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Prevention of Biofouling in Hydrocarbons by Antimicrobial Vessel and Pipeline Coating for Cost Savings and an Increase in Safety and Reliability

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Abstract

Hydrocarbons are prone to bacterial and fungal contamination. Bacteria and fungi live and proliferate in water droplets within the fuels and on surfaces surrounding them. This can cause corrosion in oil exploration and production, clogging of fuel lines in aviation and higher emissions in diesel combustion engines to state few examples. State-of-the-art is the addition of biocides to fuels, which is associated with several disadvantages like costs and environmental burden. A novel technology to prevent biofouling in hydrocarbons is presented here. By applying an anti-microbial coating to the surfaces of hydrocarbon processing units, pipelines, and fuel containers, microbial growth can effectively be reduced. The coating can be a paint or varnish, for instance, epoxy resin as already used in aircraft fuel tanks to today. It contains transition metal oxides, thus an acidic surface is produced. This acidic surface was shown to eliminate up to 10^9 colony forming units per milliliter ($\mathrm{CFU.ml^{-1}}$) of bacteria of the species of agrobacterium tumefaciens and others in diesel, kerosene, and biodiesel, where other anti-microbial coatings based on silver did not perform. The technology has the potential to bring huge cost savings to the oil and gas industry, alongside an increase in safety and equipment reliability.

Keywords: Fouling, Bacteria, Fungi, Corrosion Prevention

1. Introduction

Biofouling is defined as the gradual accumulation of waterborne organisms such as bacteria, protozoa, algae, and barnacles on the surfaces of engineering structures in water, which contributes to the corrosion of the structures and to a decrease in the efficiency of moving parts. It is a major issue not only in marine applications such as ship, but also in cooling towers and membrane processes such as water desalination (Duerr et al., 2009). Less well-known is the bacterial contamination of hydrocarbons. In water droplets, within and on surfaces around fuels such as crude oil, its distillates, and liquid biofuels, bacteria and fungi can grow. The hydrocarbons can be the sole source of energy and carbon for the bacteria (Raikos et al., 2012).

The microbial contamination of hydrocarbons gives rise to several problems, namely:

- Degradation products and deposits in the fuel tank which lead to corrosion;
- Transfer of deposits into fuel lines which leads to clogging and eventual engine stop;
- Transfer of deposits into the combustion chamber which leads to higher pollutant emissions.

For instance, in oilfields—particularly aging ones—sulfate reducing bacteria (SRB) and acid producing bacteria cause microbially influenced corrosion (MIC) and biofouling on metal surfaces.

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The SRB generate hydrogen sulfide (H_2S) and iron sulfide (FeS) as byproducts (Hamilton, 1985; Keasler et al., 2010), leading to severe corrosion.

The problem of biofouling in hydrocarbons is particularly intense in machinery that is not frequently used such as agricultural equipment, private yachts, and private planes. In humid and high-temperature environments, microbial growth in hydrocarbons is increased. Aviators know that they should keep their plane fuel tanks full during long standstills so that less condensation water, in which bacteria and fungi can grow, will form. The aviation fuel JP-8 was found to support microbial growth, with increasing temperature and water content having a positive impact on the growth profiles of the bacterial strains (Raikos et al., 2012). As the quality of fuels differs around the globe, e.g. their water content, biofouling is a frequent occurrence. Common contaminants of aviation fuel are Aspergillus flavus (Lopes et al., 1996), Staphylococcus epidermidis (Raikos et al., 2012), Agrobacterium tumefaciens (Raikos et al., 2012), and Ralstonia picketii (Raikos et al., 2012).

Today, biocides are added to hydrocarbons in refineries and to fuels aboard aircraft to reduce the extent of biofouling. There are additives available to industrial and private users alike. Private users sometimes tend to overdose the additives, which can cause damage to the engines. The biocidal activity of an isothiazolone biocide (Kathon FP 1.5) was examined by Raikos (Raikos et al., 2012). The results indicate that the biocide can suppress the growth of S. epidermidis by 73%, A. tumefaciens by 77%, and R. picketii by 81%, when used at the appropriate concentration. Common biocides in oilfields are Tetrakis (hydroxymethyl) phosphonium sulfate (THPS), glutaraldehyde, glutaraldehyde/alkyldimethylbenzyl ammonium chloride (ADBAC) mixture, 5-chloro-2-methyl-4-isothiazolin-3-one/2-methyl-4-isothiazolin-3-one (CMIT/MIT), and cocodiamines (quaternary amines) (Keasler et al., 2010)

The addition of biocides to fuels can reduce or even stop microbial growth; however, there are some disadvantages as well:

- Relatively high costs;
- Increased complexity;
- Limited spectrum of activity;
- Unwanted combustion byproducts in the exhaust gases, e.g. in the case of chlorine-containing biocides such as triclosan (5-chloro-2-(2,4-dichlorophenoxy) phenol, CAS number, 3380-34-5).

Microbial contamination is also found in drilling mud, hydraulic oil, and metal-working fluids, where organic biocides are frequently added today. It is a ubiquitous problem.

The global annual cost of fouling in the oil and gas industry is estimated at US$ 1.4 trillion. Global costs for corrosion are on a similar level, and it is estimated that 25-30% could be saved. Hence the potential cost savings from anti-microbial surfaces in the oil and gas industry are in the range of hundred millions of dollars per year.

As an alternative to adding biocides to a fluid in a container, one can coat that container with an anti-microbial surface; see Figure 1 for a schematic illustration.

Figure 1.a shows the standard solution to fight microbial growth in hydrocarbons: adding a biocide, which can be an organic or an inorganic compound. In Figure 1.b, the alternative of providing an anti-microbial surface is shown. An anti-microbial surface will either contain a biocide that is slowly leaching out, or it will provide surface conditions which are hostile to microorganisms. Examples of leaching biocides are silver ions or organic biocides which are simply mixed into the coating material (see inset in the rightmost part of Figure 1). The elution rate of the biocide has to be sufficient for the encountered germ load, and its duration should surpass the expected lifetime of the product. A non-leaching biocide is a compound that is covalently bonded to the surface and hence not consumed, or a

physical surface condition such as a micro-rough structure. Further details are given elsewhere (Hunter et al., 1995; Environment Directorate-General of the European Commission, 2012; U.S. Environmental Protection Agency, 2013; Lackner et al., 2013; Kugel et al., 2011).

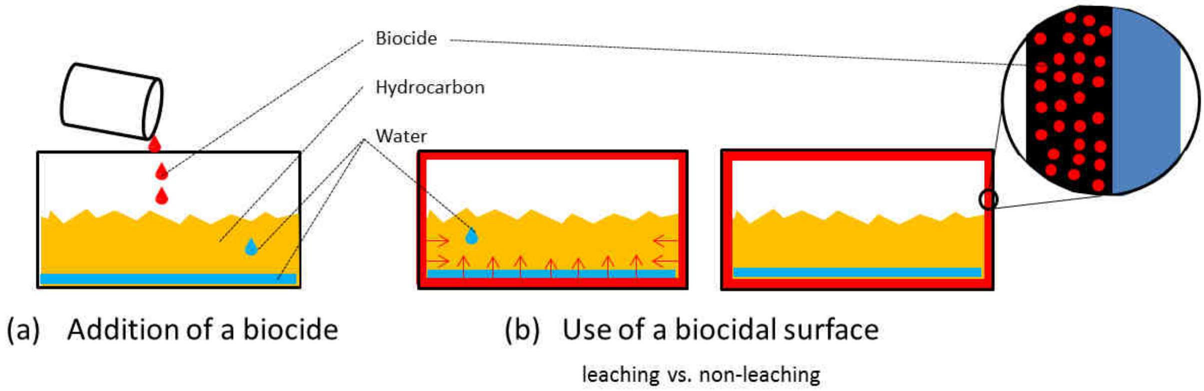

Figure 1
Strategies for keeping hydrocarbons free from bacteria and fungi: (a) adding a biocide to the hydrocarbon; (b) providing an anti-microbial surface, which can be leaching or non-leaching. See the text for details.

Also shown in Figure 1 is the presence of water; water can be found in hydrocarbons as small droplets suspended in the fuel, or accumulated as a pool at the bottom of vessels and containers, as the density of hydrocarbons is less than that of water (approx. 0.7 vs. 1.0×10^3 $kg.m^{-3}$).

A novel technology for the anti-microbial endowment of surfaces is based on the defense mechanism of the human body against microorganisms: **acids**.

This is where the human body relies on acids for microbial control:

- Acid protection mantle of the skin, pH~5.5;
- Mucosa immunity by β-defensins (cationic antimicrobial peptides);
- Acidic pH value of urine~5.5 (cranberries can lower the pH of urine, hence pushing back urinary tract infections);
- Low pH (~4) in the vagina;
- Gastric acid (pH~1) to kill bacteria taken up with food.

Furthermore, man has utilized acids for the preservation of food for a long time, e.g. with lactic acid, benzoic acid, and sorbic acid, and some acids are used as disinfectants, e.g. HCl and peracetic acid. Therefore, attempts have been made to produce anti-microbial surfaces by a reduced pH. Hauser describes a packaging film with controlled release of sorbic acid to extend the shelf life of packed food (Hauser et al., 2011). This technology is of the “leaching” type.

A particularly interesting technology has been developed by Guggenbichler et al. (Guggenbichler et al., 2008). As most acids (e.g. fruity acids and fatty acids) show a fairly high solubility in water and/or hydrocarbons, they are not suitable for a long-lasting anti-microbial endowment of surfaces. Guggenbichler found that transition metal oxides, which have a very low water solubility and negligible hydrocarbon solubility, can act as Brønsted-Lowry acids, thereby effectively killing a wide spectrum of microorganisms. MoO_3 and WO_3 were found to exhibit a strong anti-bacterial effect. To this end, fine powders of the metal oxides are mixed into various matrices. At the surface, they react with water to yield molybdic or tungstic acid, lowering the surface pH to approximately 4.5 to 5.5. The technology was shown to work in polymers, paints, and varnishes. It was initially developed for the healthcare sector (Guggenbichler, 2011). The technology is described in detail elsewhere (Zollfrank et al, 2012; Tétault et al., 2012).

Since the “acid mechanism” is non-specific, bacteria cannot develop resistances against it as is the case with antibiotics and typical organic biocides. The acidic surfaces based on transition metal oxides have been introduced in the healthcare industry (Medical Device Network, 2013). In this work, their performance in hydrocarbon-bearing systems is investigated.

2. Experimental

Aluminum plates of approximately 10×10 cm² were covered with a hydrocarbon-resistant epoxy resin containing 2% (by weight) of MoO_3. The oxide particles had a mean diameter of 1 μm. The 2 components of the epoxy system, namely resin and hardener, were mixed at the ratio of 60:40 (by weight). Prior to that, the oxide particles were added to the resin and mixed in thoroughly using a high-speed mixer to break up any agglomerates. 0.5% (by weight) of polyethylene glycol (PEG) was added to the epoxy resin as a hydrophilic additive. This addition is not mandatory; however, it increases the strength of the anti-microbial effect by making the surface more wettable (smaller contact angle of water). The resin had a pot time of about 20 min, and was applied to the samples using a brush. The thickness of the epoxy resin on the plates was around 200 μm.

Epoxy resin is chosen as a carrier for the anti-microbial agent because it is often used to treat fuel tanks of aircraft. As they are riveted and kerosene tends to creek, epoxy resin can avoid leakages. The following samples of hydrocarbons were drawn to isolate microbial contamination:

- Crude oil from a secondary oil recovery operation field;
- Jet A1 (kerosene) aviation fuel, collected from the draining point of a private plane;
- Avgas (100 LL) aviation fuel, collected from the draining point of a private plane;
- Diesel, from a regular petrol station;
- Gasoline, from a regular petrol station;
- Gasoline, from a 10-year-old lawn mower fuel tank.

By centrifugation, the water phase and hydrocarbon phase were separated whenever present. 4 different bacteria could be isolated from the Jet A1 fuel. These bacteria were grown on Columbia blood agar and identified; one of them was Agrobacterium tumefaciens. Next, these bacteria were harvested and grown on agar plates. By the McFarland standard, solutions with 10^7 to 10^9 $CFU.ml^{-1}$ were prepared for testing the samples according to the drop-on method.

3. Results and discussion

Figure 2 shows the microbiological test results. Droplets containing defined concentrations of the 4 different bacteria (10^7, 10^8, and 10^9 $CFU.ml^{-1}$ respectively) were placed on the antimicrobial epoxy resin samples. The droplets were approximately 100 μl. The samples were kept in a chamber with 100% relative air humidity to avoid the evaporation of the water. Subsequently, the samples of 10 μl each were drawn in a time series. The tests were carried out after 30 min, 1 hr., 2 hrs, and 3 hrs. The sampled water was spread on the agar plates. The incubation of these plates was done at 37 °C for 24 hrs, and Figure 2 shows the photo documentation.

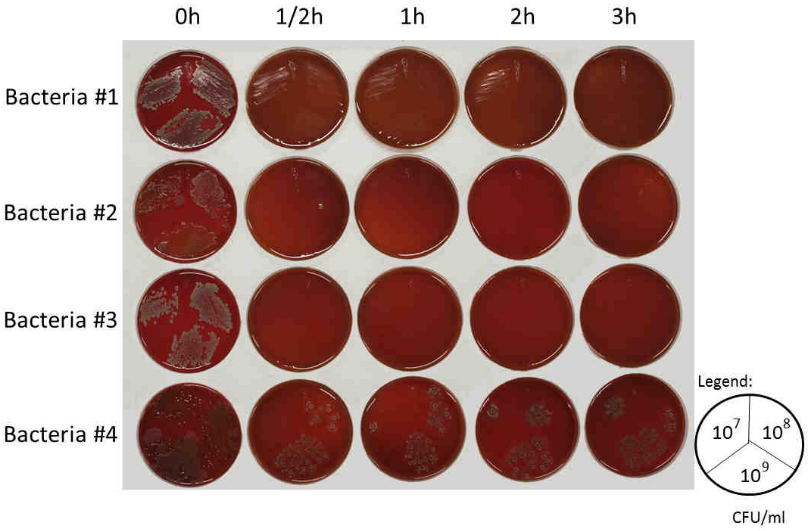

Figure 2
Rapid elimination of 10^7-10^9 CFU.ml^{-1} of the isolated bacteria is shown. On each agar plate, 3 concentrations of 1 bacterium were spread out.

In the drop-on test, the bacterial count is not measured exactly but assessed visually. One can easily distinguish between “full growth” (gray “meadow” of bacteria”) and individual colonies. Bacteria #1, #2, and #3 are eliminated after 30 min, and bacteria #4, Agrobacterium tumefaciens, after 3hrs, which is still a very good result giving the high inoculum of up to 10^9 CFU.ml^{-1}.

The drop-on method is a straight-forward, semi-quantitative test to assess the anti-microbial effect of surfaces. It is more representative than the industrial standard JIS Z2801 (corresponding to ISO 22196), where a plastic sheet is placed over the drop to artificially enhance the contact area between (hydrophobic) surface and water droplet to yield better results. The drop-on method is comparable to the ASTM standard E2149.

The mechanism of killing bacteria by the acidic surfaces is as follows: The lowered pH value of the surface induces, upon contact with bacteria, a destruction of their cell walls. This effect is non-specific. It works for gram-positive and gram-negative bacteria and also for fungi. Particularly relevant in microbial contamination is biofilm formation. Once a biofilm has been established on a surface, it can hardly be removed by conventional biocides, as the bacteria shield themselves in this biofilm; Due to the lack of nutrients, most bacteria in a biofilm have a reduced metabolism. In this “dormant” state, take-up of biocides is strongly reduced. Conventional biocides, however, need to be “digested” by bacteria, as they work from within. By contrast, the acidic technology works by contact. The prevention of biofilm formation, apart from killing bacteria, is the main mode of action of the acidic surfaces. The mechanism is visualized and explained in detail by Zollfrank (Zollfrank et al., 2012).

As Figure 2 implies, the technology of acidic surfaces has a big potential for reducing and avoiding biofouling in hydrocarbon-bearing systems. It can have a long-lasting effect, because it is based on a change of physical surface conditions mediated by the Brønsted-Lowry acids such as MoO_3 and WO_3 rather than a constant elution of a biocidal substance into the fuel (leaching biocides). Since there is no inactivation of the acid surface by sulfur-containing compounds, the technology is suitable for use in hydrocarbons. WO_3 can be used instead of MoO_3 in environments with higher water content, as its water solubility is even lower than that of MoO_3 (approx. 5 mg.l^{-1} at a pH of 7 and temperature of 20 °C). However, both are not soluble in hydrocarbons.

The epoxy resin used in this study differs from the previously used epoxy resin which was developed for high hydrocarbon resistance by the manufacturer. For the incorporation of MoO_3 and WO_3, the exact type of epoxy resin or matrix material in general is not critical, because its sole role is to fix and expose the oxide particles at the surface. Hydrophobic matrices can be modified by adding a hydrophilic additive. Antistatic agents or antifogging agents, as used in the polymer industry, or polyalcohols are well suited for this purpose. A concentration of 0.1 to 1% (by weight) normally suffices. Polyethylene glycol, as used in this study, is well suited as a hydrophilic additive for epoxy resins.

In this paper, an exemplary microbiological test of the anti-microbial epoxy resin is shown. The authors also conducted long-term tests with this technology, where no decline in anti-microbial effectiveness was found over 8 months (Guggenbichler, 2011). As the technology does not rely on the constant elution of a biocide into the environment, the duration of its activity can surpass that of the conventional anti-microbial systems of the "leaching-type".

There is a potential for the technology to be used in liquid fuel vessels and pipelines to avoid not only biofilm formation and the drawbacks associated with this phenomenon (mainly corrosion), but also other effects of the bacteria such as higher pollutant emissions during combustion, loss in efficiency, and safety compromises by clogged fuel lines and equipment failure.

The matrix for the acidic surfaces presented in this paper can be an epoxy resin, as used in this study, a paint, or a polymer, applied as a coating or a liner to the vessel or pipeline. Anti-microbial surfaces are hardly being used in the context of hydrocarbons yet. Hence the authors expect a significant increase in the use of anti-microbial surfaces to protect oil and gas exploration, production, and processing equipment, user fuel lines, and fuel tanks from biofouling in the future, leading to annual cost savings in the order of hundreds of millions of dollars and an increase in reliability and safety.

4. Conclusions

A novel technology for anti-microbial surfaces based on a reduction of surface pH was shown to give excellent results in killing bacteria encountered in hydrocarbons. There is a big potential for the technology to be used in fuel tanks aboard planes, trucks, industrial machinery, and ship to reduce or even replace the constant addition of organic biocides to the fuels, thereby savings operating costs and reducing environmental burden. The coatings can be applied to new pieces of equipment. Also, retrofitting existing installations is possible. The acidic surfaces presented here can bring substantial cost savings to the petrochemical industry, and increase the safety and reliability of equipment where hydrocarbons are stored, processed, or used.

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Nomenclature

CFU	: Colony forming units
SRB	: Sulfate reducing bacteria
MIC	: Microbially influenced corrosion
CAS	: Chemical abstracts service

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