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DRIVE TOWARDS ENVIRONMENTALLY FRIENDLY INHIBITORS FOR NATURAL GAS HYDRATE FORMATION PREVENTION

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This work summarizes methods for prevention of gas pipeline clogging by natural gas hydrate formation – with emphasis on development of environmentally friendly hydrate inhibitors. The work highlights advantages and disadvantages of current solutions and encourages future studies on new type of inhibitors based on ice-structuring proteins.
Key words: natural gas hydrate, hydrate inhibitors, flow assurance, antifreeze proteins, ice-structuring proteins, Rhagium mordax.

Nastojanja oko ekološki prihvatljivih inhibitora za sprečavanje hidrata prirodnog plina. Ovaj rad sažima metode za prevenciju začepljenja plinovoda uvjetovanu stvaranjem hidrata plina - s naglaskom na razvoj ekološki prihvatljivih inhibitora hidrata. Rad naglašava prednosti i nedostatke postojećih rješenja i potiče buduće studije o novoj vrsti inhibitora utemeljenoj na led-strukturirajućim proteinima.
Ključne riječi: hidrat prirodnog plina, inhibitori hidrata, osiguranje protoka, antifriz proteini, led-strukturirajući proteini, Rhagium mordax.

INTRODUCTION

Natural gas hydrate is a clathrate of natural gas guest molecule embedded in a cage of water host molecules formed at high pressure and low temperature conditions. Research on natural gas hydrates focuses on several areas: i) extraction of hydrates from permafrost and ocean bottom regions where enormous reserves of hydrates are present and can become a fuel of the future, ii) cheap, dense and safe methane storage in form of natural gas hydrate, iii) use of hydrates as a media for natural gas and CO_2 sequestering, and, iv) prevention of hydrate formation and clogging of gas pipelines and distribution systems [1, 2, 3, 4, 5]. This work summarizes recent advances in hydrate formation inhibition in gas pipelines.

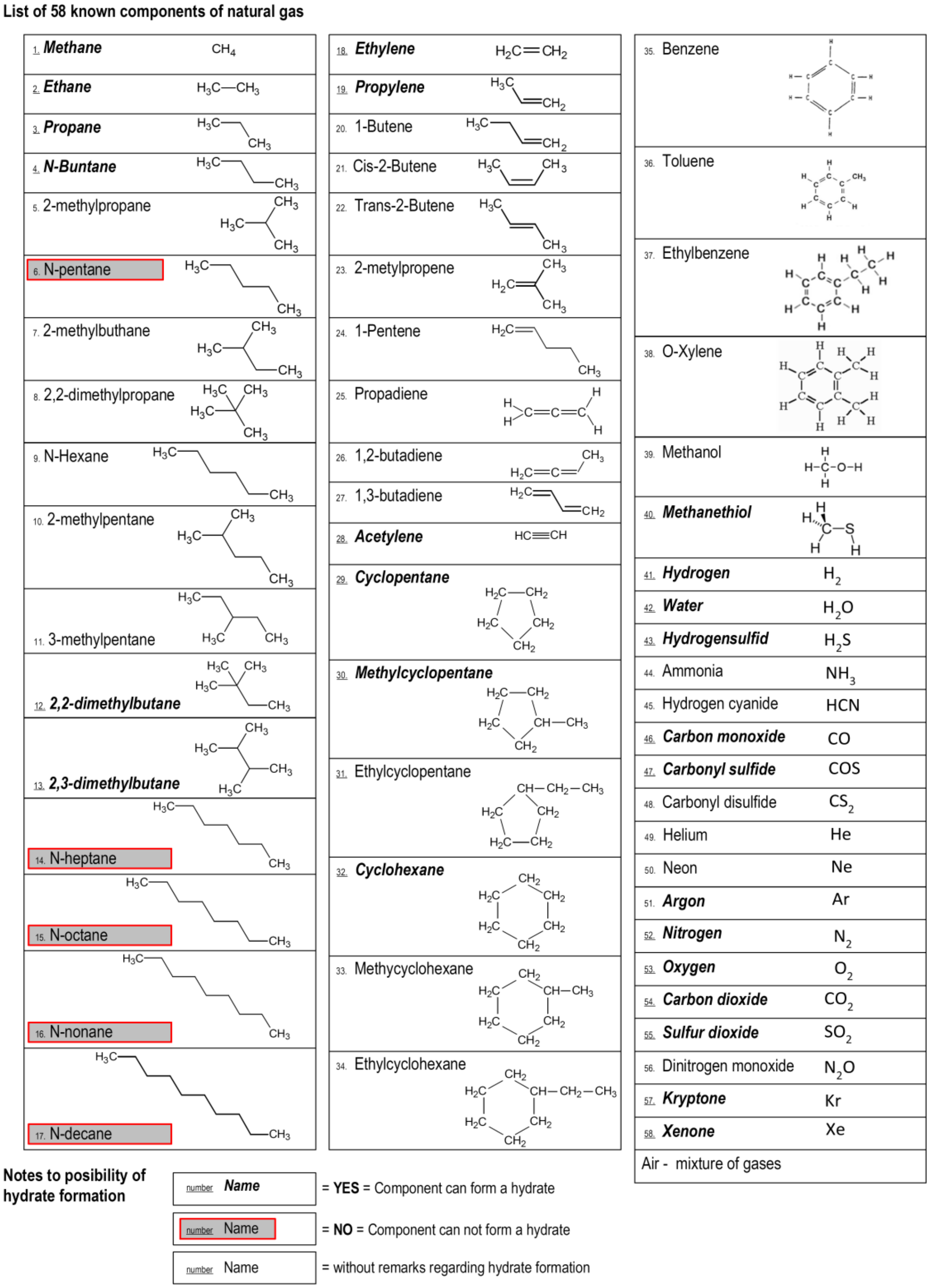
Several factors can help to reduce hydrates presence in gas pipelines, for example, i) maintaining temperature and pressure that is unfavorable for clathrate formation, ii) adding inhibitor chemicals to break hydrogen bonds of host water cages and stop or slowdown hydrate formation. As presented elsewhere water (a polar molecule, with their extraordinary properties allowed to create water clusters and cages [5]) presence in a system plays crucial role. Addition of gas hydrate inhibitor chemicals to natural gas flow is necessary part of the flow assurance procedure [6]. This work provides a summary of the common knowledge about gas hydrate inhibitors that can stop or delay hydrate formation with focus on environmentally friendly and effective solutions. This is complementary to other hydrate formation inhibition techniques that are in early stages of investigation, for example, one exploiting a metastable state between different clathrate crystalline phases to prevent clathrate formation as we present earlier [4].

An equilibrium curve highlighted in black color on pressure versus temperature diagram shown in Figure 1 defines the border between risk and no risk regions for the natural gas hydrate occurrence in a system. Tests in gas distribution systems have shown that hydrate blockage formation occurs in four steps when gas and water are present at high pressure and low temperature [7]: 1) water entrainment, 2) hydrate growth, 3) agglomeration, 4) plugging. Note that besides key contributors of methane and ethane, natural gas transported in pipelines may consists of minor contribution from 58 other components listed in Table 2 (based on data from [9]). These components may also need to be taken into account because some of them can be guests for hydrate formation. In Table 1 we list molecules that form hydrates (i.e., occur as guests) and molecules that do not form hydrates (based on data from [9]).

Table 1. The list of possible molecules which are/are not guest in gas hydrate formation [9]
Tablica 1. Popis mogućih molekula koje su / nisu dionici formiranja plin hidrata [9]

<table>
<tr><th>Hydrocarbon guests</th><th colspan="2">Non-hydrocarbon guests</th><th>Hydrate nonforming species</th></tr>
<tr><td>Methane</td><td colspan="2">Carbon dioxide</td><td>n-Pentane</td></tr>
<tr><td>Ethane</td><td colspan="2">Carbon monoxide</td><td>n-Hexane</td></tr>
<tr><td>Propane</td><td colspan="2">Nitrogen</td><td>n-Heptane</td></tr>
<tr><td>i-buthane</td><td colspan="2">Oxygen</td><td>n-octane</td></tr>
<tr><td>i-penthane</td><td colspan="2">Hidrogensulfid</td><td>n-nonane</td></tr>
<tr><td>Cyclo-propane</td><td colspan="2">Sulfur dioxide</td><td>n-decane</td></tr>
<tr><td>Methylcyclopropane</td><td colspan="2">Argon</td><td>n-undekane</td></tr>
<tr><td>Cyklo-butane</td><td colspan="2">Krypton</td><td>n-dodecane</td></tr>
<tr><td>Cyklo-pentane</td><td colspan="2">Xenon</td><td>n-Tridecane</td></tr>
<tr><td>Benzene</td><td colspan="2">Hidrogen</td><td>n-Pentadecane</td></tr>
<tr><td>Cyclo-Hexane</td><td colspan="2">Dimethylether</td><td>n-Hexadecane</td></tr>
<tr><td>Methylcyklopentane</td><td colspan="2">Acetone</td><td>n-Heptadecane</td></tr>
<tr><td>2,3-Dimethyl-1-butén</td><td colspan="2">Etylene</td><td>n-Oktadecane</td></tr>
<tr><td>3,3-Dimethyl-1- butén</td><td colspan="2">Acetylene</td><td>n-Nonadecane</td></tr>
<tr><td>2,2-Dimethylbután</td><td colspan="2">Propylene</td><td>n-Eikozane</td></tr>
<tr><td>2,3-Dimethylbután</td><td colspan="2">Karbonylsulfid</td><td>.....</td></tr>
<tr><td>cyklo-Heptán</td><td colspan="2">Metylmerkaptane</td><td>n-C100</td></tr>
<tr><td rowspan="2"></td><td>i-Propanol*</td><td>Ethanol*</td><td rowspan="2">* marked specis are used also as inhibitors</td></tr>
<tr><td>n-Propanol*</td><td></td></tr>
</table>

Table 2. Molecules & atoms occurring in a natural gas transporting via pipelines based on [9] - upgraded with chemical formulas and notes to the possibility of gas hydrate formations
Tablica 2. Popis molekula i atoma koji se javljaju u prirodnom plinu transportiranom putem cjevovoda



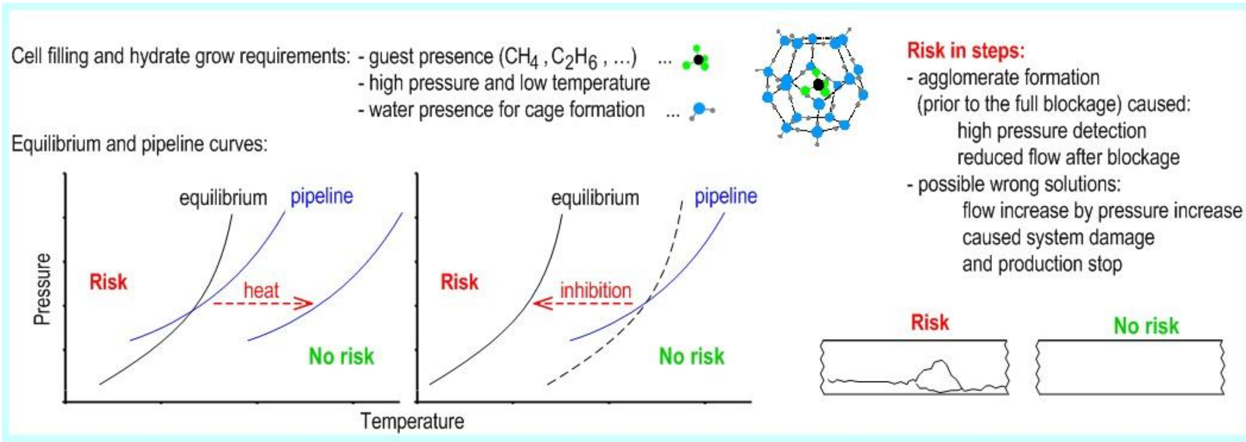


Figure 1. Thin black highlighted equilibrium curve divides the pressure-temperature diagram to regions with/without hydrate formation risk. Heating shifts the thick blue highlighted pipeline curve to the right, reducing the risk. Addition of inhibitors shifts the hydrate equilibrium curve to the left, also reducing the risk. Detailed gas hydrate formation diagram we present earlier [4]
Slika 1. Tanka crno istaknuta krivulja ravnoteže dijeli dijagram tlak-temperatura na područjima sa / bez rizika formacije hidrata. Zagrijavanje pomiče debelu plavo istaknutu krivulju cjevovoda na desnu stranu, čime se smanjuje rizik. Dodavanje inhibitora pomiče krivulju ravnoteže hidrata lijevo, također smanjujući rizik. Dodavanje inhibitora pomiče krivulju ravnoteže hidrata lijevo, također smanjujući rizik

INHIBITORS OVERVIEW

Inhibitors are added to the transport of natural gas to prevent or delay hydrate formation [8]. Commonly used inhibitors are ethylene-glycol and methanol. In Norwegian Hammerfest LNG center, inhibitors are transported by their own pipelines from the mainland and injected to the natural gas pipeline at the natural gas drilling point to ensure prevention of natural gas hydrate formation [10]. The mixture containing natural gas, water, ethylene-glycol and condensate is then transported from the ocean drilling platform to the coast with 143 km long pipeline. Those three mixture components are than taken apart for further processing by separation. The accurate dosage of monoethylene-glycol is very important due to the fact that during the transport it vanished away in both gas and condensed phase. Below, we categorize inhibitors based on their function and highlight results on alternative, environment friendly inhibitors. We will not discuss here other techniques of hydrate formation prevention that are in early stages of feasibility investigation, such as for example ethane partial pressure regulation in methane to force "competition" between multiple clathrate crystalline phases, acting as a crystallization barrier [4, 5]. Note that the cost of gas hydrate inhibitions represents 5% to 8% of gas total cost [11]. Therefore, return on investment for finding new cheap and environmentally friendly inhibitors, and complementary prevention processes, can be significant.

Thermodynamic inhibitors (TDI). Example: methanol and glycol (most commonly mono-ethylene-glycol). These inhibitors transfer the intermolecular interaction energy and change the thermodynamic equilibrium between water and gas molecules. They change chemical potential of liquid phase so that equilibrium dissociation curve is shifted to the lower temperatures and higher pressures. Alcohols and glycols form hydrogen bonds with water molecules in water solutions, and by this prohibit participation of water molecules in the hydrate formation process.

Thermodynamic inhibitors have several dissadvantages: they need to be used in high concentration to be effective (10-60 wt% in aqueous phase), they are toxic and environmentally unfriendly, and they incur considerable loses due to their volatility (contributing to high cost).

Low dosage hydrate inhibitors (LDHI). Known groups: *Kinetic inhibitors (KI); Antiaglomerants (AA).*

Kinetic inhibitors do not shift the gas hydrate formation equilibrium conditions but decellerate hydrate formation speed. They are coupled to the hydrate surface and slow crystal formation. They prevent pipeline pluging for longer time than the time of free water presence in pipelines. Dosage in low concentration can be effective (1 wt % in aqueous phase). Examples are molecules with good adsorbance at the polar surfaces of hydrate micro crystals - fatty acids, mixtures of grease alcohols and amines, and similar molecules with good water solubility, unhydrolized to insolvent parts. They form an outer casing prohibiting water bonding to hydrate crystal.

Their advantage is low cost, they are nontoxic and environmentally friendly, low dosage and low volume (21 wt %). However, they also have dissadvantages: they do not stop hydrate formation - just slow it, they are used just for temperatures lower than 10 ^{o}C, they are time dependent, and may interact with other chemical inhibitors (e.g., corrosion inhibitors) [11] .

Antiaglomerant inhibitors do not stop formation of gas hydrate crystals but prevent their agglomerations to form large hydrate plugs. Antiaglomerants cause emulsification of hydrates to hydrocarbon liquids and therefore they have no pressure and temperature limits unlike kinetic inhibitors. Their disadvantage is low effectiveness at the present time.

SEARCH FOR ENVIRONMENTALLY FRIENDLY SOLUTION

Formerly, hydrate formation inhibitors have been characterized and compared mainly by their price, volatility, solubility, dosage and sub-cooling temperature ΔT_{sub} (i.e., temperature difference between the hydrate equilibrium temperature and the operating temperature [8, 12]). Presently, the biodegradability issue is also of high importance, and new low dosage environmentally friendly solutions are being searched for.

In the North Sea region, inhibitors are categorized into three categories based on degradability percentage within a 28-day period: green (the best) > 60%; yellow 20-60%; red < 20% [13]. Parallel to usage of classical chemicals as inhibitors (like those mentioned above and all 19 listed in [8]), there is an ongoing research on employing naturally occurring antifreeze proteins – for example from Winter Flounder or other fish that live in or near to the polar region [8], or from longhorn beetle, such as Rhagium mordax [14]. This opens a promising new ways in search for an environmentally friendly inhibitor.

Note that structurally the gas hydrates differ from ice only in the configuration of neighbouring water molecules [4]. Based on such difference it appears that inhibition mechanism toward ice and gas hydrate formation is different. Antifreeze proteins allow the formation of nuclei, to which they bind, after which growth is inhibited. In hydrates the nucleation itself inhibited [14].

Note that antifreeze proteins (more generally called ice-structuring proteins (ISP)) are a diverse class of proteins that have been first identified in fish during 1950s and have since been found in cold-adapted bacteria, plants and insects [15].

Their specific activity towards preventing nucleation and grow of ice is a result of millions of years of evolution and thus not surprisingly they are quite effective KHI as well [8]. Such proteins, despite differences in structure, have common ability to adsorb to ice using specific ice-faces. They lower the freezing point of water as a result of increased local curvature of growing ice around the bonding of the adsorbent protein, resulting in a difference between freezing and melting points, phenomenon known as thermal hysteresis [16]. Example: The ice-structuring protein (ISP) from Rhagium mordax beetle is able to produce a thermal hysteresis of as much as 9°C, making it the most potent ISP found to date [17, 18]. In comparison, the ISP from fish produce thermal hysteresis of around 1-2 °C [18].

The number of studies on ice-structuring proteins has been limited because they have so far only been available in very limited amounts. However, with the recent developments in production with genetically modified bacteria and yeast, their available quantities will increase [8]. This will broaden research opportunity in search for an industrially usable, economical and environmentally friendly natural gas hydrate formation inhibitor.

CONCLUSION

Natural gas hydrate formation prevention in gas transport systems through use of inhibitor additives or other techniques plays an important role in flow assurance and pipeline clogging avoidance. This work summarizes advantages and disadvantages of current solutions based on thermodynamic, kinetic and antiaglomerant inhibitors. It highlights increasing emphasis on inhibitor environmental friendliness and biodegradebility. The work also encourages future studies on new types of inhibitors using antifreezing peptides (also called ice-structuring peptides) present in insects and fish.

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