be a result of their insolubility, and their tendency to form globules that impair gill function, rather than toxicity per se. Diesel, by contrast, contains many hydrocarbons – notably the highly toxic aromatics – that readily dissolve in water. Seawater studies found mineral diesel to be very much more toxic than biodiesels, and blends to vary in toxicity in direct relation to the proportion of mineral diesel they contained.

### 8.2. Biodegradation

The leading (and pioneering) studies of the relative biodegradability of neat vegetable oils, esters of vegetable oils, mineral diesel and diesel/biodiesel blends was once again

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<sup>24</sup> Peterson, C., et al, *Biodegradability, BOD5, COD and Toxicity of Biodiesel Fuels*, Chapter of University of Idaho publication, 1998, <http://www.uiweb.uidaho.edu/bioenergy/BiodieselEd/publication/04.pdf>.

<sup>25</sup> Most notably those conducted by CytoCulture International Ltd. Von Wedel [1999].

conducted at the University of Idaho in the 1990s, although their findings have been verified many times since.

Zhang et al<sup>26</sup> used two methods to measure the rate at which test samples were metabolised by microorganisms. One was to measure the rate at which CO<sub>2</sub> was generated (CO<sub>2</sub> is a by-product of the metabolism of hydrocarbons). Another (used to calibrate the first method) was to measure chemical changes using gas chromatography. Other methods have been used since.

Zhang's team tested neat rapeseed and soybean oils, methyl and ethyl esters of both oils, 'number two' mineral diesel, and a variety of blends of diesel and biodiesel. The control substance used was dextrose (a simple, readily metabolised sugar).

Broadly speaking, biodiesels were found to biodegrade very quickly — such that up to 85% of the test sample was mineralised after 28 days, the same rate as dextrose — and more quickly than either neat vegetable oils (of which the average mineralisation after 28 days was 75%) or mineral diesel (of which 26% was mineralised in the same period). Gas chromatography found that the primary degradation of the esters occurred well in advance of their complete mineralisation: indeed, little or none of the original fatty acid could be detected after two days.

The reason given for the faster biodegradability of biodiesel than mineral diesel is that the chemical reactions involved in metabolism are catalytic. If the enzymes (which perform as catalysts) are already present in the cells, there is no barrier to metabolism. Since the fatty acids that comprise biodiesel are naturally occurring substances, corresponding enzymes already exist. Ethyl and methyl ester biodiesels comprise mainly even hydrocarbon chains with two oxygen atoms attached, which makes them “biologically active”. The alkanes and alkenes comprising the bulk of mineral diesel are biologically inert (although they can be metabolised: microorganisms must manufacture suitable enzymes, as they don't occur naturally). Other fractions (such as those containing benzene rings) require a high input of energy from the metabolising organism. Still others are toxic.<sup>27</sup>

One consistent finding of biodegradability studies of diesel, biodiesels and blends thereof is that biodiesel blends are degraded very much faster (up to three times faster for a 50/50 blend) than diesel alone. It has been speculated that the reason for this is that microorganisms use the readily metabolised fatty acids from the biodiesel component of the blend as an energy source with which to accomplish the energy-intensive operations required to metabolise mineral diesel. So striking is the co-metabolism effect that at least one company has brought to market a product for treating spills of mineral diesel that is, in effect, biodiesel.

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<sup>26</sup> Zhang, X., et al: *Biodegradability of Biodiesel in the Aquatic Environment*, Transactions of the ASABE. VOL. 41(5): 1423-1430, 1998.

<sup>27</sup> Prince, R., *The Primary Aerobic Biodegradation of Biodiesel B20*, *Cheosphere*, Volume: 71, Issue: 8, Pages: 1446-1451. 2008.

The caveat to this is that biodiesel is insoluble in water and tends to form a relatively impermeable film on the surface of water, or suspended globules that can inhibit gaseous exchange in aquatic organisms. While not strictly a toxic effect, this is a harmful property of biodiesel that would need to be addressed in the event of a large spill of biodiesel or biodiesel/diesel blends. A suitable emulsifier, such as a detergent, ought to be promptly used to treat such a spill.

## **Appendix A: Fuel Properties of Biodiesel.**

This appendix considers the fuel-related properties of biodiesel. Consideration is first given to those properties deemed sufficiently important that they are specified in fuel quality regulations, by which time the specifications would have been debated and generally accepted by the fuel producers, distributors and engine manufacturers.

Beginning with the specifications for biodiesel, in the order in which they are listed in the Engine Fuel Specification Regulations 2008 (the current regulations that govern the quality of engine fuels in New Zealand), these properties are:

### **A1.Ester content:**

Methyl esters are the desired product of the transesterification reaction used to produce biodiesel. A minimum of 96.5% ester is required as indicated by the standard test method. This provides a check on the completeness of conversion from the feedstock oil or fat, and also a check for other contaminants.

The ester content of biodiesel is stable once it is produced and finished, unless the fuel is subject to significant degradation. And if this should occur, then it would be expected to exhibit other, more obvious characteristics such as haziness and visible contamination and sludges.

### **A2.Density:**

The term “density”, without further qualification, is normally taken as a measure of the fuel’s mass per unit volume. Biodiesel derived from used cooking oil, the main feedstock used to produce biodiesel commercially in New Zealand, has a density of around 884 kg per m<sup>3</sup> (at 15°C), greater than for mineral diesel, which typically ranges from around 825 kg per m<sup>3</sup> (at 15°C) in winter to around 845 kg per m<sup>3</sup> (at 15°C) in summer.

Due to this difference in density, if biodiesel were carefully poured into a tank of mineral diesel it would tend to fall to create a biodiesel-rich fuel mixture at the bottom of the tank, which would be relatively stable in a stationary tank. However, the motion of a mobile tank has been found to quickly mix the fuels (which are inherently miscible due to their sufficiently common hydrocarbon component, and mixing in a mobile tank a method somewhat relied on when such “splash blending” is used to produce biodiesel-mineral diesel blends – unlike James Bond, shaken is better than (quietly) stirred when it comes to blending).

Density is a useful indicator where the fuel is made up of little other than hydrogen and carbon, as is the case for mineral diesel, as density then becomes a good indicator of energy density as well. However, biodiesel also contains a significant proportion of oxygen, which does not combust and release energy, and the presence of this oxygen lowers the energy per unit mass of substance compared with mineral diesel.

Of more importance again is the volumetric energy density – the fuel’s energy per unit volume – as the vast majority of engines meter the fuel volumetrically and a decrease in

volumetric energy density is expected to result in a decrease in engine power, all else being equal. For biodiesel, with a volumetric energy density that is 6% lower than that of mineral diesel, the peak engine output is also expected to be lower by around the same amount (i.e., around 6%). But there are many other variables involved,<sup>28</sup> and in practice the differences found have been often reported as small to insignificant, even for the use of B100.<sup>29</sup>

The theoretical difference in energy density for a B20 blend is around 1%, smaller than the difference expected switching between summer and winter grades of mineral diesel.

The energy density of biodiesel is not expected to change significantly, even with fuel ageing.

### **A3. Viscosity:**

Viscosity is a measure of the fuel's resistance to flow. Biodiesel has slightly higher viscosity than mineral diesel. This is expected to result in slightly higher peak injection pressures with the use of biodiesel in older-style fuel injection systems, and slightly lower fuel delivery rates in some common rail<sup>30</sup> fuel injection systems. The practical differences that result from differences in viscosity are expected to be small under normal fuel operating temperatures.

One benefit of slightly increased viscosity is a decrease in the leakage of fuel to the lubricating oil in certain pump types.<sup>31</sup>

For biodiesel, the viscosity may increase with fuel degradation, but other factors, such as the corrosiveness of the fuel (should degradation occur), are of more concern.

### **A4. Flashpoint:**

Flashpoint provides an indication of the flammability of a substance and is often considered to assess the risks in the case of a spill. The high values normally found for biodiesel indicate that biodiesel is safer than diesel, in this regard.

The difference in flashpoint is not expected to significantly alter how biodiesel combusts in an engine, under normal engine operating conditions.

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<sup>28</sup> For example, an advance in the start of ignition found with some engines when using biodiesel can cause a small increase in power, partially compensating for the loss due to different volumetric energy density. Subtle changes in the torque curve can also give the impression of higher power, when none is actually present. Engine dynamometer tests remove this perception element and have generally found a small decrease in peak power. Roy, MM, *Performance and Emissions of a Diesel Engine Fueled by Diesel-biodiesel Blends with Special Attention to Exhaust Odor*, Canadian Journal on Mechanical Sciences and Engineering Vol. 2, No. 1, January 2011.

<sup>29</sup> A1 Movers, Auckland, and others, personal communication.

<sup>30</sup> A common rail system injects fuel from a rail that contains fuel at very high pressure and is also common to all injectors.

<sup>31</sup> For example, in in-line, jerk-type pumps, the cam lobes and main bearings of which are normally lubricated by the engine oil.

Flashpoint is also a check of the production process – a low flashpoint indicates the probable presence of methanol in amounts greater than the specification allows.

**A5.Sulphur content:**

The presence of sulphur can degrade some catalysts used in exhaust systems. Biodiesel and diesel share the same maximum sulphur content limit of 10 ppm. Modern diesels and biodiesel normally meet this specification by a good margin.

**A6.Carbon residue:**

The carbon residue number is an indicator of the amount of carbonaceous residue that may be left after a fuel's combustion. This is reported by Mittelbach as one of the most important biodiesel quality criteria, as higher results are linked to the presence of many undesirable residues. Results from a number of biodiesel producers in New Zealand indicate that this specification is also easily met.

The quality of mineral diesel is controlled with a near-equivalent test and same limit value.

**A7.Cetane number:**

Cetane number is an indicator of ignition and combustion quality, with higher numbers indicating a reduced ignition delay (the period between the injection of fuel into the combustion chamber and notable ignition of that fuel). Shorter ignition delay – and higher cetane numbers – tend to be preferred, up to a point. Because of their different chemistry, and the different pre-ignition and ignition reactions involved, it is difficult to directly compare the cetane numbers for biodiesel and mineral diesel. It's perhaps more useful to simply note that biodiesel has a higher cetane number than for mineral diesel, indicating that it should exhibit overall improved ignition properties with the engine under load.

Cetane number is not expected to deteriorate with fuel ageing; in fact, an increase in cetane is more likely, due to the formation of peroxides as some of the products of degradation.

**A8.Ash content:**

Ash is formed by the oxidation of inorganic contaminants in the fuel (and from the combustion of any inorganics from the lubricating oil that become entrained in the combustion air). The resulting ash can deposit in the combustion chamber and exhaust system, or can form abrasive particles in the lubricating oil. Ash content must therefore be kept low. Results from producers in New Zealand indicate that this specification tends to be easily met.

In a marine environment, there is a risk that ash content could become elevated by contamination of the fuel by salt water, the salts in the water yielding ashing material. This is yet another reason to avoid the ingress of water.

### **A9. Water Content:**

Water can be absorbed by biodiesel up until what is termed the saturation point. Any more water added after the saturation point remains as “free water”. The presence of free water can cause cavitation in diesel pumps, provide the conditions for rapid corrosion to occur, and for microbial growth (and associated microbial degradation of fuel, leading to sludge formation, etc.). It is important to avoid the presence of free water in the fuel.

Biodiesel’s specification of a maximum of 500 ppm water provides a reasonable margin for additional water uptake before the saturation point is reached – allowing for the absorption of around 30 ml (2 tablespoons) of water for a 50 litre vehicle fuel tank – sufficient to keep fuel systems “dry” under normal automotive conditions, but not necessarily sufficient where housekeeping is poor or where designs do not adequately protect the fuel systems from water ingress.

A common example of an inadequate design is the use of a simple U-tube fuel tank breather in marine applications, where the opening is open to the deck and not well protected from wave action. Such an arrangement provides a heightened risk of water ingress.

Biodiesel is also hygroscopic<sup>32</sup> and will absorb water from the atmosphere if left in open or simply vented tanks – a compelling reason to consider the residence time in such simple tanks, as longer residence times provide a greater opportunity for saturation levels to be reached. At that stage, a reduction in temperature can cause water to fall out of the fuel and form free water (because lower amounts of water can be absorbed by fuel at lower temperatures).

It’s common to fit water trap filters in the fuel lines supplying engines in commercial marine applications. These are expected to remove a very high proportion of any free water present. But these systems do not protect the engine against the products of fuel degradation – organic acids among others, that can pass through even the finest filters – and once at the engine, these degradation products can damage fuel injection components through corrosion or deposit and sludge build-up.

Modern engines are far more susceptible than older engines in this regard, because their fuel injection components are made to more exacting tolerances and are more vulnerable to corrosion and buildup. This is an important point, as there is anecdotal evidence to indicate that there are many cases of microbial degradation of fuel each year in the marine sector<sup>33</sup> for use of mineral diesel, but because older engines were involved, many of these occurrences came to nothing. The number of modern engines in use in the marine sector will increase over time and so will such failures unless fuel housekeeping also improves: fitting a water-trap filter is no longer sufficient to guard the engine. A similar warning is given for land-based applications.

The defences against engine damage by such fuel degradation include:

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<sup>32</sup> Attracts water.

<sup>33</sup> Discussion with various commercial fishers.

- Assuring that delivered fuel meets the quality requirements.
- Checking the main tanks for the presence of water.
- Avoiding the ingress of water. This may require tank breathers to be modified.
- Using a biocide to suppress growth, where water is found to be present. Care is required, as some biocides contain elements that aid microbial growth and may actually promote microbial growth when used in low dosage rates.

The specification limit for water in mineral diesel is 200 ppm, the lower value reflecting the lower amount of water that can be absorbed by the diesel before saturation point is reached. What's more, mineral diesel doesn't show strong hygroscopic tendencies.

#### **A10. Total Contamination:**

Total contamination is an indication of the level of fuel-insoluble material in the fuel, determined from the weight of material remaining after passing heated fuel through a fine filter. Failure to meet this specification is a sign of poor housekeeping or, in the case of biodiesel, contamination of the feedstock or poor production process control.

The test method and permitted limit are the same for biodiesel and mineral diesel.

There are many opportunities for fuel to become contaminated after delivery and engines are protected from this by fuel filters, normally placed immediately before the main fuel pump.

The contamination caused by microbial growth has already been mentioned.

One particularly relevant characteristic of biodiesel is that it exhibits greater solvent properties than mineral diesel and when the biodiesel proportion of a blend is sufficiently high for this property to assert itself, it can result in the loosening of dirt and deposits from fuel tanks, lines and other fuel components. The loosened material then becomes entrained in the fuel. An engine's standard fuel filter is expected (and specified) to prevent this type of material from damaging the engine, but it may require replacement soon after the first switch to fuels of higher biodiesel content. Some commercial road transport operators have also added a pre-filter to provide added convenience and protection.

#### **A11. Copper strip corrosion:**

The copper strip corrosion test is an indicator of the tendency of a fuel sample to cause corrosion to copper, zinc and bronze parts and is normally easily met for biodiesel.

Of more concern in the marine context are the biodiesel degradation reactions that may be catalysed<sup>34</sup> by the presence of such "yellow" metals, given the relatively prevalent use of such metals (for example, copper fuel lines are frequently used due to their good resistance to corrosion in the marine environment). "Metal inhibiting" additives are sometimes used to counter this risk. Additives used to promote oxidation stability (see

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<sup>34</sup> Metals such as copper can act as catalysts, causing reactions to occur at greater rates than had they been absent.



below) are also expected to suppress the degradation reactions but in a less-effective manner.

#### **A12. Oxidation stability:**

A fuel has to be sufficiently stable in storage, handling and use in an engine that it does not degrade before it is injected into the combustion chamber – the products of degradation threatening damage to the engine. Yet a hydrocarbon is expected to undergo reactions once provided with heat and oxygen: – after all, it is expected to combust in the combustion chamber of an engine.

Some hydrocarbons are sufficiently unstable that they will undergo reactions at ambient temperatures. An example is linseed oil, which at one time was a common base for paints and would harden (“dry”) with exposure to oxygen (in the air), and harden more quickly with exposure to oxygen and higher temperatures. Biodiesel has chemical similarities to linseed oil (and therefore similar reaction tendencies), and use in an engine exposes it to oxygen and elevated temperatures – which is why there has been much research into developing tests aimed at providing an indication of the “thermal-oxidation” stability of biodiesel, in order to provide an indication as to whether it is fit for use in an engine.

The thermal-oxidation test for indicating “oxidation stability”<sup>35</sup> of biodiesel currently referred to in both the European standard and the New Zealand regulations is the Rancimat test, which originated in the food industry. The Rancimat test involves bubbling air through a sample held at 110°C and noting the time it takes for an observable change in the amount of acids produced (from the degradation of the sample). A minimum “induction” time of 6 or 10 hours is required depending upon the regulations and end use of the biodiesel. In the case of biodiesel derived from common feedstocks, achieving these induction times normally requires the use of additives.

The number is somewhat arbitrary – there is no direct correlation with the number and how the fuel may degrade in an engine application – but it is still the only stability indicator that has generally wide acceptance in the industry,<sup>36</sup> and it does serve the purpose of demanding that a fuel exhibits a minimum resistance to degradation.

The oxidation stability of biodiesel also decreases with time,<sup>37</sup> and is expected to decrease more rapidly in hostile storage conditions. Hence the oxidation stability can be seen as a buffer to the onset of serious degradation. And the marine environment can see cases of 6-monthly refuelling, significant use of yellow metals in the fuel system, and the risk of fuel contamination by water, all of which would test this stability “buffer”. The options to manage the consequent risk include:

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<sup>35</sup> The specification referred to by the standard is “oxidation stability” even though a thermal-oxidation test is used.

<sup>36</sup> Mittelbach et al. Biodiesel, The Comprehensive Handbook, Publisher: Martin Mittelbach, 2006 ISBN: 3-200-00249-2

<sup>37</sup> Tang, H., et al, *The Oxidative Stability of Biodiesel: Effects of FAME Composition and Antioxidant*, Lipid Technology, Volume 20, Issue 11, pages 249–252, November 2008

1. Keeping the fuel fresh through receiving fresh fuel and maintaining frequent (less than 3-monthly) turnover.
2. Ensuring any fuel storage tank is clean, free of water, protected from the elements or the sun<sup>38</sup> and from any contaminants, including water.
3. Beginning with a fuel with a high oxidation stability “buffer” in the first place. This may call for an oxidation stability of up to 20 hours in the more extreme applications<sup>39</sup>.

Mineral diesel is relatively stable by comparison, and although it is still tested for oxidation stability, a different test method is used.<sup>40</sup> Blends of biodiesel and mineral diesel appear to exhibit stability pro rata to the proportion of biodiesel.

#### **A13. Acid value:**

Acid value, also referred to as Total Acid Number (TAN), is intended as a check of the manufacturing process for biodiesel – to identify whether the finished product contains acidic properties which may cause corrosion. A simplified method can be used to check for post-production degradation of fuel, as organic acids are among the early products of the degradation of biodiesel. This is hardly a back-yard mechanic-type test, but could prove useful for fuel distributors and the odd enthusiast.

#### **A14. Methanol, glyceride and glycerol content:**

These fuel quality specifications provide checks on the production process. The presence of methanol (i.e., the excess not sufficiently removed after processing) lowers the flashpoint and lubricity. The presence of glycerides and glycerol risks the build-up of deposits on the injectors, with the follow-on risk that these deposits may interfere with the atomisation of the fuel (and in turn lead to fuel dilution of the lubrication oil, and even damage to the engine).

#### **A15. Metals:**

Biodiesel is checked for its content of the metals sodium, potassium, calcium and magnesium, to limit the carry-over of these metals from the production process.

#### **A16. Phosphorus:**

Some feedstocks used for making biodiesel contain amounts of phosphorus that could damage the catalysts used in advanced exhaust after-treatment devices and the specification limits the amount of phosphorus permitted to contamination levels. Engines used in marine applications are unlikely to be fitted with exhaust catalysts and therefore this quality requirement is of little consequence for the marine sector for normal fuel sources.

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<sup>38</sup> Exposure to the sun can result in a marked increase in diurnal temperature changes, and result in increase tank breathing, risking higher water ingress unless the tank is protected from this.

<sup>39</sup> Based on possible oxidation stability degradation rates given by Tang et al.

<sup>40</sup> Mittelbach et al. Biodiesel, The Comprehensive Handbook, Publisher: Martin Mittelbach, 2006 ISBN: 3-200-00249-2.

### **A17. Additional properties:**

The EFSR 2008 specifies that diesel offered for retail sale (i.e., on the public forecourt) may contain up to 5% biodiesel and must be fit for common purposes – there is therefore an onus on the part of the fuel supplier to ensure that the fuel will operate without fault under the conditions that may be experienced in common use. Blends of biodiesel above a B5 level are available for non-retail sale (i.e., they are sold under a contract). Regulations do not require fuel sold under contract to be fit for purpose, although it seems an obvious “catch-all-other” specification for the receiver to demand in order to avoid unforeseen quality issues.

The greatest risk, for a B5 blend, is the possibility of crystallisation of some fractions of the biodiesel at low temperatures which, if severe, can result in filter blocking. The risk is greatest where tallow- and palm-derived biodiesels are used. Some that otherwise meet the EFSR 2008 specification show filter-blocking tendencies at temperatures of around 14°C when in neat form<sup>41</sup> – sufficient to block fuel filters if the fuel is left to “soak” at ambient temperatures found in many New Zealand locations even in summer. In general, however, fuel temperatures in the marine environment tend to be moderated by the thermal inertia of the surrounding water and filter-blocking with a B5 blend is not expected, even where tallow-derived biodiesel is used. As has been mentioned elsewhere in this report, biodiesel derived predominantly from used cooking oil (the biodiesel most commonly used in New Zealand), by comparison, typically has a “cold filter plugging point” (CFPP<sup>42</sup>) of around –6°C<sup>43</sup>, meaning that you would not expect crystallisation-related filter blocking problems to occur until the temperature of the fuel approaches this value. Sub-zero fuel temperatures would be unusual for a New Zealand marine application.

### **A18. Volatility:**

Diesel is a mixture of many different hydrocarbons with quite different boiling points – if you were to gradually raise the temperature of a diesel sample in an open beaker, you would expect the weight of that sample to steadily decrease, weight loss by temperature increase, between around 160°C and 340°C. The vast majority of the sample would have evaporated by the time 340°C had been reached.<sup>44</sup>

If the same experiment were conducted with biodiesel, little would evaporate from the beaker right up until the temperature reached around 340°C.<sup>45</sup>

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<sup>41</sup> Testing carried out by Fuel Technology for a New Zealand client, noting that some poor quality tallow-derived biodiesels exhibited filter blocking tendencies at higher temperatures. Results provided with permission.

<sup>42</sup> CFPP is defined by a number of test methods including ASTM D6371, IP309 and CEN EN116, and as its name suggests, it provides an indication of the temperature around which filter blocking may occur.

<sup>43</sup> Typical results for BDNZ B100, derived from mainly used cooking oil, used with permission.

<sup>44</sup> Based on results provided in Lane, J.C. In Kirk-Othmer, *Encyclopedia of Chemical Technology*; Third Ed.; John Wiley & Sons: New York, NY, 1980, Vol. 11; pp. 682-689.

<sup>45</sup> Based on the boiling point of the main esters involved, *Handbook of Chemistry and Physics*, 61<sup>st</sup> Edition, CRC Press.

What's more, biodiesel has a slightly greater heat of vaporisation than mineral diesel,<sup>46</sup> greater surface tension,<sup>47</sup> and greater density, which together with the decreased volatility, serve to increase the proportion of fuel that survives the evaporation and combustion processes that take place during the combustion stroke. Surviving fuel can be entrained back into the combustion gases, to be expelled on the exhaust stroke (with possible implications for the after-treatment of exhaust gases), or may impinge upon the cylinder walls (possibly causing localised dilution of the lubrication oil) and eventually mix with the lubricating oil. The last results in undesirable fuel dilution of the engine's lubricating oil.

And lower volatility results in lower evaporation losses from the lubrication oil once the biodiesel is there. The overall result is a higher degree of fuel dilution of the lubrication oil when biodiesel fuels are used, which has been measured even for the use of blends with biodiesel proportions as low as B20.<sup>48</sup>

The dilution rate of engine oil is expected to increase as the proportion of biodiesel increases, as engine load decreases, and as engine temperature decreases – idling after a cold start presents some of the most favourable conditions for the dilution of engine oil. Some advanced engine designs may also use late or supplementary injection of fuel as part of their emissions control mechanism (but these will unlikely be found in use in the marine sector). These designs are also more susceptible to dilution of lubricating oil by fuel.

With viscosity a fraction that of lubrication oil, the presence of fuel in the lubrication oil will significantly reduce lubricity of the oil, initially, at least, and increase the risk of engine damage. Goughs, one of several engine oil test laboratories in New Zealand, uses a combination of flashpoint and viscosity to estimate the amount of fuel dilution of lubricating oil<sup>49</sup>. Caterpillar recommends a maximum of 4% fuel dilution (at which time the lubrication oil should be changed).

Engine manufacturers have responded to the heightened risk of lubrication oil dilution by recommending more frequent oil change periods with the use of biodiesel. This doesn't take engine operation into consideration, meaning that there is some opportunity for a more tailored approach in specific applications. And the marine sector does see some extremes in this regard, ranging from relatively low-risk main propulsion engines operating under high load for a high proportion of the time, through to high-risk generator sets, that may operate at high speed and under little or no load for the majority of time.

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<sup>46</sup> Valeri I et. Al., *The Construction Of The Combustion Models For RME Bio-Diesel Fuel For ICE Application*, [http://publications.lib.chalmers.se/records/fulltext/local\\_88943.pdf](http://publications.lib.chalmers.se/records/fulltext/local_88943.pdf)

<sup>47</sup> idem

<sup>48</sup> Jääskeläinen, H., *Compatibility of Biodiesel with Petroleum Diesel Engines*, Dieselnet publication, [http://www.dieselnet.com/tech/fuel\\_biodiesel\\_comp.html](http://www.dieselnet.com/tech/fuel_biodiesel_comp.html)

<sup>49</sup> Micheal Hooper, Manager, Goughs Oil Analysis Laboratory, personal communication.

In theory, it is also possible to monitor the oil and only replace it when necessary. However, lubrication oil containing biodiesel has also been found to become more viscous over time<sup>50</sup> which renders the traditional, low-cost tests for estimating lubricating oil dilution unreliable and therefore unsatisfactory for this purpose.

#### **A19. Lubricity as a fuel**

The fuel in a compression-ignition engine acts as the lubricant for many fuel injection components and must therefore exhibit sufficient lubricity to prevent wear and deterioration of the performance of the fuel injection system. Biodiesel has been found to exhibit better lubricity properties than modern diesel fuels<sup>51</sup>, and has sometimes been considered as an additive specifically to improve the lubricity of mineral diesel.

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<sup>50</sup> Jääskeläinen, H., *Compatibility of Biodiesel with Petroleum Diesel Engines*, Dieselnet publication, [http://www.dieselnet.com/tech/fuel\\_biodiesel\\_comp.html](http://www.dieselnet.com/tech/fuel_biodiesel_comp.html)

<sup>51</sup> Knothe, G., et al. *Lubricity of Components of Biodiesel and Petrodiesel. The Origin of Biodiesel Lubricity.*, Energy Fuels, 2005, 19 (3), pp 1192–1200, DOI: 10.1021/ef049684c.

## **Appendix B: Defining Compatibility and Differences in Opinion that May Result**

### **Defining compatibility**

For the purposes of this report, a “compatible” fuel is one that won’t cause any “significant degradation” to the integrity of any component of an engine system (there may, of course, still be a difference in opinion over what is considered to be “significant degradation”). And for present purposes, “compatibility” doesn’t consider the performance output of the engine (e.g., power or emissions), unless any performance change produced is sufficient to compromise the mechanical integrity of any engine component.

At proportions of up to 5% biodiesel blended with mineral diesel (the proportion permissible for retail sale<sup>52</sup> in New Zealand without the need to give notice that the fuel contains biodiesel), the influence of any differences in the chemical nature of the biodiesel component is expected to be insignificant – and no compatibility issues or significant change in performance compared with the use of straight diesel is expected to arise. For this reason, virtually all New Zealand representatives of the various engine manufacturers accept the use of up to 5% biodiesel – or, in the case of some European-origin manufacturers, who follow the specification for diesel in Europe, up to 7% biodiesel for retail sales.

As the proportion of biodiesel in a blend increases, the blend takes on more of the characteristics of the biodiesel component. And given that some materials used in some past and current engine builds suffer in the presence of 100% biodiesel, the risk of problems occurring when fuels containing biodiesel are used rises accordingly, if:

1. The incompatible materials are present and make contact with the fuel;
2. The proportion of biodiesel in the fuel is sufficiently high for the different chemical characteristics of the biodiesel to be exhibited; and
3. The change in performance of the material actually leads to compromise.

As an example, consider the use of an o-ring in a fuel system assembly (although the same arguments could be used for any engine component made from elastomers – flexible materials – such as hoses, lip-seals and other fuel system components). These flexible materials tend to some extent (and the extent varies) to absorb the various hydrocarbons that make up the fuel. For a specific o-ring material, some hydrocarbons are absorbed more than others and, as these materials tend to swell as more hydrocarbon is absorbed, different o-rings may grow to an extent that depends on the composition of the fuel.

Due to material selection, this growth is usually not significant and the function of the o-ring – to make a seal – is not compromised. However, some o-ring materials still in use have been found to be affected to a greater extent when biodiesel fuels are used. And for

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<sup>52</sup> That is, sold at public forecourts.

some of these materials, swelling of the o-ring may occasionally prevent reassembly – it simply can't be pushed back into the same groove from which it was removed.

To elaborate on this point:

1. The flexible materials used in the manufacture of fuel components have had to evolve with changes in fuel formulation. Natural rubber in fuel systems has become a thing of the past, as has the use of some earlier synthetic replacements, due to their incompatibility with modern fuels. The materials now specified for use with modern diesel formulations also tend to be compatible with biodiesel.
2. It can, however, be difficult for some manufacturers to identify exactly which materials were used in past engine builds (the engine “manufacturer” can be merely the last assembler in a long, compounding assembly chain), which introduces uncertainty. Modern parts tracking practices and specific material selection will resolve this.
3. Should an incompatibility be found with the use of a blend, there is no specific proportion of biodiesel at which this might occur (i.e., when the different characteristics of biodiesel suddenly assert themselves). The changes involved are more likely to be incremental and simply reach a stage at some point where they become noticeable, or even significant, and there are other factors such as the age, condition and exact formulation of the material that can also come to bear.
4. The engine manufacturer may view any *risk* of variation in o-ring growth as an incompatibility, due to their potential liability for remediation costs. But it should be noted that some o-ring growth can be found with the use of straight diesel; the difference is that since there is a wealth of experience with the amounts of growth and their significance, this tends to be regarded as acceptable. The approach to biodiesel is unlikely to be so lenient until the extent of its effects are known and quantified.
5. End-users may be less wary of effects such as the swelling of o-rings than manufacturers. Once aware of a potential problem, they may be happy simply to replace an o-ring (for example) when servicing is necessary, and will not experience any compromise in the performance of the component (or the engine) before or after the service.

### **Difference in Opinion**

The foregoing shows how there can be differences in opinion on the perceived *level of compatibility* (i.e., what is and what is not considered to be a significant change in how a material or component performs), and on the *level of acceptability* (depending upon the person providing or considering that opinion). While there is a range of such opinions amongst different groups, including manufacturers, end-users, mechanics and so on, it's possible to generalise about them (based on past discussions with the various groups):

#### ***Engine manufacturers:***

- Engine manufacturers have a great deal at stake when considering whether to approve biodiesel and its blends for use in their products. They seek to serve their clients well, and any failure in their duty of care leaves them liable to both

financial losses and to damage to their reputation. They will naturally demand a very high degree of assurance that the use of biodiesel fuels will not compromise the function or level of service (including durability) of the engine.

- They are, however, responsive to the market, and will shift their position if there is sufficient demand or competitive advantage in doing so, and if it is technically feasible. Market demand, for example, has led many manufacturers to accept the use of B20 and fuels of even higher biodiesel content.
- In the New Zealand context, manufacturers will tend to provide their expert opinion and recommendations through their representatives. Some representatives, however, may not be as well informed as others. Some may not accept the use of the higher biodiesel blend ratios the same engine manufacturer will accept in other countries<sup>53</sup>. For specific applications, some representatives may secure approval for the use of blends containing higher biodiesel proportions than those normally recommended by the engine manufacturer<sup>54</sup>.

***The uninformed user:***

- Will look to the engine manufacturer for expert advice, and work strictly to the recommendations provided by them (including working to the interpretation offered by the engine manufacturer's local representative).

***The mainstream early adopter:***

- Will consider information from various sources including from the engine manufacturer, the fuel provider, their mechanic, web-based material and opinion, the experience of others (for example, looking for similar vehicle models in lists of those already operating on the target fuel blend), etc.
- Is more likely to switch when an engine is out of warranty (and the potential voiding of warranty is not a concern. This is further discussed below).
- Perceives benefits in using biodiesel fuels which are greater than or at least offset the perceived risks.

***Informed user:***

Similar to the *mainstream early adopter*, but takes the level of understanding of the risks and benefits to far greater depth, resulting in a well-informed assessment. Of course, the scale of the task of becoming well informed in this area should not be underestimated. An engine presents a very complex application involving high temperatures and very high pressures, very tight tolerances (especially when it comes to modern-day diesel injection equipment), complex interactions, together with a large range of conditions in which the engine is used, a wide variation in the way the engine is operated, and occasionally the use of degraded fuel. Deciding between different fuel options requires genuine expertise in the field in order to make a truly informed decision.

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<sup>53</sup> This is despite using same engine models.

<sup>54</sup> As demonstrated by MTU and Hitachi in specific applications in New Zealand.



## **Appendix C: Microbial Degradation**

Microbial degradation, caused by what is sometimes referred to as “diesel bug”, refers to the degradation caused by a range of bacteria and fungi that specialise in feeding off hydrocarbon fuels. Diesel bug is believed to affect hundreds of (mineral) diesel vehicles a year in New Zealand, and the resulting acids and other products of fuel degradation can quickly damage fuel injection components to the point where they must be replaced. And whilst a quality fuel filter may capture some of these products, this is not a defence against acids and some sludges, which will pass through them. Many in the industry argue that modern fuel injection systems are far less tolerant of the effects of diesel bug, due to their close tolerances, and that unless fuel housekeeping is improved to suit, this will lead to increased occurrences of diesel bug-related damage as the fleet modernises.

Diesel bug requires nutrients (which may come from fuel additives or from contaminated water ingested by the fuel), mild to warm temperatures, and the presence of free water in order to feed and grow – and the first defence against their growth is to avoid the presence of free water. Biodiesel can absorb a greater amount of water before free water precipitates, and this property can serve to dry out tanks that contain small amounts of water, actually reducing the risk of biological degradation. But biodiesel is also more hygroscopic in nature than mineral diesel and will attract a greater amount of water from the air above the fuel, which then leads to a greater chance of free water forming as the temperature lowers again (as lower temperature reduces the amount of water that can be absorbed by the fuel). There is a lesser risk of this occurring in marine applications where temperature variability is generally lower, but the risk is also heightened by the widespread use of simple vents on marine vessel fuel tanks.

## **Appendix D: Engine Manufacturer Information on the Compatibility of Biodiesel**

The follow lists the various responses from engine manufacturers or their representatives on the compatibility of their engines with biodiesel.

### ***Caterpillar***

*Information source: internal, Caterpillar technical bulletin.*

Use of up to 5% biodiesel accepted in a range of engine types, up to B30 in others. Advise that Caterpillar dealer should be contacted if going above this proportion. Recommend that use of “S-O-S Service Oil Analysis” in order to determine the oil drain period that is optimum.

### ***Cummins***

*Information source: Cummins website*

Various, newer (2008 and later) engine models can use up to B20. Otherwise the use of up to 7% biodiesel is accepted.<sup>55</sup>

### ***Detroit***

*Information source: Detroit Diesel Corporation Engine Requirements Brochure.*

A maximum of 5% biodiesel is accepted (despite reference to EN590, which at the date of the brochure allowed up to 7% biodiesel). Biodiesel was also required to be supplied by a BQ-9000 Accredited Producer, which is generally only relevant for producers in the United States. Detroit also only recommend fuel standing in an application for a maximum of one month.

### ***Deutz***

*Information source: Deutz AG Service Fluid Recommendation*

Specific engines are approved for the use of fuel containing up to 20% biodiesel if the biodiesel proportion meets ASTM D6751-09a, and up to 100% biodiesel if the biodiesel proportion meets EN 14214.

### ***Hitachi***

*Information source: internal, Hitachi technical bulletin.*

Use of up to 5% biodiesel accepted with fuel meeting EN590. Shortened service periods recommended (even at this level of biodiesel content). Hitachi have also approved the use of B20 in a specific industrial application.

### ***Isuzu***

*Information source: New Zealand agent plus US National Biodiesel Board (US) statement.*

The New Zealand agent states the use of up to 5% biodiesel is currently accepted and that up to B10 will be accepted for a specific model due for release in January 2012. A statement by the National Biodiesel Board (US) says that Isuzu has accepted the use of

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<sup>55</sup> [http://cumminsengines.com/every/customer/biodiesel\\_faq.page](http://cumminsengines.com/every/customer/biodiesel_faq.page)

B20 in specific engines in the US (these appear to be US-specific engine models for use in on-road applications).

**John Deere:**

*Information source: US website plus New Zealand agent*

The use of fuels containing no more than 5% biodiesel is preferred, but up to B100 can be used in all engines if the biodiesel meets EN 14214. The use of John Deere-supplied detergent/dispersant fuel additive “is required” if the biodiesel proportion is above 20%.<sup>56</sup>

**Kubota:**

*Information source: US Kubota website plus personal communication, New Zealand agent.*

One section of the Kubota US website suggests that the use of fuels containing up to 5% biodiesel only are accepted, whereas another page lists engines approved for the use of fuels containing up to 20% biodiesel.

**Lister-Petter**

*Information source: Lister-Petter UK, via New Zealand agent (Lister Petter Oceania)*

The use of fuel containing up to B20 is accepted across the engine range.

**Lombardini Marine:**

*Information source: Lombardini technical information.*

The use of fuel containing up to 30% biodiesel accepted for FOCS and CHD engines. Use of biodiesel not accepted in JMT-type engines. Warranty void if fuel-related problems occur.

**MAN**

*Information source: MAN Service Information<sup>57</sup>*

Up to B100 can be used in specific engine models (and if the biodiesel has sufficiently low phosphorus content, in the case of engines fitted with certain particulate trap devices, but these are unlikely used in the marine sector). MAN recommends the use of two tanks of diesel before the downtime of an engine for more than one month.

The New Zealand agent for MAN trucks and buses reports acceptance of the use of up to B7 only.

**Mitsubishi**

*Information source: personal communication, New Zealand agent.*

The use of fuel containing up to 5% biodiesel accepted.

**MTU**

*Information source: New Zealand Agent plus MTU service information.*

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<sup>56</sup> [http://www.deere.com/en\\_US/rg/servicesupport/faqs/biodiesel/index.html](http://www.deere.com/en_US/rg/servicesupport/faqs/biodiesel/index.html) and [http://www.deere.com/en\\_AU/equipment/power\\_systems/marine/vol\\_2\\_2010\\_powersource\\_comm.pdf](http://www.deere.com/en_AU/equipment/power_systems/marine/vol_2_2010_powersource_comm.pdf)

<sup>57</sup> [http://www.biofuelxpress.com/6storage/877/4/180911en\\_man04042009uk.pdf](http://www.biofuelxpress.com/6storage/877/4/180911en_man04042009uk.pdf)

The use of fuel containing up to 7% biodiesel accepted for all engines. Up to 20% biodiesel has been accepted for specific applications.

### ***Perkins Marine***

*Information source: Perkins Marine Product Bulletin (provided by New Zealand agent) and Perkins Marine website material.*

The use of fuel containing up to 20% biodiesel approved for specific models of marine and generator engines (these tend to be engine models built after late 2007). Otherwise the use of up to 5% biodiesel is accepted in accordance with EN590 (which at the date of the Product Bulletin allowed a maximum of 5% biodiesel in diesel). Recommendations provided include the same oil service period but halved fuel filter replacement periods. The use of fuel containing a maximum of 5% was recommended if the engine was infrequently used.

### ***Scania***

*Information source: internal Scania technical information.*

The use of up to 8% biodiesel accepted for all engines. Some specific engine models can use up to 100% biodiesel. A retrofit kit was (information dated April 2010) to be made available to adapt other engines to 100% biodiesel capability. Recommendations include: changing the fuel filter at 20 hours for first three times if engine had been previously run on mineral diesel; and shortened oil service periods (but recommended oil change periods were dependent upon the type of engine operation with stop-start operation requiring more frequent oil change periods).

### ***Volvo Penta***

*Information source: US website plus internal, Volvo Penta technical information.*

The use of fuel containing up to 5% biodiesel accepted, in compliance with EN 590 (which actually allows up to 7% biodiesel). Information stated that some customers may use fuels with greater biodiesel proportion and recommendations were provided for this. Volvo Penta also declared relief from any liability for fuel-related damage when fuel containing higher proportions of biodiesel were involved.

### ***Wartsila***

*Information source: Wartsila website and personal communication Wartsila.*

Wartsila can provide engines able to operate on a range of fuels including 100% biodiesel.

### ***Yanmar Marine***

*Information source: Yanmar website and agent-provided Yanmar Marine technical information.*

Whilst the website stated acceptance of the use of fuel containing up to 5% biodiesel only, the technical information stated the acceptance of up to 20% biodiesel in specific engines. Recommendations included: replacement of fuel hose, fuel feed pump, water separator, and O-rings; checks on oil level and water level of separator; use of biodiesel no more than 3 months old; and running the engine on diesel before closing down the engine for long periods.