Multifunctional biomass-based chemicals

H_2S scavenging

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ARTICLE

Multifunctional Biomass Based Chemicals: H_2S Scavenging

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Multi-valent biomass based H_2S scavengers have been prepared in a few steps from cheap and available chemicals and evaluated using state-of-the-art *in situ* Raman spectroscopy under reaction conditions relevant for industial applications. The chemicals are based on using carbohydrates as a flexible scaffold, where the exact properties can be tuned to meet specific applications. Different functional groups can be introduced and the solubility and partitioning can be controlled by simple means. The chemicals presented here have been developed with the aim to be used as H_2S scavengers in the oil and gas industry in order to limit the use of enviromentally concerning chemicals of fossil origin.

Introduction

Biomass has become increasingly important for the synthesis of bulk chemicals, which can substitute the ones of fossil origin.[1,2] Carbohydrates are among the most abundant molecules in nature, and several are produced on an industrial scale at a low price. Glucose, as an example, is the most common molecule in the biosphere, and hence an important chemical for biomass-based chemicals and in line with concepts of e.g. the European Commission's chemical strategy (The Green Deal). In addition to its low price, glucose also comes with 4-5 alcohols groups and an aldehyde/hemiacetal, which can be modified in a selective manner. This multi-functional scaffold gives access to highly functionalized molecules in a few steps. This we wish to explore as a concept for tailoring chemicals for industrial purposes, here exemplified by H_2S scavenging. H_2S is an unwanted highly toxic by-product in several industries from agriculture and food production to the oil and gas industries.[3] In addition to its toxicity and pungent smell, it does also cause problems by being corrosive and by forming insolvable salts, with costly consequences in the production facilities. Reducing the level of H_2S is therefore a major concern. The methods used to remove H_2S strongly depend on the industry as well as place of action. If the concentration is high (above 1000 or 3000 ppm), the absorption of H_2S with solvent regeneration and recovery of pure H_2S (to be conveyed to the Claus process for producing sulphur[4]) is preferred. Other technologies are preferred when there is limited space for absorption or adsorption columns and downstream processing of H_2S. To meet this challenge H_2S scavengers have therefore been developed so that the H_2S can be removed just by adding chemicals. This is often also economically more attractive, especially for low concentrations of H_2S (dozens to hundreds ppmv).[5,6] For thousands ppmv and above, scavenging would be too expensive and an absorption unit is preferable.[7] A particular challenge is the use of scavengers in the offshore oil and gas production with limited space and long distances to the infrastructures on shore. In some cases (e.g., scavenging of natural gas stream), the scavengers used offshore need to react fast in a confined space (i.e., low available reaction time). In addition, the excess scavenger as well as the products formed, upon reaction with H_2S, have to be environmentally benign and disposable at sea, if they cannot be re-injected in subsea wells. The environmental impact is determined by toxicity, bioaccumulation potential and persistency (PBT) and newly developed solutions should include those parameters already in the design phase to comply with initiatives such as Safe-and-sustainable-by-Design (SSbD) (European Commission, 2022).[8] Consequently, an initial assessment of the mentioned parameters should be carried out as early as possible, preferably in the design phase. Today, the most used H_2S scavengers are triazine based and MEA-triazine is estimated to account for more than 80% of the H_2S scavenger oilfield market. One of the most used H_2S scavengers is 1,3,5-tris(2-hydroxyethyl)-hexahydro-*s*-triazine, commonly referred to as MEA-triazine.[9] It is typically used as a 40-60 wt.% aqueous solution of technical quality and it is known to be relatively toxic in the aquatic environment. Additionally, when used it generates a peculiar wastewater, also known as spent H_2S scavengers, with a high concentration of organics and high pH. This wastewater causes operational challenges such as precipitation (scaling) and fouling making re-injection in subsea wells often unfeasible, thus discharge to sea is commonly practiced.[10] In terms of volumes, it is a relative small discharge compared to the total discharge from the oil and gas industry, and it is hence typically less than 0.1% of the volume of

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produced water discharge. However, due to the high concentration of moderately toxic chemicals, its Environmental Impact Factor is estimated to be between 10% and 20% of the total discharge into the sea of offshore oil and gas installations.[11] Due to the high impact of the discharge to the marine compartment it is important to assess the potential environmental impacts of alternative solutions before further development. In this work we present our findings on synthesizing and assessing environmental impacts at the design level for conceptually new biomass based multi-valent chemicals exemplified by H_2S scavengers. The scavenging properties are evaluated using a state-of-the-art *in situ* Raman spectroscopy method. The first generation of these conceptually new "green" scavengers are prepared from carbohydrates and their kinetic profile benchmarked against MEA-triazine. The environmental impact was assessed using four regulatory relevant test species covering three trophic levels including two marine (*Aliivibrio fishceri* and *Skeletonema costatum*) and freshwater species (*Raphidocelis subcapitata* and *Daphnia magna*) and test for readily biodegradability by aerobic biodegradation (OECD 301F).

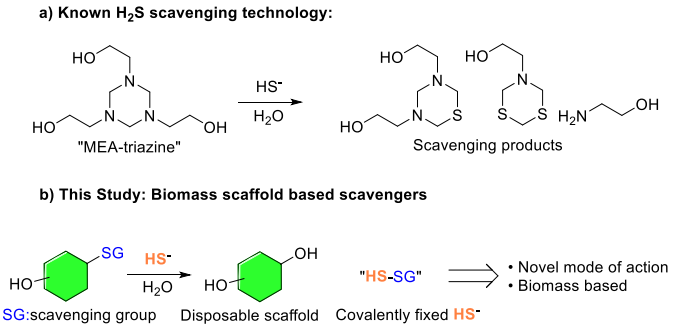
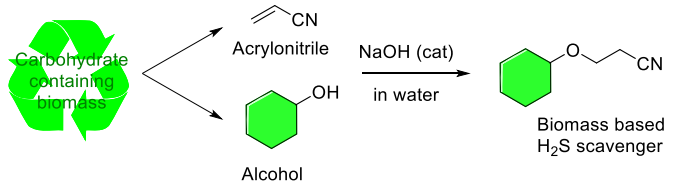


Figure 1 -a) 1,3,5-tris(2-hydroxyethyl)-hexahydro-*s*-triazine (MEA-triazine) and its products when reacting with HS^- (H_2S dissociated in water). b) Conceptually new H_2S scavenger based on biomass functionalized with functional group able to capture HS^- in a covalent manner.

Hexahydro-triazines react with H_2S at basic pH to form thiadiazine and dithiazine (Figure 1a) and these have been found to cause problems with fouling and hence alternative scavengers are in high demand.[12] Complete reaction between the MEA-triazine and H_2S would give trithiane, but in reality this product is not formed due to low reactivity of the dithiazine. This has recently been studied in more detail and the protonation ability has been found to be crucial for the reactions to proceed. Hence MEA-dithiazine is not protonated under the applied reaction conditions and does therefore not react.[13]



Scheme 1 General concept and synthesis of biomass based H_2S scavengers.

With the aim to discover fundamentally new H_2S scavengers, free from triazine and formaldehyde, we considered alternative functional groups able to react with H_2S. Addition of H_2S to alkenes and alkynes are well-known reactions, but often too slow. Reaction with C-N / N-N multiple bond is also well known and H_2S is an example used as a reductant for the azido group. Azides are however often unstable and shock-sensitive and hence not safe. Reactions with nitriles are less common, but have found uses in various technical application.[14] Interestingly, the reaction between the cyano functionality and H_2S was already described by Völckel in 1841.[15] Kindler studied the reaction in more detail and found that benzonitrile derivatives reaction with H_2S depended on the substituents on the benzene.[16,17] Generally, aliphatic nitriles are found to be less reactive and elevated temperatures or catalysts are needed for their transformation into thioamides.[14] As most aromatic compounds are of fossil origin and often environmental hazardous we decided to study aliphatic nitriles as H_2S scavengers. As mentioned above the low reactivity can be overcome by using catalysts or additives and we therefore sought to construct multivalent nitrile based H_2S scavengers, as our hypothesis was that more nitriles, or other functional groups, could have a rate enhancing effect on the reaction. As the spatial arrangement and intermolecular distances were considered important for such intramolecular catalysis we focussed our research on using well-defined biomass based templates as our platform. Carbohydrates stands out as candidates for such platform as multiple functional groups (alcohols) are placed specifically in a confined space. Furthermore, even though structurally complex, carbohydrates are often cheap and considered renewable. Glucose is, as an example, the most common molecule in the biosphere and a commodity chemical, which is produced on a huge scale in its pure form. Several other carbohydrates are closely related to glucose and hence also cheap and readily available. Examples are fructose, inositol, glucono lactone and mannose. Only very few examples of nitrile containing carbohydrates have been reacted with H_2S. A rare examples is by Popsavin et al., who synthesized a thiazofurin derivative from a xylofuranosyl cyanide to get the corresponding thioamide for the construction of a thiazole.[18]

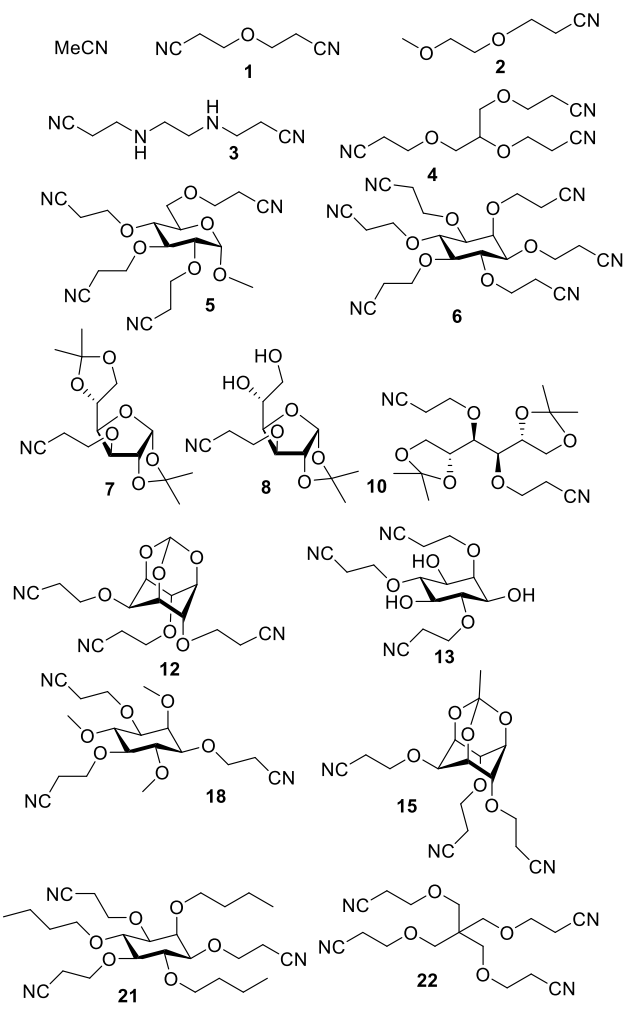


Figure 2 Nitriles synthesized and studied as H_2S scavengers.

There are, however, no examples of nitriles or nitrile containing carbohydrates used for H_2S scavenging. Linking nitriles with carbohydrates most obviously involve C-O bond formation and in order to limit waste, catalytic reactions were preferred. The oxo-Michael addition is a simple reaction performed under base catalysis with water present. Linking acrylonitrile to alcohols under such conditions is a known approach for cyanoethyl ether synthesis. Hence, we aimed at studying the use cyanoethylated carbohydrate derivatives as H_2S scavengers under basic conditions. Acrylonitrile is an industrial chemical, and its synthesis from biomass has recently gained increased interest and several routes have been developed. Carbohydrates[19,20] and glutamic acid[21] have earlier been used as feedstock, but the price is still to the high site.[22,23]

Results and discussion

Synthesis of H_2S scavengers

In order to compare scavengers with difference nitrile content, orientation of cyanoethyl groups, size and solubility in water, we set out to synthesize a library of cyanoethyl ethers based on simple alcohols and on carbohydrate templates. Dicyanoethyl ether **1** and 3-(2-methoxyethoxy)propanenitrile **2** were readily synthesized from the corresponding alcohols and acrylonitrile (see SI for details). There have been reports stating that the reaction between nitriles and H_2S is promoted by amines.[24] An amine functionality was therefore included in our construct by reacting ethylene diamine with acrylonitrile giving compound **3** in an almost quantitative yield. More challenging were the syntheses using biomass based polyols. The simplest was glycerol, which upon reaction in acrylonitrile containing sodium hydroxide in water gave the triether **4** in 64 % yield. Moving to the even more heavily functionalized biomass based chemicals methyl α-D-glucoside was transformed into the per cyanoethyl ether **5** with a good yield. Inositol is a carba-sugar isomer of glucose and it contains 6 alcohol groups in comparison to the 4 in glucose. Hence the hexacyanoethyl ether **6** of inositol was synthesized according to a literature procedure.[25] An advantage using carbohydrates is the well-developed protective group chemistry, which selectively gives access to specific protective group patterns. In this context, we decided to use simple low molecular weight chemicals to modify our templates. The preferred protective groups are based on carbonyl compounds, as they potentially also react with H_2S, like formaldehyde, and hence the overall scavenger properties might be improved. Diacetone glucose was functionalized with a cyano ethyl at the free 3-OH giving **7**. This fully functionalized and hence less hydrophilic glucose derivative prefers the oil phase. Selective removal of one isopropylidene group afforded the 5,6-diol **8**, which is hydrophilic, exemplifying how the template can be used for tailor made chemicals with optimal partitioning properties. Mannitol, i.e. reduced mannose, was reacted with acetone under acid catalysis and gave the diacetone mannitol, which subsequently was cyanoethylated on the two remaining alcohols giving **10**. Orthoesters are also common protective groups in carbohydrate chemistry and even more importantly they have been found to react with H_2S.[26,27] Orthoesters are commonly used to selectively protect 3 out of the 6 alcohol groups in inositol and hence this was exploited. The known orthoformate of inositol was easily prepared on a large scale and could subsequently be cyanoethylated using the standard oxo-Michael conditions giving the product **12** in 68% isolated yield. To change the partitioning of the chemical, the orthoester could easily be removed, liberating 3 alcohols and at the same time causing the ring conformation to flip from the axial rich to the more stable equatorial rich **13**. As this also change the spatial arrangement of the cyanoethyl groups we decided to also synthesize the all cis tri-cyanoethylated derivative **18**, with methyl ethers on the remaining positions. The different inositol derivatives (**12, 13** and **18**) allowed us to study the importance of the arrangement of the cyanoethyl groups from being ax-ax-eq in **12** to eq-eq-ax in **13** and finally eq-eq-eq in **18**. To study whether the orthoester had an influence we synthesized

analogue **15** with an orthoacetate group instead of the orthoformate group. The choice of orthoester can be used to influence the partitioning of the scavenger. Instead of the orthoester the partitioning could also be affected by the installation of alkyl groups such as the methyl ethers on derivative **18.** The partitioning could once again be tuned by installing more fatty alkyl groups here exemplified by butyl ethers in **21**. Pentaerythritol is a readily available polyol and was cyanoethylated to form product **22** which could be compared with the biomass based polyols.

H_2S scavenging properties studied by Raman spectroscopy

The diverse biomass derivatives, synthesized in this work by functionalization with nitriles, were studied with respect to their H_2S scavenging properties and compared with the commercial H_2S scavenger MEA-triazine (technical). The comparison was carried out in basic aqueous solutions, since these are the conditions employed in one relevant industrial application of MEA-triazine, where basic aqueous solutions of MEA-triazine are injected in natural gas streams to remove H_2S. Raman spectroscopy has recently been used for *in situ* monitoring of the aqueous phase scavenging reactions of bisulfide (HS^-), i.e., the prevalent form of H_2S at high pH, with MEA-triazine.[28–30] Bisulfide has a characteristic peak at 2574 cm^{-1} in Raman spectra, which overlaps with neither MEA-triazine peaks nor peaks of reaction products, thus allowing to monitor the progress of the H_2S scavenging reactions.[13,28,29]

In this work, an in-house made experimental setup allowing to monitor the disappearance of bisulfide ion and the pH in a batch stirred configuration, at controlled and constant temperatures up to 75°C, was used. Details of the setup can be found elsewhere.[13]

The library of nitriles prepared were tested using the abovementioned experimental setup and compared with MEA-triazine at an initial pH 10, which upon reaction changes (See SI for details). Somewhat surprising, the best performing scavenger was the orthoester protected inositol carrying 3 cyanoethyl groups (**12**) see figure 3. More densely cyanoethylated polyols, like **5** or **6**, were less efficient in H_2S removal and shifting from the axial rich **12** to the equatorial rich **18** did also influence the scavenging properties negatively. Making the compound more lipophilic caused problems with the solubility in the aqueous model system and hence a lower performance. Based on the initial Raman study, compound **12** was chosen as the most promising compound and its synthesis scaled up to 50 g. A detailed kinetic study was performed following the consumption of HS^- in the model system. Compared with MEA-triazine, under the same conditions, **12** was almost as fast. A technical product of **12**, i.e., not purified to the same extent, was found to match the performance, which is relevant for the intended technical use. While the use of MEA-triazine caused the pH to increase substantially, which in turn led the reaction to stall until lowering the pH by adding HCl,[13] the use of **12** did not change the pH to the same extent. In contrast, the new inositol based scavenger continued scavenging and could remove all traces of HS^- in the setup in approx. 40 min (see figure 3). The perusal of the Raman spectra showed no peaks corresponding to the expected values for thioamides, which suggested an alternative mode of action compared to the expectations. In addition, the spectra indicated that a new nitrile containing compound appeared, which was puzzling. Control experiments were therefore performed in the absence of HS^- and it was revealed that under the basic conditions used, the scavenger slowly turned into a new nitrile containing compound, which by using a reference compound, was confirmed to be acrylonitrile. The scavenger is actually working as an acrylonitrile releaser under these conditions via a retro-Michael addition. Changing the pH towards neutral slowed the scavenging reaction, which is in line with a slower release of acrylonitrile from **12**. In order to test whether released acrylonitrile in fact is the active scavenger, reagent grade acrylonitrile was used under the same conditions. Similar kinetic were observed and hence we can conclude that acrylonitrile is the actual scavenger.

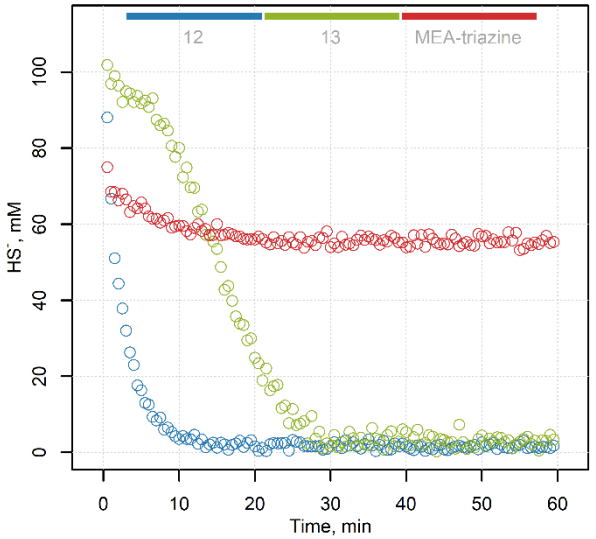


Figure 3 Study of the reactions between scavengers (**12**, **13** and MEA-triazine) and HS^- at an initial pH of 10 at 75 °C. The concentrations of HS^- are estimated based on Raman spectra acquired during the reactions.

Our initial goal was to develop a biomass based H_2S scavenger to be used off-shore as the current available chemicals have an unacceptable impact on the marine environment. As the mode of action of the chemicals developed in this project involves acrylonitrile release, this clearly disqualifies for use offshore, where the spent H_2S scavengers are often discharged into the sea. The limited pH increase and the highly efficient removal of HS^- at high pH might be advantageous, compared to MEA-triazine, and may find use in special applications.

Environmental impact assessment

Data describing the ecotoxicity of chemicals is necessary for pre- and post-market registration by European and international regulations e.g. REACH. Herein, the requirement for PBT assessment by REACH was combined with the criteria for the PLONOR list for chemicals used in offshore oil and gas

extraction in the North Sea Region governed by the OSPAR commission. The PLONOR list criteria used for comparison of the synthesized H_2S scavengers were 1) chemicals must not be carcinogenic, mutagenic or toxic for reproduction, 2) should exceed LC/EC50 of 100 mg/L, 3) should not be bioaccumulative and 4) should be readily biodegradable. The benchmark substance used for comparison of the most active synthesized H_2S scavengers (**4**, **12** and **13**) was MEA-triazine. Based on QSAR estimations, the proposed structures did not raise concern for potential bioaccumulation. The most active of the synthesized H_2S scavengers (**4**, **12** and **13**) exerted no inhibition of luminescence (*A.* fisheri) , growth (*S. Costatum* and *R. subcapitata*) or lethality (*D. magna*) at the highest concentrations tested (100 mg/L). Benchmarked against MEA-triazine the new synthetic scavengers had at least 15-times lower toxicity for the freshwater algae (EC50, MEA-triazine, 6.66 mg/L), and at least 5-times lower toxicity for the marine algae (EC50, MEA-triazine, 21 mg/L).[31] For assessment of biodegradability, scavengers **4**, **12** and **13** did not pass the criteria for readily biodegradability (>60% theoretical oxygen demand). Energetically the CN bond is unfavourable however biodegradation and utilization both as nitrogen and carbon source for bacterial growth has been demonstrated.[32–34] Consequently, further research with adapted bacterial cultures would be needed to assess the mineralization of the chemicals.. In summary, the presented results would characterize the H_2S scavengers as posing little risk and be accepted for discharge to the marine environment.[35]

Conclusions

In conclusion we have developed a conceptual new type of industrial chemicals with limited environmental impact based on simple biomass, where the advantages of multi-valency is easily incorporated using the functional groups available. The concept has been illustrated by synthesizing H_2S scavengers, where the optimal chemical carried 3 cyanoethyl groups and an orthoester. The benefits from having more reactive groups in the same molecule as well the tailored spatial order was demonstrated from comparing a large number of other easily available derivatives, exemplifying the flexibility and modularity of the concept. With the many handles available in e.g. carbohydrates different functionalities can be included and hence multi-functional chemicals will be the next step in this ongoing research.

Author Contributions

AMK did the synthesis supervised by CMP, who designed the concept. FRMR performed the kinetic studies based on Raman Spectroscopy supervised by SK and MM. CMP and MM wrote a draft manuscript with contribution from all authors. LMS carried out the environmental impact assessment.

Conflicts of interest

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