



Automotive Fuel Oxygenate Issues 机动车燃料增氧剂问题

U.S. Grains Council
美国谷物协会

December 2016
2016年12月

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Why Use Oxygenates ?

为何使用增氧剂？

- More complete combustion to CO₂ and water because oxygen is part of the fuel.
氧气助燃使燃烧更加充分，产生二氧化碳和水
- Complete combustion reduces carbon monoxide (CO) and ground-level ozone (O₃)
充分燃烧减少了一氧化碳 (CO)和地表臭氧 (O₃) 的产生
- Examples of oxygenates are:
增氧剂包括：
 - Ethanol 乙醇
 - Methyl tert-Butyl Ether (MTBE)
甲基叔丁基醚(MTBE)
 - Ethyl tert-Butyl ether (ETBE)
乙基叔丁基醚(ETBE)
 - Tertiary Amyl Methyl Ether (TAME)
三戊甲基醚(TAME)
 - Tertiary Butyl Alcohol (TBA)
叔丁醇(TBA)



Oxygenate Mandate in the United States

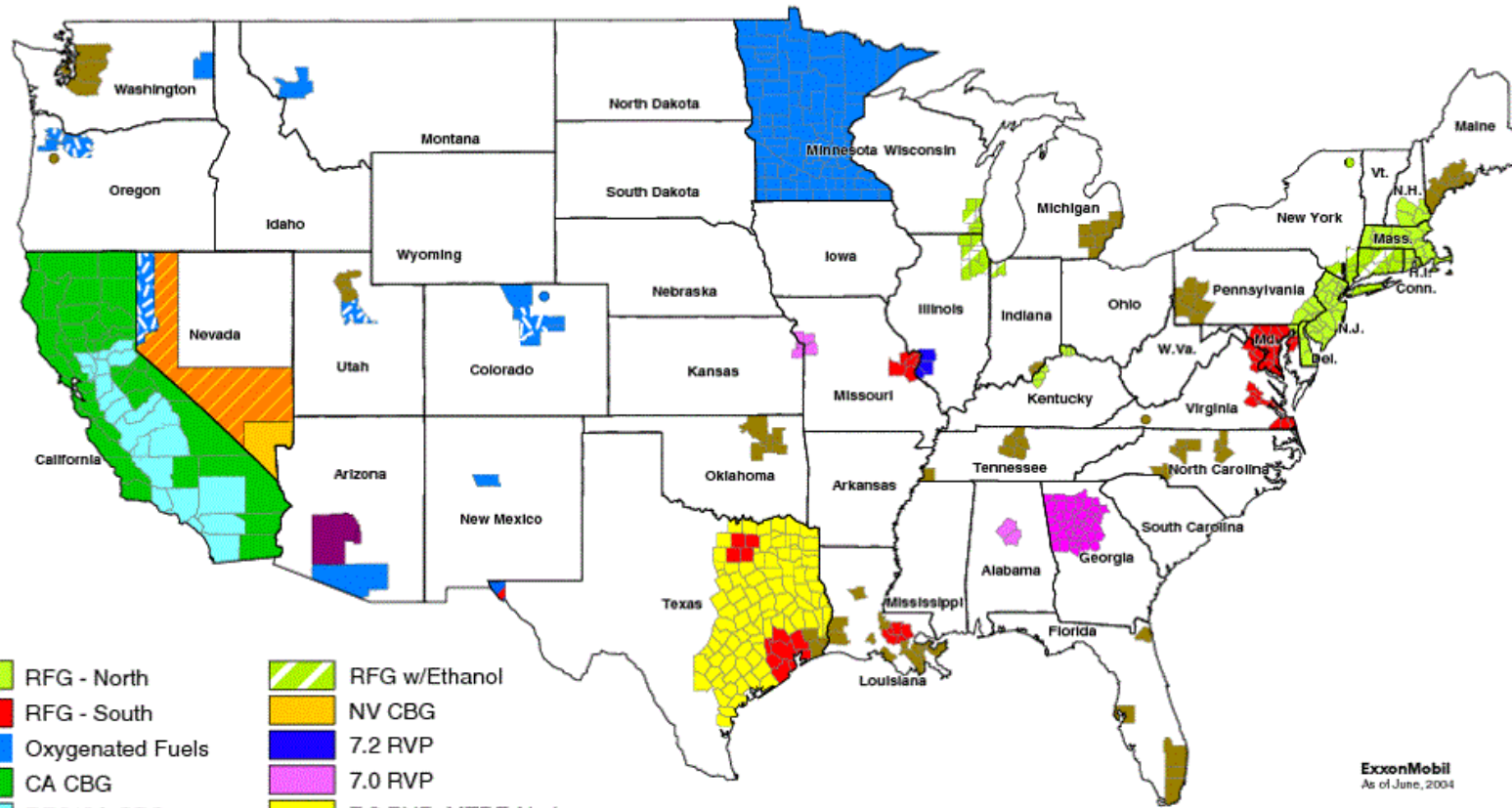
氧化添加剂在美国的强制使用

- Since 1992 fuel with 2.7% oxygen required during cold months in cities with high carbon monoxide.
1992年以来，一氧化碳排放较高的城市被要求寒冷月份应在燃油中添加2.7%的增氧剂。
- From 1995 to 2005 Reformulated Gasoline with at least 2% oxygen required in cities with high ground-level ozone.
从1995年到2005年，地表臭氧浓度较高的城市被要求使用至少添加了2%增氧剂的新配方汽油。
- Ethanol was the oxygenate of choice in the Midwest, but MTBE was used in most other areas for economic reasons and its blending characteristics.
中西部地区选择乙醇作为增氧剂，但多数其他地区使用甲基叔丁基醚(MTBE)，主要是出于经济原因以及其良好混配性的考虑。



美国各地汽油使用要求

U.S. Gasoline Requirements



- | | | | |
|--|-------------------|--|---------------------------|
| | RFG - North | | RFG w/Ethanol |
| | RFG - South | | NV CBG |
| | Oxygenated Fuels | | 7.2 RVP |
| | CA CBG | | 7.0 RVP |
| | RFG/CA CBG | | 7.8 RVP, MTBE-No Increase |
| | AZ CBG | | 7.8 RVP |
| | Oxy Fuels/7.8 RVP | | 7.0 RVP, 30 ppm S |
| | Oxy Fuels/7.0 RVP | | 300 ppm S |
| | Conventional | | |

ExxonMobil
As of June, 2004

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Renewable Fuels Standard in the US

美国可再生燃料标准

- A volume requirement for renewable fuels established.
确立了可再生燃料使用量的要求
- Automobile engine technology improved combustion efficiency.
汽车发动机技术发展提高了燃烧效率
- Oxygenate requirements removed for reformulated gasoline in 2006.
2006年去除了新配方汽油的增氧剂要求
- However, MTBE producers denied liability protection for any harm done by MTBE use in fuel.
不过，甲基叔丁基醚 (MTBE) 生产商拒绝为在燃油中使用 MTBE 产生的任何危害承担责任。

MTBE Problems

MTBE的问题

- Vapor has a sharp and disagreeable odor when fuelling vehicles.
为车辆加油时散发的汽体有刺鼻的异味。
 - Many consumer complaints.
许多消费者对此有所抱怨。
- Spills of MTBE persist in groundwater.
MTBE泼洒后会在地下水中持续存在
 - Not easily treated.
不易处理
 - More persistent than other gasoline components like BETX.
与其他汽油成分如BETX（苯系物）相比更不易清除
 - Disagreeable taste at very low concentrations.
即使浓度极低亦有难闻气味



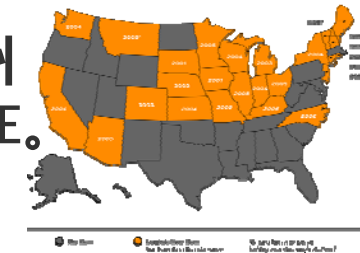
Use of MTBE in the U.S. has been replaced by Ethanol

在美国MTBE在使用中已被乙醇替代

- USEPA (Environmental Protection Agency) policy since 2000 to phase out MTBE use entirely.
美国环境保护署的政策从2000年开始分阶段完全淘汰MTBE的使用。

- State of California and New York banned MTBE in 2004, which was 40% of prior MYBE consumption. 25 States had banned it by 2005.
2004年加利福尼亚州和纽约州禁用了MTBE，这两个州此前占总消费量的40%。到2005年25个州禁用了MTBE。

- Almost no MTBE is now used in the United States.
现在MTBE几乎已在全美国停用。





Oxygenate Anti-knock and Octane Properties

增氧剂的抗爆性和辛烷特性

- In gasoline engines the spark plug ignites the fuel-air mixtures at the ideal time.
在汽油发动机中火花塞在恰当的时间点燃油气混合物
- Engine knock occurs when some of the fuel explodes early due to temperature, pressure and fuel properties.
当燃料因为温度、压力和燃料特性提前点燃，就会发生发动机爆震
- Knock causes locally high pressure in the engine cylinder and may damage the engine.
爆震会导致发动机汽缸局部高压，可能会损坏发动机。
- Octane rating is a measure of the performance of a fuel in high compression gasoline engines.
辛烷值是衡量燃料在高压压缩比汽油发动机中性能的一个指标

Alkyl Lead 烷基铅

- From the 1920s to the mid-1970s alkyl lead compounds like tetraethyl lead were used to prevent knock and increase octane ratings.

从20世纪20年代到70年代中期，烷基铅，如四乙基铅，被用于防止爆燃和提高辛烷值。

- USEPA policy win 1979 was to phase out lead in fuel due to its neurotoxicity.

美国环境保护署在1979年争取到将燃油中的铅逐步淘汰，因为铅具有神经毒性。

- Lead was banned in fuel in the U.S. in 1995.

美国于1995年禁止在燃料中添加铅。

- Alkyl lead in fuel also damaged catalytic converters required on U.S. cars in 1975, resulting a phase out before the 1995 ban.

燃油中的烷基铅还会损害美国汽车按1975年规定安装的催化转化器，因此在1995年禁令之前已开始被逐步淘汰。



MTBE as Anti-Knock 作为抗爆剂的MTBE



- Used in fuels starting in 1979 at 3-7% by volume.
从1979年开始用于燃料，添加量为3 -7%。
- Cost less than ethanol and has good fuel blending properties.
成本低于乙醇，混配性较好。
- In the U.S., tax incentives for renewable fuels have made grain-based ethanol less expensive than MTBE, ETBE, TAME or TBA
在美国，可再生燃料的税收激励使谷物乙醇比MTBE，ETBE，TAME或TBA更经济。

Octane Rating 辛烷值

- Engines designed for higher octane fuels are more efficient in using energy.
设计使用高辛烷值燃料的发动机能源利用的效率更高。
- Adding either Ethanol or MTBE raises the octane rating of regular gasoline.
添加乙醇或MTBE能提高普通汽油的辛烷值。

	Gasoline 汽油	Ethanol 乙醇	MTBE
Blending RON 混合研究法辛烷值	90-100	108-115	116-120
Blending MON 混合马达法辛烷值	81-90	90-112	100-104

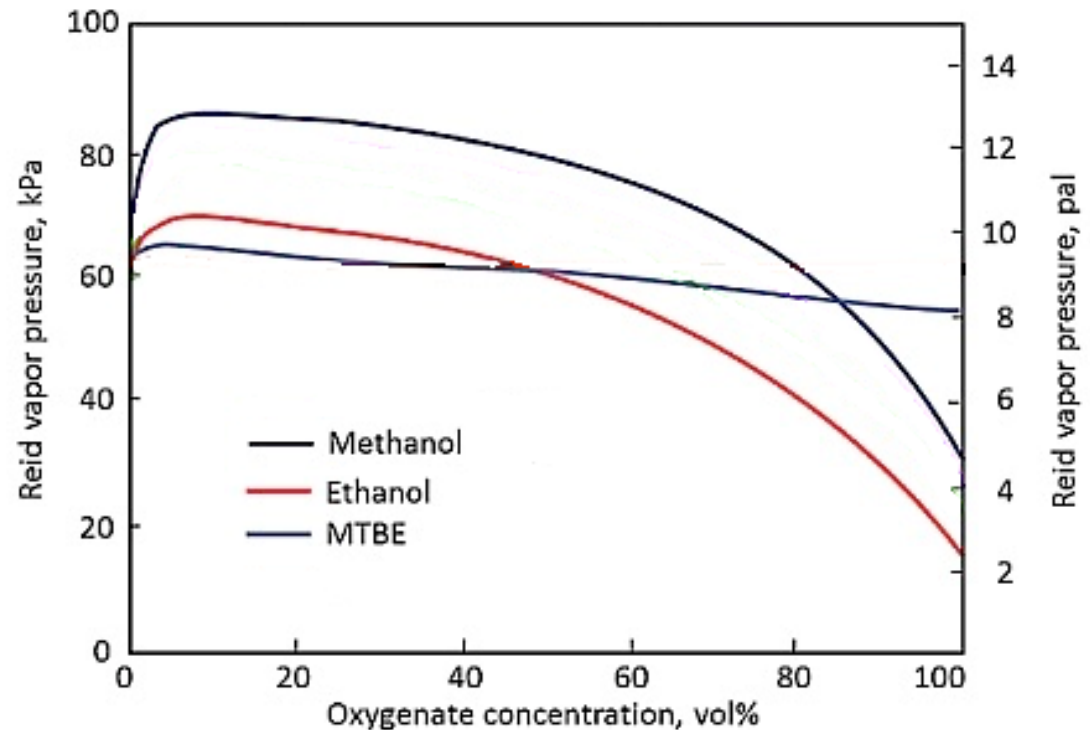


Other Properties of Fuel Additives

燃料添加剂的其他特性

Volatility 挥发性

- Lower volatiles mean less air pollution.
挥发性低意味着更少空气污染
- Ethanol and MTBE form azeotropes with gasoline resulting in higher volatility fuel blend at lower concentrations.
乙醇和MTBE与汽油生成共沸，导致在低浓度情况下混合燃料挥发性提高
- Gasoline for blending must have lower volatility to compensate.
作为补偿，用于混配的汽油必须具有低挥发性。



Furey 1985

Oxygen content 含氧量

- Ethanol 35%
乙醇35%。
- MTBE 18%
MTBE18%。



Water Solubility

水溶性

- MTBE has negligible bulk water solubility and can be blended into fuels at existing refineries and moved through existing bare metal piping.

MTBE在大容量水中溶解度较低，可忽略不计，可在现有的精炼厂与燃油混合，并可在现用裸金属管中流动。

- Ethanol will dissolve any water it contacts which can lead to corrosion problems in bare metal tanks and piping.

乙醇会溶于其接触到的任何水体，因此在裸金属罐和管道中会产生腐蚀问题。

- Ethanol is usually splash blended at the final fuel terminal into the delivery trucks which have lined tanks. Retail tanks are usually have fiberglass liners and non-metal hoses not susceptible to corrosion.

乙醇通常以在销售终端向有内胆的油罐车内倾倒的方式掺入燃油。零售油罐通常配有玻璃纤维内胆和非金属软管，不易产生腐蚀问题。



Comparative Toxicity of MTBE and Ethanol

MTBE和乙醇的毒性对比



- Acute toxicity is low for both
两种物质的急性毒性均较低
 - Ethanol LD50 8300 mg/kg bw/day
乙醇 LD50 (致死剂量) 8300 mg/公斤体重/每天
 - MTBE LD50 4000 mg/kg bw/day
MTBE LD50 (致死剂量) 4000 mg/公斤体重/每天
- Ethanol NOAEL 2400 mg/kg bw/day
乙醇 无可见有害作用水平 2400mg/公斤体重/每天
- MTBE NOAEL 714 mg/kg bw/day
MTBE 无可见有害作用水平 714mg/公斤体重/每天
- LD50 = mean lethal dose LD 50 = 平均致死剂量
- NOAEL = no observed adverse effect level
NOAEL= 无可见有害作用水平

Occurrence

自然生成

- Ethanol is produced by the human body due to metabolism by intestinal microflora resulting in typical blood alcohol levels of 0.062 to 0.73 mg/L.
乙醇可能作为肠道菌群代谢的产物在人体中生成，因此人的血液酒精浓度一般为0.062到0.73毫克/升。
- MTBE is not known to occur naturally.
未发现自然生成MTBE的情形。



Carcinogenicity

致癌性

■ Ethanol 乙醇

- Not directly a carcinogen but its metabolite acetaldehyde is.
并非直接致癌物，但其代谢产物乙醛是致癌物。

- IARC carcinogen rating based on human (epidemiologic) studies of high concentration exposures.
国际癌症研究机构的致癌物评级是基于暴露在高浓度环境下的人体（流行病学）研究

■ MTBE

- Multiple organ cancers at high concentrations in some animal species but not others.
对于某些动物种类高浓度MTBE可导致多种器官的癌症，而对其他动物并无此作用。
- No human studies.
无相关人体研究。

Taste and Odor Thresholds

味觉和气味阈值

	Ethanol 乙醇	Benzene 苯	TBA 叔丁醇	MTBE 甲基叔丁基醚	TAME 甲基叔戊醚	ETBE 乙基叔丁醚
Taste threshold in water (µg/L) 水中味觉阈(µg/L)	--	500	--	20-40	128	47
Odor threshold (ppm) 气味阈 (ppm)	49	0.5	21	0.053	0.027	0.013



Rise and Fall of MTBE Production in the U.S.

MTBE生产在美国的兴衰

- Before 1979
1979年之前 minimal
极少
- By Jan 1992
到1992年为止 3,038,000 bbl/month
3,038,000 桶/月
- By Jun 2000
到2000年6月为止 7,260,000 bbl/month
This was peak production.
7,260,000桶/月
此为产量峰值
- By Feb 2015
到2015年2月为止 520,000 bbl/month
520,000 桶/月



MTBE is produced from 合成MTBE的原料

- C4 olefins (one double bond) from refined crude oil
源自精炼原油的C4烯烃（一个双键）
 - Too volatile to use all that is produced in gasoline blending
在汽油混合中产生，挥发性过强无法使用全部
 - Readily available
容易获得
- Methane or Methanol
甲烷或甲醇
 - From natural gas or petroleum
源自天然气或石油



Ethanol can be produced from 合成乙醇的原料

- Petroleum – via ethylene and steam
石油 – 通过乙烯和水蒸汽
- Natural Gas – via syngas (CO and H₂)
reforming
天然气 – 通过合成气（一氧化碳和氢）转化
- Grain-based starch – conventional
fermentation and distillation
谷物淀粉 – 传统的发酵和蒸馏法
- Cellulosic conversion – enzyme
modulated conversion to fermentables
纤维素转化 – 通过酶的调节转化为可发酵物



Ethanol Production in the U.S. bbl/month

美国乙醇产量 桶/月

■ 1981	168,000
■ 1990	1,512,000
■ 1995	3,000,000
■ 2000	3,500,000
■ 2005	8,000,000
■ 2010	28,000,000
■ 2015	29,500,000



Peak MTBE vs. Ethanol in US

MTBE和乙醇的产量峰值 美国

- MTBE 7,260,000 bbl/month (2000)
MTBE 7,260,000 桶/月 (2000)
- Ethanol 29,585,000 bbl/month (2016)
乙醇 29,585,000 桶/月 (2016)



What happened to U.S. MTBE production capacity?

美国MTBE的产量现状如何？

- Units at refineries were put into mothballs, sold overseas, or converted to other products.
精炼厂的相关设施被闲置起来，出卖给海外企业，或转产成他产品。
- Several merchant (stand alone) facilities still operate for export production. Most are located on the U. S. gulf coast.
少数商户（独立的）的设备仍在运营，主要用于出口。多数位于美国墨西哥湾沿岸。
- U. S. MTBE production is now only 7% of the peak in 2000.
如今美国MTBE产量只是2000年峰值时的7%。





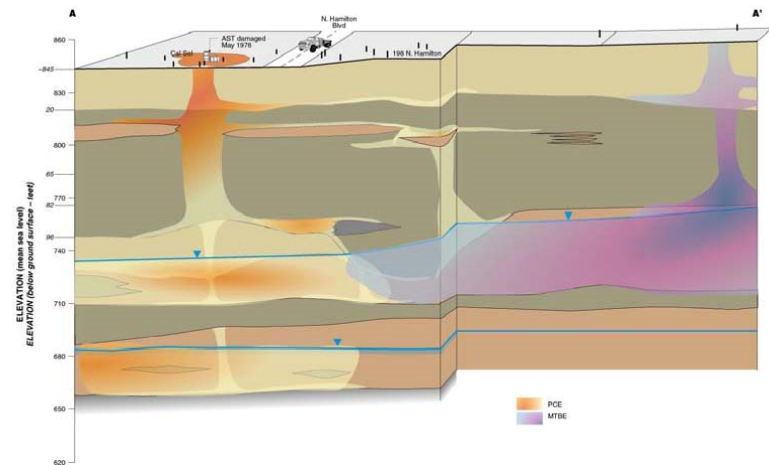
MTBE in the Environment MTBE与环境



MTBE Fate

MTBE的归宿

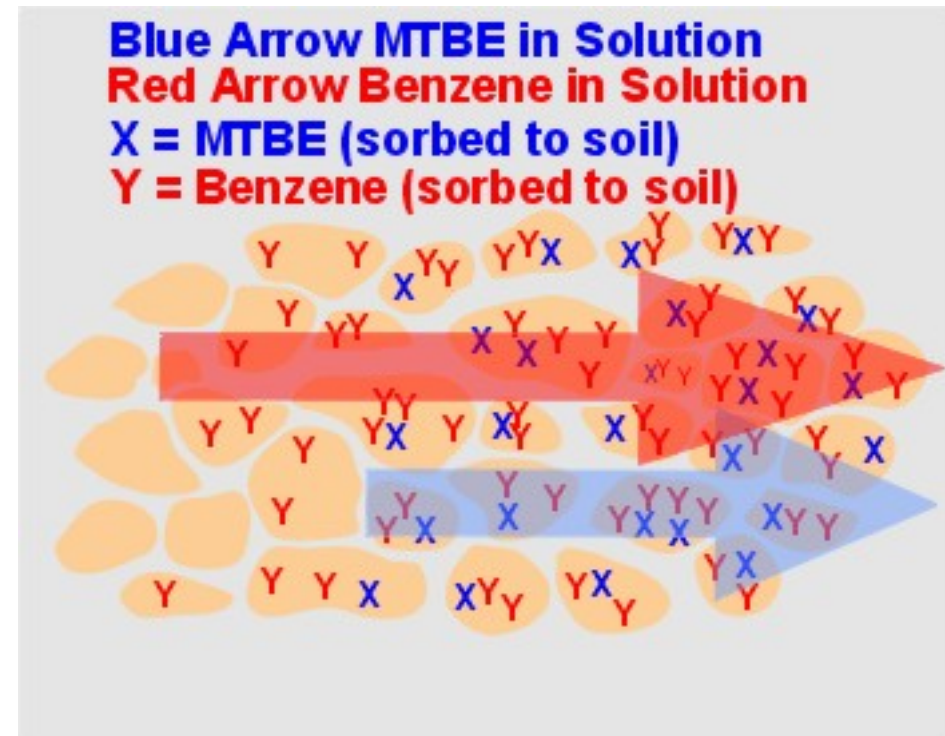
- Short half-life in air of 2.4 days
在空气中的半衰期短，为2.4天。
- Spills on surface soils quickly evaporate
泼洒到土壤表面会迅速蒸发。
- Large spills or underground tank leaks soak into soil and persist.
大量泼洒或地下储藏罐泄漏，浸入土壤后会持续存在。



MTBE in Groundwater

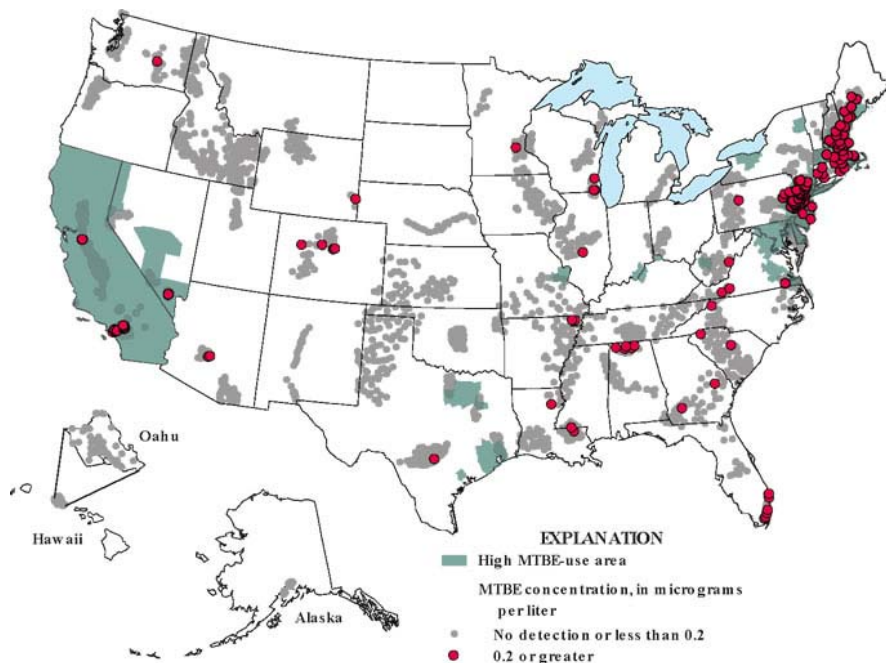
MTBE与地下水

- Moves readily from soil to groundwater.
会迅速从土壤进入到地下水中
- Vapors do not readily escape from deep soil or groundwater.
不易从深层土壤或地下水中蒸发
- Moves with groundwater flow but only 4.3% soluble in water.
随地下水流动，但水溶率只有4.3%。
- Very low and disagreeable odor/taste threshold.
不良气味/味觉阈值很低。



U.S. MTBE in Groundwater

美国地下水中的MTBE



- Numerous studies have shown that MTBE contamination in public and private drinking water wells is widespread in the U.S.

多项研究显示，全美国MTBE对公共或私有饮用水井造成的污染很普遍

- More likely to occur in urban areas.
常见于城市地区

MTBE in Groundwater Difficult to Remediate

地下水中的MTBE治理很难

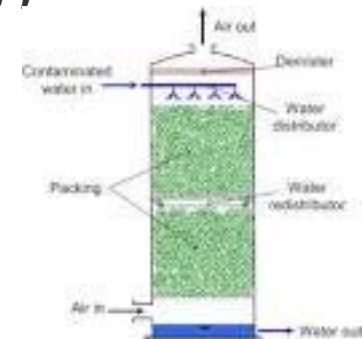
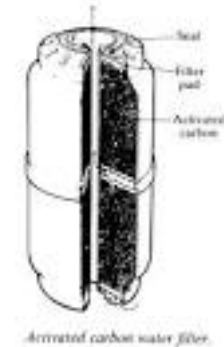
- Activated carbon filtration is not cost effective. A two cubic foot bed lasts a month or less in residential usage.

活性炭过滤成本较高。在住宅中二立方英尺的吸附层只能使用不到一个月。

- Air stripping is possible, but only with high air flow to water ratios, which is energy intensive.
- 空气脱吸法虽然可行，但只有在高汽液比的条件下才能实现，能耗很高。

- Biodegradation may occur, but only very slowly.
- 可以生物降解，但速度十分缓慢。

- Cleanup costs estimated as high as \$30 Billion U.S. dollars 清洁工作大约花费300亿美元



Ethanol Easier to Remediate

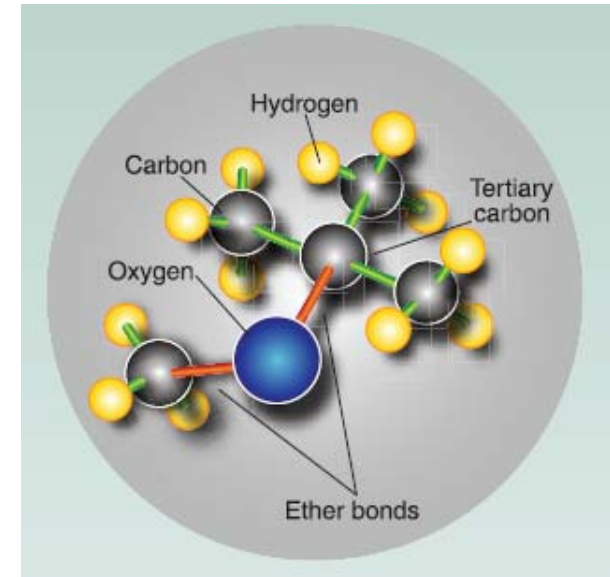
乙醇影响较易修复

- Biodegradation occurs quickly.
生物降解发生迅速
- Because it is 100% soluble in water it is diluted quickly.
因其100%溶于水，稀释速度快
- Nutrient (NPK) and pH management may be helpful in some soils.
对于某些土壤养分（氮磷钾）和pH值调节可能有益。



Why doesn't MTBE biodegrade? MTBE为何不能生物降解？

- Soil microorganisms put energy into breaking bonds and get more energy out when the bond breaks. They prefer substrates with the higher net energy gain.
土壤微生物耗费能量使分子断键，键断时能得到更多能量。它们更喜欢净能收益高的基底物。
- MTBE has a tertiary carbon to which three other carbons are attached. More energy is needed to break those tertiary carbon-carbon bonds, so the net energy gain is less.
MTBE带有叔碳原子，与三个其他碳原子相连。叔碳原子断键需要更多能量，因此净能收益较低。
- Microbe enzymes work in 2-carbon bites. Ethanol is ideal. The geometry of MTBE prevents the enzyme from accessing a 2-carbon portion.
微生物酶擅长切割双碳，因此乙醇是更为理想的选择。MTBE的几何结构不利于酶接触双碳部分。



Summary 小结

- Ethanol can be produced from grain using readily available and mature technology. It reduces dependence on petroleum. It is renewable and does not contribute to greenhouse gas increases.

乙醇可以利用现有成熟技术从谷物中提取。它降低了对石油的依赖性。乙醇是可再生资源，且不会导致温室气体增加。

- MTBE poses a risk to groundwater due to its disagreeable taste and odor at very low concentrations. It must be produced from petroleum and natural gas. It contributes to greenhouse gas accumulation.

低浓度的MTBE即具有异味，对地下水有威胁。它必须从石油和天然气中提取，会增加温室气体的累积。

