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EI literature review

Implications of biofuels on microbial spoilage and corrosion within the fuel distribution chain and end use

EI LITERATURE REVIEW

IMPLICATIONS OF BIOFUELS ON MICROBIAL SPOILAGE AND CORROSION WITHIN THE FUEL DISTRIBUTION CHAIN AND END USE

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Foreword

Recent EU regulations allowing the use of biofuels have not fully considered the potential adverse impact of microbial activity in distribution, storage and end use. These impacts may cause significant implications for fuel quality and stability and also the integrity of distribution and storage infrastructure. However there is substantial evidence that some problems resulting from microbial activity in biofuels are already occurring.

Microbial growth in fuel tanks and systems leads to operational problems including filter clogging, tank gauging malfunction and rapid corrosion of fuel tanks and fuel system components. This is a known issue sporadically encountered in hydrocarbon diesels and, to a lesser extent, in conventional unleaded gasoline. By virtue of their ready biodegradability, it is probable that widespread use of biodiesel and bioethanol will lead to increased problems of microbial spoilage and corrosion.

Remedial measures are costly and can result in system downtime and use of chemical biocides. Some biodiesel suppliers, contrary to generally accepted best practice[64], are reported to dose biocides on a continuous or semi-continuous basis to prevent problems. This appears contradictory that apparently "environmentally friendly" fuels need treatment with chemical biocides which are preferentially water soluble and potentially have an adverse environmental impact and implications for disposal of water drained from storage tanks.

This literature review aims to review the current knowledge base, including technical research and operator experience in order that an informed judgement can be made on the existing and potential impact of microbiologically related problems in fuel distribution, storage, supply and end use associated with a more widespread use of biodiesel. Following the identification of knowledge gaps and subsequent recommendations from this literature review, a microbiology laboratory study will be commissioned to analyse test blends of biodiesel and bioethanol.

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1 SUMMARY

Numerous anecdotal reports have suggested that biofuels will be more susceptible to microbial spoilage than hydrocarbon diesel. In reality very few reports have been published on investigations into the susceptibility of biofuels[1] and their blends to microbial degradation. Only six reports were found specifically addressing this issue, all of which were related to biodiesel and its various blends. No reports investigating the susceptibility to microbial spoilage of bioethanol, biobutanol and ETBE were found, therefore for these fuels and blends estimations on their propensity to microbial spoilage had to be made based on their physico-chemical characteristics.

The six reported investigations into the biodegradability of various biodiesels showed that biodiesels derived from different feedstocks have varying degrees of susceptibility to biodegradation, primarily due to the original fatty acid composition, ester solubility and partitioning in water [13, 33, 38, 39, 40, and 41]. However these studies were somewhat contradictory. Two of the studies demonstrated that microbial growth was far more prevalent in RME biodiesel than in hydrocarbon diesel, as would be expected by the physico-chemical properties of the fuel. However one study conducted on SME biodiesel reported antimicrobial activity of the biodiesel, possibly due to the presence of antimicrobial fatty acids as components within SME, whereas another study reported that growth in SME was highly prolific in comparison with hydrocarbon diesel. Two studies into the microbiological properties of SME and CME biodiesels concluded that these fuels had comparable biodeterioration susceptibilities to hydrocarbon diesel. As so few investigations have been carried out, and given the results from the aforementioned studies, it is clearly apparent that much more experimental work is required to obtain a full picture of the susceptibility of biodiesel to biodegradation.

In the absence of published reports on the susceptibility to microbial spoilage of bioethanol, biobutanol and ETBE based fuels, assumptions based on their physico-chemical characteristics had to be made in order to assess their susceptibility to biodegradation. These often conflicting factors include:

— water partitioning of the alcohol or ether;
— tendency to render the fuel hygroscopic;
— antimicrobial activity of the alcohol or ether;
— biodegradability of the alcohol or ether, and
— blend ratio of the biofuel.

The factors above are discussed in detail in this review.

Although ethanol is a well known potent antimicrobial agent, low concentrations in water represent a utilisable carbon source for many micro-organisms. Anecdotal evidence suggests that bioethanol increases the risks and associated problems of microbial growth in fuels; however the literature search conducted to compile this report found no published studies relating to this. However, ethanol is highly miscible in water and is very hygroscopic; ethanol and its breakdown products can be used as carbon sources by a great many micro-organisms. This suggests that fuels containing bioethanol will be more prone to spoilage than fuels containing biodiesel. Conversely, if the partitioning of bioethanol into the free water phase leads to antimicrobial levels of ethanol (>5% (v/v) for most

[1] Biofuel in this context refers to transport fuels containing percentage biocomponents greater than allowed in 'standard' fuels (e.g. >5% ethanol in EN228 or >5% FAME in EN590 diesel).

micro-organisms) being present in the free water then susceptibility of bioethanol based fuels to biodegradation is likely to be reduced. Blend composition may be crucial in determining the susceptibility of bioethanol to microbial spoilage. Any water drawn into the fuel is joined to ethanol by hydrogen bonding, after the ethanol is saturated with water, both phase out of the fuel and descend to the bottom of the fuel storage tank as a water/ethanol liquid. For instance, higher bioethanol concentration may lead to greater water pick-up, potentially leading to more water and ethanol breakout as condensation, increasing the potential for microbial growth. However, higher bioethanol concentration may lead to greater bioethanol concentrations in any free water present, reducing the potential for microbial growth. The converse may be true for lower bioethanol blends.

No reports describing the propensity of ETBE to microbial degradation and spoilage were found. However, the antimicrobial properties of various ethers against a wide range of micro-organisms have been reported in many articles; one article reports that petroleum ether is more antimicrobial than 97% ethanol. In addition, ether is far less soluble than ethanol so there will be less potential substrate present in the aqueous phase of fuel systems. This suggests that ETBE fuels will be less susceptible to microbial spoilage than bioethanol fuels, however the ability of organisms to utilise ETBE as a carbon source is not known. In addition, it should be noted that reduced solubility may result in ETBE being present in the water phase at sub-inhibitory concentrations so potentially increasing the likelihood of microbial growth.

No reports were found investigating the propensity of biobutanol to microbial spoilage; however several factors suggest that any such problems will be less likely to occur than in bioethanol fuels. Increased carbon chain length reduces the solubility of an alcohol in water; therefore less biobutanol will be present in the aqueous phase as a carbon source for microbial growth. Increased carbon chain length also reduces the ability of micro-organisms to breakdown biobutanol. Antimicrobial activity of alcohols also increases with chain length, again reducing the risk of microbial problems occurring in biobutanol fuels in comparison with bioethanol fuels. As discussed for bioethanol, blend composition may be critical in determining the susceptibility of biobutanol blend fuels to microbial spoilage. However, as with ETBE, reduced solubility may result in biobutanol being present in the aqueous phase at sub-inhibitory concentrations that may represent a utilisable carbon source for microbial growth.

In conclusion, there has been very little work carried out investigating the susceptibility of biofuels to microbial degradation and the consequences of this on the fuel distribution chain and end use. Given the political and legislative pressures calling for increased use of biofuels, for example the EC is proposing a binding target of 10% biofuel use by 2020, there is an urgent need for laboratory work in this area to be carried out.

2 INTRODUCTION

Although biofuels are often considered 'new fuels' they have in fact been in use since the earliest internal combustion engines were developed. One of the first prototypes of the diesel engine invented by Rudolf Diesel in 1892 was designed to run on vegetable oil, and several of Henry Ford's first internal combustion engines were designed to run on bioethanol rather than petrol [1]. However, the subsequent low cost of crude oil for most of the 20th century limited demand and development in the production of biofuels. Around the time of World War Two, biofuels made a brief reprise due to limited petroleum crude oil supplies; the oil crisis of the 1970s and resultant high prices encouraged many countries to commence research into the development of alternative fuels; additional work was carried out in the 1980s on biodiesel development in South Africa in response to economic sanctions [1,2]. Brazil pioneered large scale production of bioethanol during the Middle Eastern oil embargo of the 1970s [3], and in the early 1990s farmers in Austria started cooperatives to produce and use biodiesel commercially [2].

In 2007 crude oil reached record prices and the United States and Europe are becoming increasingly dependent on oil imports from the politically unstable Middle East. Europe currently imports 80% of its oil needs and the 2004 European Commission Green Paper raised concerns over Europe's security based on its dependence on energy imports [4]. Furthermore, in response to growing alarm about the effects of greenhouse gas emissions from burning fossil fuels on global warming, the European Union signed the Kyoto protocol in 1997, committing the EU to an 8% reduction in annual greenhouse gas emissions by 2010 compared with the 1990 level [5]. The EC White Paper of 2001 on European Transport Policy (ETP) highlighted the need to encourage the use of non-fossil transport fuels [6]. The United States President G.W. Bush signed the Energy Policy Act of 2005 (EP Act 2005), which included the Renewable Fuels Standard (RFS) and established the first nationwide baseline for the use of fuels derived from renewable sources. The RFS required petroleum refiners to use at least four billion gallons of renewable fuel beginning in 2006, increasing to 7,5 billion gallons by 2012. In January 2006 President Bush called for a 75% reduction in the dependence of imported fossil fuels by 2025 through the use of biofuels [7]. At least four United States Bills of Congress encouraging the expansion of the use of biofuels have been introduced since February of 2007 alone [8,9,10,11]. In addition to the environmental concerns of burning fossil fuels, the reliance on imports of fossil fuels and high prices, suggests that if crude oil consumption continues at the present rate, then crude oil reserves could be depleted in less than 50 years [12].

For the reasons above, alternative sources of energy such as biofuels have never been more in the political and economic spotlight. Biofuels are liquid or gaseous fuels made from plant materials, either from agricultural crops or from forestry or municipal waste products. Liquid biofuels can be divided into two categories:

1. Fuels derived from fermentation of plant material and subsequent distillation, such as bioethanol, biobutanol and ethyl tertiary butyl ether (ETBE, produced by reaction of bioethanol with isobutylene).
2. Fuels derived from vegetable oil crops i.e. biodiesel.

EU regulations allowing the use of biofuels have not fully considered the potential impact of microbial activity in distribution, storage and use. There are significant implications for fuel quality and stability and also the integrity of distribution and storage infrastructure.

There is substantial evidence that some problems resulting from microbial activity in biofuels are already manifest. Microbial growth in fuel tanks and systems leads to operational problems including filter clogging, tank gauging malfunction, and rapid corrosion of fuel system components. By virtue of their ready biodegradability, it is probable that widespread use of biofuels will lead to increased problems of microbial spoilage and corrosion. There is some evidence that this has already been the case, with numerous anecdotal reports of filter blockages in pumps delivering biodiesel in service stations and complaints to fuel suppliers from motorists, truck and bus operators and marine users. Some complaints are also due to cold flow properties of biodiesel. However, note that some of these issues occur when biofuels are first implemented into systems due to their solvent properties and removal of existing hydrocarbon residues.

Some laboratory work has evidenced that biofuels, notably those based on plant seed methyl esters (biodiesel), are more prone to microbial spoilage but studies have been limited, particularly with regard to differences between different biofuel types. The objectives of this review are to summarise specific studies into the biodegradation and deterioration of different biofuel types and subsequent consequences which will form the foundation for further laboratory based investigations. This review will:

- Provide a background in biofuel feedstocks, biofuel manufacturing processes and the advantages and disadvantages associated with the use of these alternative fuels.
- Describe the impact of different feedstocks on biofuel microbial stability.
- Define the effects of parameters such as water solubility and partitioning of esters and other readily degraded hydrocarbon components, water absorbing properties of the fuel, access to microbial nutrients, and the use of biocides in biofuels.
- Appraise current methods to assess the microbial stability of biofuels and the relevance of existing methods for assessing oil biodegradability.

The focus of this review will be on the two main biofuels, biodiesel and bioethanol, though some consideration will be given to biobutanol and ETBE.

It should be noted that there have been very few peer-reviewed articles published concerning the problems associated with microbiological contamination of biofuels. A number of the sources of information used in compiling this review came from government, trade organisation or commercial web-sites. In some cases, information derived from certain web-sites, particularly those with commercial interests, *may* be of questionable reliability; this should be taken into account whilst reading this review.

2.1 SEARCH RESOURCES

The literature search was carried out using the following information resources:

British Library Direct
http://direct.bl.uk

Directory of Open Access Journals
http://www.doaj.org