



# MTBE / ETBE Transport over inland waterways

Guidelines

UPDATE MARCH 2012



The European Fuel Oxygenates Association



# EFOA

## EUROPEAN FUEL OXYGENATES ASSOCIATION

- Founded in 1985, EFOA is a non-profit, technical organisation.
- EFOA is a sector group of CEFIC, the European Chemical Industry Council.
- Its role is to represent the European Fuel Ether industry in a wide variety of technical and government initiatives.
- EFOA is recognised by the European Commission as a stakeholder on fuel quality and biofuels.
- We have 11 members representing the majority of the European ether capacity.



### Our Mission

- EFOA is dedicated to the promotion of ethers as fuel components towards a cleaner and sustainable future.

## PREAMBLE 2<sup>ND</sup> EDITION

**Fuel ethers are oxygen containing petrol blending components. Their high octane ratings and clean burning characteristics help mitigate the problem of air pollution. They also allow for quicker and easier bio-ethanol use and deliver additional CO<sub>2</sub> emission savings.**

Ether usage varies across Europe but at the current time they represent somewhere between 3 & 4% of the EU petrol pool (about 5 million tonnes).

Apparently random short-term concentration peaks of fuel-ethers MTBE (Methyl-tert-Butyl ether) and ETBE (Ethyl-tert-Butyl ether) were analysed regularly throughout the year in the Rhine at the International Monitoring station at the Dutch-German border in Bimmen-Lobith and other measuring stations. The peaks last less than 24 h and vary in severity typically up to 15 µg/l, far below any health risk but in a range of magnitude causing a possible risk of taste and odour tainting of drinking water produced from Rhine water.

EFOA led analysis of the data and investigations about possible sources resulted in indications that barges transporting the substances on the Rhine are the probable source, especially after they have unloaded the product and contain liquid and vapour residues of the products only. Deeper analysis of the measured concentration data have demonstrated that most of the incidents with higher concentrations are happening in the Rhine from Duisburg to just north of Wesel.

EFOA believes that this problem can be solved by raising awareness of the properties of fuel ethers and the need for correct product handling and residue management. For this reason we have prepared the following Code of Best Practice when transporting fuel ethers by barge.

This version is a revision of the original March 2008 edition. As well as including the update from October 2009 this version also includes two recent positive developments in the control of barge product residues.

In June 2010 the International Safety Guide for Inland Navigation Tank-barges and Terminals (ISGINTT), the result of a project where all stakeholder groups involved in tank-barge operations where involved, was released with the purpose to improve safe transport of dangerous goods at the interface of inland tank barges with shore facilities.

While the ISGINTT guide provides detailed information about physical-chemical hazards and some toxicological hazards the EFOA Code of Best Practice addresses more environmental aspects, especially the releases in the Rhine.

Also after an extended ratification process the CDNI treaty about waste from barges came into force at the end of 2009 (Übereinkommen über die Sammlung, Abgabe und Annahme von Abfällen in der Rhein- und Binnenschifffahrt, which is stored by the Central Commission for Navigation on the Rhine CDNI). The provisions for avoiding loading residues and the mandate to install treatment stations also for loading residues is welcomed by EFOA.

# DISCLAIMER

**In order to address the problem of incorrect product handling and residue management EFOA has developed this code of best practice (CoP) covering the loading and unloading of fuel ethers from barges.**

The CoP is based on the experience and expertise of the EFOA member companies in handling ETBE and MTBE.

Whilst it is intended to be a summary of best practice, it is recognised that other quality systems and processes may be equally effective in achieving the desired level of environmental protection.

The systems described in the CoP are entirely voluntary. Individual companies may decide to apply the CoP either in full, or in part, or not to apply it at all, according to their own judgment.

In addition, the information included in the CoP is provided without prejudice.

The CoP is freely available on our internet site <http://www.efoa.org>.

# CODE OF BEST PRACTICE (CoP) COVERING THE LOADING AND UNLOADING OF FUEL ETHERS FROM BARGES

**The purpose of this code of best practice is to minimise the vapour and liquid residues that are generated during the shipment of MTBE and ETBE in order to reduce the potential for their release into water.**

It is designed with the input of the barge industry and is aimed at barge and oil logistics personnel. Producers and users of the substances need to fully brief their logistic partners with regard to suitable quality assurance systems. By doing so they would help guarantee that inappropriate handling of transported substances will be avoided.

All operations must be conducted in accordance with the relevant national regulations and the requirements of international regulations (for example ADNR / ADN 2011 regulations) as appropriate. The recommendations from ISGINTT guide should be observed as well.

## 1 Barge selection

EFOA suggests that producers and consumers of ethers consider the following options for enhancing their quality assurance systems.

- All consignors involved in the transport of MTBE/ETBE should undertake inspections of barges or participate in a common inspection scheme (e. g. European Barge Inspection Scheme). This will enable each consignor to satisfy himself of the suitability of barges employed and ensure that appropriate safety standards are maintained.
- Greater control over the types of barges used to transport ethers may be achieved by taking full control of the logistics chain. Companies should therefore think about what terms and conditions of sale would best deliver adequate control.

### **Selection of barges should take into consideration the following points:**

- Barges with previous cargo MTBE or ETBE are preferred. Implementing a policy of dedicated barges for ether shipments will also bring benefits. Not only will it minimise product residues by eliminating the need for cleaning and degassing, it will reduce the number of personnel along the supply chain who handle ethers thus allowing for greater levels of training.
- Efforts should be made to also ensure that the following cargo will be compatible with MTBE and ETBE (see No. 5).
- Barges are preferred that have separate ballast and product tanks, as well as vapor return- and efficient stripping facilities according to the latest technical standards.
- Barges equipped with deep well pumps or equivalent are preferred. Double-hulled barges with diamond shaped tanks are among the vessels which use these pumps in order to minimise product residues.
- Barges with low-emission sampling points are preferred.
- Possibility of efficient line draining should be available on the barge.
- The use of barges with authorised slop tanks for carrying loading residues should ensure better waste management.

## 2 Loading

These operations should be carried out according to the latest edition of the ADNR-checklist as well as the ISGINTT guide with information for volatile substances with flash points below 60°C.

Sampling after loading are to be carried out according to the latest available ADNR-rules, by taking into consideration UN regulated waiting time between end of loading and sampling. Sampling of ships tank should be executed with lowest emission possible, ideally via a closed sampling system. Loading lines should be emptied into ship product tanks to avoid emissions or spillages as recommended in the ISGINTT guide.

The loading location should be able to handle barge vapour residues. Closed loading systems are preferred, i.e. vapour return facilities, incineration or vapour absorbing systems should be considered. When the previous cargo was incompatible then the barge should be presented clean, dry and odourless and at atmospheric pressure. **Any necessary cleaning should not result in a release of the substances to water.** Contaminated water must be treated according to the regulations.

Barges with previous cargo MTBE/ETBE or compatible product should be accepted, without intermediate cleaning, but liquid free. This would minimise the risk of unintended releases.

The cargo should be accompanied by EFOA handling recommendations (see Annex 1). We recommend that the following UN numbers are used; for MTBE UN2398, hazard class 3, packing group II, for ETBE UN1179, hazard class 3, packing group II.

As recommended by the ISGINTT guide, a safety data sheet should be available before loading and go along with the travelling barge.

## 3 Unloading

These operations should be carried out according to the latest edition of the ADNR-checklist.

Vapour handling: barges should either to be connected to a vapour return line of the land tank in to which the product is to be discharged or land tank to be connected to an off-gas handling system i.e. vapour return facilities, incineration or vapour absorbing system.

Resting of barges: unloading facilities should always provide installations or appropriate connections to use the efficient stripping system of barges. This is in order to ensure that barges product tanks can be rested and are liquid free as far as the latest technical standards allow.

**The provisions from the ISGINTT guide about Efficient Stripping and Draining of Cargo Tanks and Line draining should be observed:**

In general, all cargo loaded should be completely discharged at the unloading terminal. A terminal should have arrangements to receive drainings and should effectively cooperate in this matter.





Arrangements for facilitating draining of the barge's tanks can comprise of:

- Suction by a terminal's pump.
- Discharge by a barge's pump (stripping pump).
- Purged by inert gas or air through a stripping line.

For these purposes recommended interface system on the barge side are

- EN 14 420-6 DN 50 (male connection)
- EN 14 420-7 DN 50 (male connection)

It is recommended that terminals are equipped with one of the above mentioned female connections.

If a terminal is equipped with self sealing couplings the terminal should provide appropriate connectors for the previously mentioned male connectors.

When engaged in efficient stripping, the tanker must be able to provide a liquid pressure of at least 300 kPa (3 bar). The back pressure required to achieve product flow ashore should not exceed 300 kPa (3 bar).

On completion of discharge, the tanker's cargo deck lines should be drained into an appropriate tank and then discharged ashore or into a remainder (slop) tank.

When draining is complete, and before hoses or marine arms are disconnected, the barge's manifold valves and shore valves should be closed and the drain cocks at the barge's manifold should be opened to drain into fixed drain tanks or portable drip trays.

Cargo manifolds and marine arms or hoses should be securely blanked after being disconnected. The contents of portable or fixed drip trays should be transferred to a slop tank or other safe receptacle ashore.

In case of remaining loading residues the CDNI treaty demands that either the charterer or the land installation have to advise to the barge where to treat the residue and to pay for the costs. Therefore it is in the interest of all parties to use the efficient stripping system.

**ⓘ It is very important that receivers ensure sufficient time and tankage is available to achieve complete unloading.**

Receivers should make every effort to remove all liquid product from the barge on-shore. Pumps and lines must also be emptied on-shore as this minimises the residual material the barge has to handle. See section on cleaning and disposal of wastes.

According to CDNI a certification of unloading must be signed by the barge crew and unloading station.



## 4 Transit

MTBE and ETBE vapours are heavier than air. Therefore in case of release near the river surface the vapours will naturally go towards the river. Also in comparison with typical organic substances the water solubility for ethers is relatively high (e.g. 42 g/l for MTBE). Thus in transit, ideally vapours should not be vented. If there is no other option, venting must be done in accordance with the ADNR and the EC-VOC-Directive (94/63). In addition it is recommended to:

- Not vent when humidity levels are high e.g. raining or snowing
- Vent vapours above the deck level to minimise risk of water contact

Ballasting should always be restricted to dedicated ballast tanks. No ballast should be taken into or released from product tanks.

During transport no product movements to be made i.e. emptying of lines, swapping of product between tanks or other activities concerning ship lines, tanks, pumps etc.

## 5 Previous Cargoes and Cleanliness

Annex 2 details a list of compatible cargoes with ETBE and MTBE.

The tank that carries MTBE/ETBE shall not have carried substances that result in dangerous reactions/effects. Examples of such substances can be found in the EPA's Chemical Compatibility Chart or the US Coast Guard compatibility charts (Title 46, Code of Federal Regulations, part 150, October 1995).

Tanks to be loaded with MTBE/ETBE shall not be cleaned with materials which are reactive with ethers e.g. strong acids or oxidising agents (consult material safety data sheet: [see annex 3](#)).



## 6 Cleaning and Disposal of Wastes

In all circumstances barge product tanks should be drained and free of liquids after discharging by using an efficient stripping system of the barge in connection with the discharging installation to be proved by an independent inspector.

Any cleaning of barges tanks, as well as the disposal of any product residues and wash waters must be done in a proper form at authorised disposal facilities and according to the applicable laws.

It is strongly recommended that operations should be organised to minimise waste levels.

### → Literature

ISGINTT GUIDE	INTERNATIONAL SAFETY GUIDE FOR INLAND NAVIGATION TANK BARGES AND TERMINALS	<a href="http://WWW.ISGINTT.ORG/300-DE.HTML">HTTP://WWW.ISGINTT.ORG/300-DE.HTML</a>
CDNI treaty		<a href="http://www.ccr-zkr.org">http://www.ccr-zkr.org</a>
ADNR /ADN 2011	Regulation about transport of dangerous goods on the Rhine	<a href="http://www.ccr-zkr.org/">http://www.ccr-zkr.org/</a> <a href="http://www.unece.org">http://www.unece.org</a>



# ANNEX 1

## ETHER: HANDLING RECOMMENDATIONS FOR WATER PROTECTION

Un-Nos: 2398, 1179

Addendum to ADNR instructions

January 2011

### DANGEROUS GOOD

**Methyl-tert-Butyl-Ether (MTBE), UN-No. 2398,**  
**Ethyl tert-Butyl-Ether (ETBE), UN-No. 1179,**  
 Colourless liquids with strong turpentine-like odour and taste

### NATURE OF HAZARD FOR WATER

- - Partly soluble in water with limited evaporation from water.
- - Removal from water is difficult.
- - Slow biodegradation.
- - Strong odour and taste even by very small concentrations means hazards to drinking water production and purification plants.

### AVOIDING SPILLS

- - Any risk of spill in water has to be avoided.
- - Transport of MTBE compatible loads only, without tank cleaning where ever possible.
- - Degassing in atmosphere not during rainfall.
- - Condensate of degassed MTBE should not rinse in surface water (1000 m<sup>3</sup> tank may contain 150-200 kg ether vapour after unloading without degassing).
- - Washing water from tank cleaning operations to be treated in authorized treatment stations.
- - Avoid ballasting in product tanks. Ballasting only in completely cleaned product tanks from both vapour and liquid MTBE. Ballast water from product tanks which were not completely cleaned before ballasting has to be treated in authorized treatment stations.

### IN CASE OF SPILLAGE

- - Do not allow entrance in water.
- - Take up mechanically or with an absorbent material.
- - To be disposed of to authorized stations.

 EMERGENCY CALL 112

### FURTHER INFORMATION



Regarding other hazards please refer to Safety data Sheet or ADNR.

## ANNEX 2

INSTRUCTIONS FOR PRODUCT LOADINGS OF ETBE/ MTBE	
accepted preload	actions needed *
Gasoline, max. 50 ppm Sulphur	1
Gasoline, max. 10 ppm Sulphur	1
Diesel, max. 50 ppm Sulphur	2
Diesel, max. 10 ppm Sulphur	2
Heating Oil, undyed	2
Heating Oil, dyed	2
Jet A-1 / Kerosene	6
AVGAS 100 LL	2 + 5 or 4 + 5
Middle distillate -components	2
Gasoline-Components	1
Light distillate fuel (LDF)	2
Alcohols (Methanol, Ethanol)	1
FAME (Bio-diesel)	2
TBA (t-butyl alcohol)	1
MTBE/ ETBE	1

\* see barge remarks



### INSTRUCTION FOR PRODUCT CHANGE BY MINERAL OIL PRODUCTS AND -COMPONENTS FOR INLAND WATER-, COASTER AND SEA-GOING SHIPS

In accordance with the International Transport Guidelines the degassing of barges transporting dangerous goods (ADNR – Paragraph 7.2.3.7) is authorized under certain conditions.

As of 1<sup>st</sup> January 2006 the degassing (ventilation) of gasoline is forbidden in Germany as per the 20<sup>th</sup> Emission Protection Rules (BImSchV – UN No. 1203; VK 91, VK 95 and VK 98).

For the above reasons after transporting petrol a barge should not be vented. If venting is unavoidable it must be done with a certified efficient stripping system and this system must have a current valid certificate.

Nbr	Required action	Remark
1	<b>Normal emptying</b>	Tanks and pipelines have to be drained and empty. Attention should here be paid to dead ends, lows, sample lines and deck lines.  No special cleaning measures are necessary.
2	<b>Special emptying</b>	Ship has to be equipped with a certified «efficient stripping system (ESS)».  Tanks, pipelines, pumps and filters have to be completely emptied with an «effective stripping system». This must be documented in the cargo journal.  Or, where allowed, by A1-products as pre-loading:  Tanks, pipelines, pumps and filters have to be empty and gas free.  «Gas free» means: certificate of one expert mentioned in the ADNR, with the remark «safe for entry but not for fire activities».  Or by A3-products as pre-loading:  A certificate of a surveyor must confirm that the ship is cleaned of residues. The disponent has then to decide if a product change is possible with the asserted residue quantity. In case of need ckeckings and analyses for all three cases can be requested.
3	<b>Not recorded</b>	
4	<b>«Dedicated»</b>	Direct loading only if same pre-loading.
5	<b>AVGAS 100 LL</b>	For the transport of AVGAS 100 LL only coated ships are allowed.  After stripping of the previous loading complete emptying has to be guaranteed by an independent surveyor.
6	<b>Not permitted</b>	A direct product change is not allowed. Either «Dedicated» (see § 3) or another product, compatible with the list.

INSTRUCTION FOR PRODUCT CHANGE BY MINERAL OIL PRODUCTS AND -COMPONENTS FOR INLAND WATER-, COASTER AND SEA-GOING SHIPS															
LOADING	PRE-LOADING .....														
	Gasoline max. 50 ppm Sulphur	Gasoline max. 10 ppm Sulphur	Diesel max. 50 ppm Sulphur	Diesel max. 10 ppm Sulphur	Heating Oil undyed	Heating Oil dyed	Jet A-1 / Kerosene	AVGAS 100 LL	Middle distillate, -components	Gasoline Components	Light distillate fuel (LDF) without bio parts	Ether (MTBE, ETBE)	Alcohols (Methanol, Ethanol)	FAME (Bio-diesel)	TBA (t-butyl alcohol)
Gasoline, max. 50 ppm Sulphur	■	1	1	1	2	2	2	2	2	1	2	1	1	2	1
Gasoline, max. 10 ppm Sulphur	1	■	1	1	2	2	2	2	2	1	2	1	1	2	1
Diesel, max. 50 ppm Sulphur	2	2	■	1	2	2	2	2	2	2	2	2	2	1	2
Diesel, max. 10 ppm Sulphur	2	2	1	■	2	2	2	2	2	2	2	2	2	1	2
Heating oil, undyed	2	2	1	1	■	1	1	2	1	2	2	2	2	2	2
Heating oil, dye	2	2	1	1	1	■	1	2	1	2	2	2	2	2	2
Jet A-1 / Kerosene	6	6	2	2	2	6	■	6	6	6	6	6	6	6	6
AVGAS 100 LL	2+5 or 4+5	2+5 or 4+5	2+5 or 4+5	2+5 or 4+5	2+5 or 4+5	2+5 or 4+5	2+5 or 4+5	■	2+5 or 4+5	2+5 or 4+5	2+5 or 4+5	2+5 or 4+5	2+5 or 4+5	2+5 or 4+5	2+5 or 4+5
Middle distillate -components	2	2	1	1	1	1	1	2	■	2	2	2	2	2	2
Gasoline-Components	1	1	1	1	2	2	2	2	2	■	2	1	2	2	1
Light distillate fuel (LDF)	2	2	1	1	2	2	2	2	1	1	■	2	2	2	1
Ether (MTBE, ETBE)	2	1	2	1	2	2	2	2	2	2	2	■	1	2	1
Alcohols (Methanol, Ethanol)	2	2	2	2	2	2	2	2	2	2	2	1	■	2	1
FAME (Bio-diesel)	2	2	1	2	2	2	2	2	2	2	2	2	2	■	2
TBA (t-butyl alcohol)	1	1	1	1	2	2	2	2	2	2	2	1	1	2	■

Description of numbers see annex 2, page 12.

■ = «dedicated»



# ANNEX 3

## Material Safety Data Sheet

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Safety data sheets or product safety summary reports for ETBE and MTBE can be found on the website of any supplier of fuel ethers.

Web links to some examples are given below :

### ETBE

<http://www.lyondellbasell.com/Products/ByCategory/refining/EthylTertiaryButylEther/TechnicalInformation/>

<http://www.nesteoil.com/default.asp?path=1,41,535,547,555,12751>

[http://chemicals.sabic.eu/datasheets/safety\\_datasheet/\\_en/](http://chemicals.sabic.eu/datasheets/safety_datasheet/_en/)

### MTBE

<http://www.lyondellbasell.com/Products/ByCategory/refining/MethylTertiaryButylEther/TechnicalInformation/>

<http://mtbe.evonik.com/product/mtbe/en/Pages/default.aspx>

[http://www.eni.com/en\\_IT/products-services/other-products/cleanfuel/mtbe/mtbe.shtml](http://www.eni.com/en_IT/products-services/other-products/cleanfuel/mtbe/mtbe.shtml)

[http://chemicals.sabic.eu/datasheets/safety\\_datasheet/\\_en/](http://chemicals.sabic.eu/datasheets/safety_datasheet/_en/)







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*EFOA is a sector group of Cefic,  
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