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Development of Skeletal Kerosene Mechanisms and Application to Supersonic Combustion

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A Review of Kinetic Hydrate Inhibitors from an Environmental Perspective

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ABSTRACT: Kinetic hydrate inhibitors (KHIs) have been used in the upstream petroleum industry for about 25 years to prevent plugging of flow lines with gas hydrates. The main ingredients in current commercial KHI formulations are one or more water-soluble polymers which contain both hydrophobic and hydrophilic functionalities. Although the vast majority of KHIs are low in acute toxicity and bioaccumulation, very few commercial products show good biodegradability, and for that reason, there is always some concern of long-term chronic toxicity from partially degraded products if discharged into the environment. This report reviews all efforts to develop more biodegradable KHIs, and outlines the fact that some classes of so-called "green" chemicals are not necessarily readily biodegradable or low in toxicity. The review also covers methodologies to recover or destroy KHIs and reduce their discharge to the environment.

1. INTRODUCTION

In the late 1980s, the upstream oil industry began research projects to develop low dosage hydrate inhibitors (LDHIs) to go alongside low dosage inhibitors that were already available for other flow assurance issues such as wax, asphaltene, and scale formation. All of these low dosage inhibitors are noncolligative, which means they do not depend on the ratio of the number of solute particles to the number of solvent molecules in a solution. LDHIs are usually subdivided into two main classes, kinetic hydrate inhibitors (KHIs) and anti-agglomerants (AAs). AAs allow gas hydrate formation under controlled conditions, causing a dispersion of small transportable particles to form.[1−5]

AAs will not be discussed further in this review. The key ingredient in KHI formulations is a water-soluble polymer or oligomer which contains both hydrophobic and hydrophilic functionalities. These functionalities interact with both free water and water found in gas hydrate particles to prevent macroscopic hydrate formation and plugging of flow lines in oil and gas fields. The exact KHI mechanism is still not clear, but there is good evidence that nucleation inhibition and crystal growth inhibition are involved with many of the oligomers and polymers.[6]

2. COMMERCIAL KHI POLYMERS

Polymers that have been used in many field applications include those based on the monomers *N*-vinyl caprolactam (VCap), *N*-vinylpyrrolidone (VP), or *N*-isopropylmethacrylamide (NIPMAm) as well as hyperbranched poly(ester amide)s (HPEAs) based on diisopropanolamine and various carboxylic anhydrides. (Figure 1).[1,4] Polymerization of the monomers VCap, VP, and NIPMAm by themselves or with any other vinylic monomer will form polymers with polyvinyl backbones which are generally poorly biodegradable. This in accordance with the generally observed degradation rate of water-soluble synthetic polymers having a hydrocarbon backbone, whose biological attack is very limited until their molecular weight drops below about 1000 g/mol, and which is often too low for optimal KHI performance.

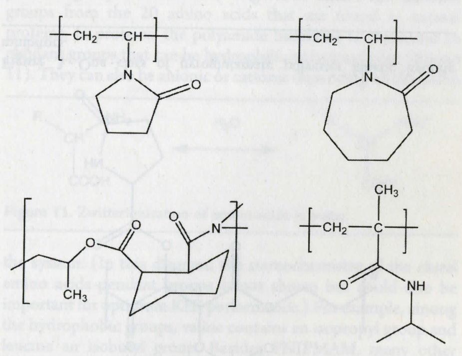

Figure 1. Repeating units in classic commercial KHI polymers: clockwise from top left, *N*-vinyl-2-pyrrolidone, *N*-vinyl-2-caprolactam, *N*-isopropylmethacrylamide, and a polyesteramide unit made from diisopropanolamine and hexahydrophthalic anhydride.

This general trend holds true, with the noticeable exception of polyvinyl alcohol (PVA) homopolymer, for many water-soluble materials, including poly(*N*-vinyl-2-pyrrolidone), poly(acrylamide)s, and several other polycarboxylates.[7] In a later study in water-soluble polymers, efficient mineralization in a reasonable time frame (<1 month) was recorded only for polyacrylic acid with molecular weights lower than 1000 g/mol.[8]

Seawater biodegradation is one of three key ecotoxicological tests conducted under the OSPAR guidelines for chemicals used offshore in the North-East Atlantic region including the North Sea. Operators sometimes adopt these guidelines for other offshore areas which do not have sufficient environmental

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