METHANOL INSTITUTE

Methanol Safe Handling Fact Sheets

Prepared by:

Alliance Consulting International
San Diego, California, USA

Prepared for:

Methanol Institute
Arlington, Virginia, USA

Edition: 1.0

Date: October 2008

List of Fact Sheets

Methanol Chemical Fact Sheet

Chemical Formula and Properties

From a molecular perspective, the methanol molecule contains a single carbon, and is thereby the simplest alcohol derived from the alkane series of normal, saturated hydrocarbons: methane (CH_4), ethane (C_2H_6), and propane (C_3H_8). The two- and three-carbon alkane-derived alcohols are ethanol and propanol, respectively.

Systematic names for alcohols are extracted from the names of the corresponding alkane group by dropping the "-e" ending and adding "-ol." Common alcohols, methanol (CH_3OH), ethanol (C_2H_5OH), and 2-propanol (C_3H_5OH) have similar physical and chemical properties.

As the number of alkyl groups that comprise the alcohol increases, the length of the straight alkyl chain increases, the molecular weight of the alcohol molecule increases, and freezing and boiling point temperatures of the liquid phase increase.

Because alcohols are universally used to synthesize other more complex organic chemicals, it is common practice to indicate generalized alcohol structures using the capital letter "R," where "R" represents the alkyl or substituted alkyl groups. The chemical formula of alcohols is commonly written in shorthand in terms of their oxygen-containing functional group as follows: ROH.

The general formula for alcohols (R-OH) indicates a structural similarity between alcohols and water (H-OH). In fact, some properties of alcohols, and specifically of methanol, resemble properties of water. This is expected; the functional hydroxyl group in water and methanol (the hydroxyl group, OH^-) is centrally involved in chemical reactions involving these substances.

Table 1. Three Representative Alkane-Derived Alcohols

Molecular Structure	Systematic Name	Common Name	Liquid Freezing Point	Liquid Boiling Point
CH_3OH	Methanol	Methyl alcohol; wood alcohol[1]	-144ºF, -97ºC	149ºF, 65ºC
CH_3CH_2OH	Ethanol	Ethyl alcohol; grain alcohol[2]	-175ºF, -115ºC	172.4ºF, 78ºC

[1] Reference to methanol as "wood alcohol" is an artifact of an earlier time (prior to 1926). During this period, methanol was produced by destructive distillation of wood. The year 1926 marked the initial production of synthetic methanol in Germany.

Molecular Structure	Systematic Name	Common Name	Liquid Freezing Point	Liquid Boiling Point
CH_3CHCH_3 | OH	2-Propanol[3]	Isopropyl alcohol	-194.8ºF, -126ºC	206.6ºF, 97ºC

Chemical reactions involving alcohols typically fall into one of four classes:

1. oxidation-reduction reactions
2. addition reactions
3. elimination reactions
4. substitution reactions

Water and alcohols both react with alkali metals to produce hydrogen ($H_{2\ (gas)}$), a highly flammable, explosive gas. In the reaction with alcohol, the molecule that is analogous to the hydroxide ion (OH^-) in water-based reactions is called the alkoxide ion (RO^-) in alcohol-based reactions.

Water-based reaction: $HOH_{(liquid)} + Na_{(solid\ metal)} \rightarrow Na^+ + OH^- + H_{2\ (gas)}$

Alcohol-based reaction: $ROH_{(liquid)} + Na_{(solid\ metal)} \rightarrow Na^+ + RO^- + H_{2\ (gas)}$

Alcohols react with hydrogen bromide (HBr), hydrogen chloride (HCl), or hydrogen iodide (HI) in a substitution reaction to produce alkyl halides.

Reaction with hydrogen bromide: $ROH + HBr \rightarrow RBr + H_2O$

Reaction with hydrogen chloride: $ROH + HCl \rightarrow RCl + H_2O$

Reaction with hydrogen iodide: $ROH + HI \rightarrow RI + H_2O$

Concentrated sulfuric acid has a high affinity for combining with water. When alcohols with hydrogen (H) and hydroxyl (OH) groups on adjacent carbon atoms are treated with sulfuric acid, the alcohol is dehydrated to give the corresponding unsaturated alkene series molecule and water in an elimination reaction.

In summary, methanol is classified as a hazardous material by regulatory agencies as hazardous to life safety in the sense that it is flammable, toxic, reactive with alkali metals and strong oxidants, and 100% miscible in water. Because of these properties, methanol requires careful handling and storage, in all quantities and container types.

---

[2] Grain alcohol, or ethanol, is produced by fermentation of grain. Typically small amounts of methanol are produced along with ethanol. Because methanol is a potent poison, it is necessary to separate the methanol before consuming the ethanol.

[3] The numerical prefix that precedes “propanol” indicates the structural location of the hydroxyl group molecule relative to the alkane group molecule.

Chemical Synthesis of Methanol

Manufacture of synthesis gas was first established industrially by the so-called “water-gas” reaction in Germany in 1926. Prior to that time destructive distillation was the primary source of methanol. Since 1926, production processes have evolved through a number of configurations, moving from coal as a feed material with high-energy consumption requirements to a wide range of feedstocks for production of synthetic gas, reduced energy consumption, and improved yields.

Water gas reaction (1926): $C_{(coal)} + H_2O_{(steam)} \rightarrow CO + H_2$

Today, two methods are used to make synthesis gas from natural gas (methane): steam reforming and partial oxidation. The most predominant of these and the one described here is the method known as “steam reforming,” wherein steam is reacted with methane at 1652ºF (900ºC) by passing the gas phase through a tube of nickel oxide catalyst. Two reactions (Rxn) are possible. depending on operating conditions.

Rxn 1: $CH_{4\,(methane)} + H_2O_{(steam)} \rightarrow CO + 3H_2$

Rxn 2: $CO + H_2O \rightarrow CO_2 + H_2$

Process parameters must be controlled within a narrow operating envelope in order to drive Rxn 1 and suppress Rxn 2.

Raw, or crude methanol, is distilled to produce refined, high-purity product.

Earlier processes operated at pressures up to 350 bar (5000 psi) at 662ºF (350ºC) to drive the reaction. Newer processes rely on catalyst activity rather than pressure and temperature to drive the reaction.

Methanol Fuel Applications Fact Sheet

Given current world crude oil supply and demand, it is apparent that changes in fuels, vehicles, and driving habits are inevitable. It is likely that methanol will represent an option in that change.

In present usage, over 50% of refined petroleum is consumed as gasoline and diesel fuel to power internal combustion engines. Environmental, energy efficiency, and economic considerations aside, the technical feasibility of using methanol as a motor fuel to replace gasoline poses a fundamental challenge.

The feasibility of switching from a petroleum-based to a methanol-based economy is in large measure dependent on the abundance of and variety of sources for obtaining methane gas. A fundamental difficulty is the high energy necessary to generate hydrogen gas required for methanol synthesis using existing technology.

While direct substitution of methanol for gasoline is technically feasible, substitution will likely present some challenges as well. Below are some of the issues raised by this question.

Questions on Substitution of Methanol for Gasoline

Can methanol be used in existing internal combustion engines?

Methanol has a higher octane number than gasoline, which allows engine design to take advantage of higher cylinder compression ratios, which in turn increase engine efficiency. A fuel consisting of 100% methanol can deliver a 30% increase in engine efficiency. In other words, the engine is capable of delivering more work per unit of fuel. The heat of vaporization of methanol compared to gasoline is greater, thereby cooling the air in the engine to a larger extent than with gasoline. This in turn allows a leaner fuel air mixture, which may reduce air emissions. Methanol also has a lower combustion temperature which can help to reduce nitrogen oxide (NOx) emissions.

There are also challenges. Gasoline is a continuously boiling liquid over the temperature range of 70º to 430ºF (21º to 221ºC), which enable easy starting in cold weather. Methanol is a constant boiling liquid with a boiling temperature of 150ºF (65ºC), thus making methanol-fueled automobiles more difficult to start in cold weather. However, the flash point of methanol is 52ºF (11ºC) compared to that of gasoline – approximately 113ºF (45ºC). Difficulty associated with cold weather starting is overcome by addition of 15% gasoline: i.e., M-085 fuel.

Is the heat of combustion of methanol similar to that of gasoline?

The heat of combustion of methanol is about 60% that of gasoline. Hence, while efficiency is better, the energy derived from the fuel is somewhat less. A generally used multiplier of 1.65 gallons of M-85 fuel is used to provide the same energy content or driving range as that of a gallon of gasoline. The advantage of increased efficiency is substantial.

Will currently used alloys and synthetics withstand extended contact with methanol?

In general, integrity of existing materials will not be compromised. Exceptions to this are lead, magnesium, and aluminum, as well as certain gasket, belt, and hose materials, which may be subject to mild corrosion attack and/or long-term degradation. In order to preserve the strength-to-weight advantage provided by aluminum and magnesium engine components, it may be necessary to add corrosion inhibitors to the fuel to protect these materials. This is substantially the same as currently used proprietary engine performance gasoline additives. Likewise, some synthetic materials may need to be substituted prior to using 100% (i.e., neat) methanol as fuel in an automobile designed to burn gasoline.

Can methanol be distributed through existing terminal and station-based dispensing systems?

Yes, provided fuel is protected from absorbing water and/or corrosion inhibitors are added to the fuel. Dry methanol is compatible with commonly used ferrous alloys. Wet methanol can be corrosive to these alloys. This is substantially the same issue as that for automobile fuel system and engine components. This issue is readily eliminated by adding corrosion inhibitors to the fuel as is done currently with gasoline and by replacing gasket and hose materials with currently available alternatives.

Are the toxic and fire hazards associated with methanol acceptable to the public?

Toxicity hazards upon exposure to methanol are greater than those of gasoline; however, exposure in the event of a spill is less likely than with gasoline due to the low vapor pressure of methanol compared to gasoline. Fire and explosion hazards are substantially less than those of gasoline. The lower flammability limit for gasoline is about 1.5 vol% in air. The lower flammability limit of methanol is 6 vol%, four times that of methanol. The combination of lower vapor pressure and higher lower flammability limit combine to make the likelihood of ignition of vapor from a methanol spill much less than the likelihood of ignition of vapor from a gasoline spill. Also, small methanol spills can be diluted to non-hazardous concentrations with water spray, an additional advantage over gasoline.

The objective of product stewardship and the purpose of this Fact Sheet are to educate fuel handlers, automobile repair facilities, and the driving public regarding precautions and safe handling procedures for methanol. These procedures are substantially the same as those for gasoline: “Do not breathe the vapors; do not swallow the liquid, and do not allow liquid to touch your skin.” Motorists have long been protected from exposure to benzene and other harmful organic compounds in gasoline. The public can likewise be protected from exposure to methanol.

Direct Substitution as an Automobile Transportation Fuel

Several tactics are anticipated for use of methanol as automobile transportation fuel:

- direct substitution of methanol for gasoline
- direct substitution of methanol as a blend with gasoline
- direct substitution as a methanol-derived additive to gasoline that improves fuel economy, reduces tail pipe emissions, and expands the gasoline pool

Each of these strategies is technically feasible and is capable of benefiting motorists. The task of educating the public and the responsibilities of methanol stewardship belong to you, methanol producers and handlers.

Product Stewardship Implementation Fact Sheet

Implementing product stewardship in an organization involves all levels of management and employees. Follow the ten PSPs and make them a part of everyday business activity. The outline below provides a brief how-to guide on implementing each step of the PSPs.

Implementation Plan

1. **Establish Leadership and Accountability.**

   Senior leadership should establish a policy covering product stewardship. Ideally, this should be integrated into the company's overall policy statement. Adequate resources in the form of skilled personnel should be assigned to establish, review, and attain each product's stewardship performance goals. Financial resources should also be committed to sufficiently support plans to roll out and continuously improve product stewardship. Integrate product stewardship responsibilities across the company and involve applicable groups in procurement, marketing, and sales decisions. Leadership needs to:

   - Create a culture of openness and willingness to change,
   - Address poor product stewardship performance and resolve difficult issues,
   - Change performance goals or a product management strategy,
   - Modify support resources, and
   - Encourage all employees to monitor and respond to external changes or challenges impacting its products or marketing strategies.

2. **Establish and maintain a database of information on environment, health, and safety hazards pertaining to new and existing products.**

   Ensure that the company has at its disposal the most complete and current set of EH&S information available about its products. To accomplish this, the company must establish a database of EH&S information that is continuously updated and maintained. Information in the database may include the following:

   - Product testing and registration data;
   - Compliance with legislation and regulations regarding the product(s) that might affect marketing, storage, environment, etc.;
   - Customer and distributor surveys and record of visits;
   - Ongoing government agency work related to toxicology and/or health effects of the product;
   - Technical reviews of products and similar products; and
   - Disposal restrictions and risks.

Leadership should designate a responsible person / party for maintaining the database and collecting information from internal and external sources. The database should be accessible to employees with product stewardship risk assessment responsibilities.

3. **Use a risk-based approach to select suppliers and product raw materials and components.**

   A process is required to assess raw materials and select those materials having an acceptable level of risk. During raw material component selection, consider EH&S hazards to minimize product risk throughout its life cycle. Elements to consider include packaging choices, inherent properties of the material, environmental impact, and contaminants and impurities. When looking at suppliers, consider the quality and EH&S management systems of the supplier and the potential to affect product and employee safety, cause public concerns, or negatively impact the environment. Actively seek input and advice from suppliers on their product and risk management experience to build both business relationships and an understanding of the commitment to product stewardship.

4. **Use the EH&S information collected to extend the product assessment review across the full product commercial life cycle.**

   It is important to assess the risk of an existing, new, or reformulated product, or group of products, during storage, handling, and disposal while within company control and then beyond the point of sale. Examine the EH&S risk of existing, new, or reformulated products over their life cycles by conducting a Life Cycle Analysis (LCA). Evaluate the health and safety hazards and exposures of products using existing EH&S information, or Product Risk Characterization (PRC) tools. Use the PRC tool to prioritize products with respect to risk. It is critical that there is a process to re-assess and re-characterize product risk.

Life Cycle Analysis (LCA):

Life Cycle Analysis (LCA) consists of three phases:

- Phase I – Life Cycle Inventory (LCI): Establish a quantitative inventory of energy use and environmental burdens / releases associated with any specific product.
- Phase II – Analysis: Assess and analyze the energy use, burdens, end use risk, and environmental fate relative to products and processes.
- Phase III – Action: Implement action to improve energy use and mitigate EH&S impact.

5. **Establish a security plan specifically directed at protecting all relevant stakeholders, including the public, from the deliberate misuse of company products or supplies.**

   The company must clearly define security responsibilities for managing the product stewardship aspects of its products. Assign a product security priority to each product based on its inherent / end use security hazards and the product exposure. Priority levels can be categorized into high, medium, and low. Develop a security risk management plan for high- and medium-priority products. The security plan should address the deliberate misuse of company products and raw materials as a result of terrorism, activism, vandalism, and malicious acts. The plan should be specifically directed at the protection of company employees, nearby neighbors, and second parties from the potential impact of the threat scenarios.

6. **Identify, document, and implement safety, health, and environmental risk-management strategies.**

   The key to mitigating product risk is to understand the various components of product risk that arise across the product life cycle and, on an iterative basis, to identify and implement action to control or reduce the highest potential risks. A thorough management of change process that considers the effect on product risk will ensure the ongoing assessment of product risk. Procurement, Sales and Marketing, Manufacturing, Government Affairs, and R&D need to agree on where risk is acceptable and where mitigation and controls are most needed. Consider categorizing risk into three levels: unacceptable, acceptable with controls, and acceptable as is / exceeds standards.

Unacceptable Risk	Immediate and often long-term strategies for mitigation are required. These are highest priority to address changes and seek improvements.
Acceptable With Controls	Verify that controls are in place, and monitor performance. Without continued focus and ongoing control efforts, incidents may occur.
Acceptable As Is / Exceeds Standards	Continue to do what is reasonable and required. If others can benefit from your experience, seek to share with others. This industry-leading risk management practice may be communicated in “Best in Class” recognition or awards.

   Once the risk has been identified, a risk mitigation strategy should be implemented. Companies should try to balance reactive and proactive product risk management strategies.

7. **Incorporate product stewardship education into existing employee training programs throughout the company, and provide additional training to employees who have product stewardship responsibilities.**

   Ensure that employees are trained and knowledgeable on the proper handling, use, recycling and disposal of products. Employees who are involved with products after sale and delivery should have the training and education necessary to:

   - Understand product and packaging hazards and identify product deviations;
   - Know and apply proper use, handling, reuse, recycling, and disposal procedures;
   - Recognize adverse health or environmental effects;
   - Encourage customers to influence their downstream customers and product users in the standards of Responsible Care; and
   - Be alert to the customers’ comments or perceptions, and take action to respond to product-related issues and concerns.

   The company should establish a process where employees, especially Sales and Marketing personnel, can feed back information on new use, identified misuses, or adverse effects for use in product risk characterization in an efficient and effective way.

8. **Reach out to direct product receivers and second parties, and inform them of product stewardship practices.**

   Companies are expected to extend the principles of product stewardship to customers and other parties. The long-term result of implementing this practice is improved EH&S performance. Companies can provide information and training on EH&S issues to second parties, including direct product receivers. On an ongoing basis, actively seek and document feedback from customers and distributors on their end use and risk management experiences with the product. External advisory committees may be established to promote this dialogue. Establish minimum standards and selection criteria for distributors and direct product receivers, and assess performance against this standard. Repeat information sharing on a regular basis, and follow up routinely to reinforce EH&S information, provide additional training, and/or invite stakeholders to observe your systems or practices in place, etc.

9. **Consider the concerns of those not in the direct product flow to help reduce both real and perceived hazards.**

   Those not in the direct product flow may have thought about product stewardship efforts from a different perspective. This input may assist the company to become more effective. Actively seek feedback from relevant stakeholders, such as government bodies, neighbors, and environmental groups. Involve R&D early with customers and their customers to assist in product design and to minimize potential difficulties in use, handling, recycling, and disposal. Participate in industry organizations and local, national, and international public forums as a way to both give and receive the benefit of experience. Be aware of international agencies, websites, standards bodies, and forums where product stewardship and risk management of chemical products information may be in development, available, or exchanged.

10. **Measure how well the product stewardship practices are implemented.**

    Performance indicators tracked on a regular basis will demonstrate that the key elements of product stewardship are “alive and well.” The metrics can be used to identify and implement changes to promote continuous improvement. Performance indicators need to be defined. They can be either activity based or outcome based. Activity-based indicators measure the progress of product stewardship activities compared to defined targets. Outcome-based indicators measure anecdotal or quantitative absolute results. Senior leadership should integrate product stewardship performance metrics and goals into employee assessment processes, and take action to address poor performance, change performance goals, modify support resources, or change a product commercial strategy. Companies should assess the status of their product stewardship activities at a similar time each year, as well as randomly. Continuous improvement may require further training, a transfer of resources, or management insisting on accountability for agreed commitments.