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Short overview of the toxicity and (modelled) degradability of model substances of the 1st generation biofuels

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Short overview of the toxicity and (modelled) degradability of model substances of the 1st generation biofuels

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Abstract

Biofuels are increasingly used as alternatives for commonly used mineral oils and petrol. Because of moral and economic considerations, there is discussion on the merits of this substitution, and there is concern regarding possible adverse effects of emissions of biofuels and combustion gases on human health and ecosystem health. Finally, there is concern on the persistence of biofuels in the environment.

The study reported here was aimed at gathering information on the environmental (bio)degradability and toxicity of biofuels. A short literature study was supplemented with model calculation on the biodegradability of the biofuels, using one of the most advanced software packages available for this purpose.

Fiscal privileges currently stimulate the use of ethyl-t-butyl ether (ETBE) as additive to biofuels. ETBE is obtained from bio-ethanol. For ETBE too, the biodegradability and toxicity were determined in this study.

The general finding of this research is that biofuels are relatively easily degradable in the environment, and that their toxicity is limited. Problems are expected with regard to the additive ETBE. This chemical is less prone to degradation and it is virtually non-degradable in anaerobic environmental compartments. Thereupon, ETBE is highly water soluble, allowing the chemical to migrate freely in the environment.

Key words: biofuels, environment, biodegradability, toxicity, ETBE

Rapport in het kort

In het algemeen zijn biobrandstoffen gemakkelijk afbreekbaar in het milieu en zijn de schadelijke effecten voor de gezondheid en het milieu beperkt. Wel zijn problemen te verwachten van de stof ethyl-t-butyl ether (ETBE), die wordt toegevoegd om verontreinigingen die vrijkomen bij de verbranding van biobrandstoffen te verminderen. ETBE is moeilijk afbreekbaar en kan vooral in zuurstofarme milieus, zoals sommige grondwatersystemen, lang aanwezig blijven. Daarnaast kan de stof zich gemakkelijk verplaatsen tussen de milieucompartimenten aarde, water en lucht. Momenteel is weinig bekend over mogelijke schadelijke effecten van ETBE voor de gezondheid en het milieu. Gebruik van ETBE wordt momenteel in de Europese Unie fiscaal gestimuleerd. Dit blijkt uit een korte literatuurstudie van het RIVM, aangevuld met berekeningen van de mate waarin biobrandstoffen afbreekbaar zijn.

Biobrandstoffen worden in toenemende mate gebruikt als alternatieven voor de gangbare minerale oliën. Aanleiding voor het onderzoek zijn maatschappelijke vraagtekens bij grootschalig gebruik van voedselgewassen als brandstofvoorziening en de landbouwgrond die nodig is voor de teelt ervan. Daarnaast is er de vraag of de gassen die vrijkomen bij de verbranding van biobrandstoffen ongewenste effecten hebben op de gezondheid of milieu. Meer onderzoek is nodig om mogelijke schadelijke effecten van ETBE te kunnen vergelijken met de schadelijke stoffen die bij de verbranding van biobrandstoffen vrijkomen.

Trefwoorden: biobrandstoffen, milieu, afbreekbaarheid, toxiciteit, ETBE

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1 Introduction

Biofuels are for various reasons increasingly used as substitutes for the commonly used mineral oils and petrol. There is discussion on the merits of this substitution, partly because of moral considerations, partly because of economic considerations and partly with regard to possible additional adverse effects on humans and on ecosystems (as compared to currently used fuels). Thereupon, considerations of persistence may apply to biofuels. In this project, a screening was made of information on (biological) degradability and toxicity of chemicals/chemical structures that are typically present in biofuels. The most advanced models currently available for predicting biodegradability of chemicals were applied for this purpose. The chemicals investigated were biodiesel and so-called Pure Plant Oil (PPO).

PPO is oil that may be generated from for instance rapeseed, sunflowers or soybeans. PPO in general consists of esters of long (multiple) unsaturated fatty acids with glycerol (1,2,3-propanetriol) as the backbone, in which the triglyceride moiety is the predominant ester. A schematic representation of a triglyceride is given in Figure 1.

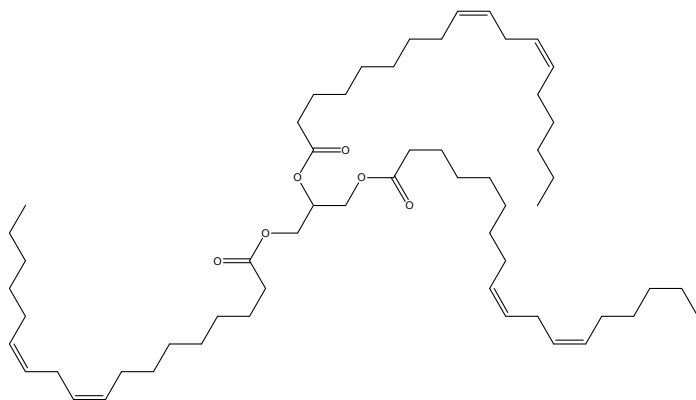


Figure 1: Schematic representation of (cis, cis) linoleic acid triglyceride.

Biodiesel is generated by esterification of fats and oils originating from plants or animals. Methanol is usually used for this esterification as methanol is the cheapest alcohol and is also most reactive (1). Dependent on the starting material, a mixture is obtained of methyl esters of the fatty acids present with varying chain lengths. It is reported in literature that biodiesel generated with soy oil, rapeseed oil and "waste cooking"-oil as starting materials, the esters of linoleic acid (doubly unsaturated, i.e. two double bonds present in each backbone), oleic acid (singly unsaturated) and palmitic acid (fully saturated, i.e. no double bonds) are the most predominant basic chemical structures. Jointly, these three esters contribute to about 80% of biodiesel (2).

Biodiesel that is prepared from animal fats consists for about 55% of esters of the three fatty acids just mentioned, whereas the remaining percentage is a complex non-defined mixture of various nature (3). A schematic representation of a methylated fatty acid is given in Figure 2.

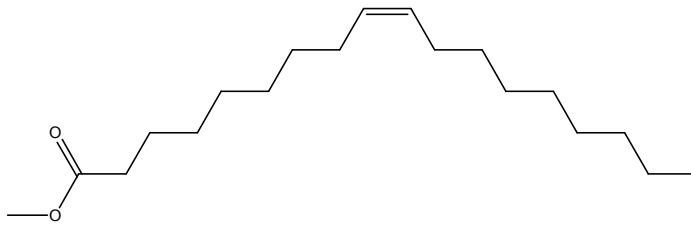


Figure 2: Schematic representation of (cis) oleic acid, methyl ester.

As with any fuel, additives are also used in case of biofuels. Ethyl t-butyl ether (ETBE) is a chemical that is used as an additive to biofuels to increase the octanol number and to decrease the emission of pollutants resulting of combustion of the fuels. ETBE may be obtained from bio-ethanol and is currently (due to fiscal privileges for ETBE in the EU) increasingly taking the place of MTBE (methyl t-butyl ether) for this purpose. The biodegradability and toxicity of ETBE were also investigated, whereas bio-ethanol was not considered as it is well known that ethanol is easily degraded following release in the environment by biotic and abiotic degradation pathways.

2 Methods

The software package CATABOL, v. 5.097 (Laboratory of Mathematical Chemistry, OASIS, Bulgaria) was applied to get an impression of the degradability of the biofuels mentioned above. CATABOL is a software package that is capable of predicting the extend of biodegradability of organic chemicals. Thereupon CATABOL is suited of forecasting which metabolites are being formed following degradation of the parent compound.

CATABOL is based upon two types of information:

- A training set of 743 chemicals for which data are available on their experimentally determined Biological Oxygen Demand (BOD) in a standardized MITI-biodegradability test, developed and standardized by the Japanese Ministry for Trade and Commerce (MITI).
- A library of transformations of chemical fragments and their degradation products. Each transformation step is assigned a probability indicating the likelihood of a certain transformation step.

CATABOL is capable of predicting whether a chemical will be fully mineralized (i.e. complete degradation to yield mineral end products and water), or whether persistent metabolites will be formed. Formation of persistent metabolites in general is unwanted as such metabolites may reach unacceptably high concentration in the environment.

Organic contaminants may, apart by biodegradation (removal by degradation induced by micro-organisms in water, soil or sediment), also be degraded by chemical transformation. An important transformation route for organic chemicals which are present in air, is degradation by reaction with hydroxyl radicals (OH·) and ozone (O₃). Hydroxyl radicals and ozone are being formed in the atmosphere/stratosphere under the impact of sunlight. As is the case for removal of biofuels by means of biodegradation, no experimental data are available regarding rates of abiotic degradation of biofuels. In this case too, however, a software package is available for predicting rates of removal of organic chemicals by reaction with hydroxyl radicals and ozone molecules in the atmosphere (so-called Advanced Oxidation Processes, AOP). AOPWIN, v1.91 (US-EPA, 2000) was used for this purpose.

On the basis of the information provided in the Introduction, the following chemicals were used as representatives of chemicals typically present in biofuels, including their so-called SMILES – a system that is used for representing the chemical structure in such a way as to allow for structure recognition in software packages used to generate information related to the chemical structure of the substance:

1 - Typical chemical structures present in PPO:

Triglyceride of (cis, cis) linoleic acid

SMILES:

C(OC(=O)CCCCC/C=C\C/C=C\CCCC)C(OC(=O)CCCCC/C=C\C/C=C\CCCC)C(OC(=O)CCCCC/C=C\C/C=C\CCCC)

Triglyceride of (cis) oleic acid

SMILES:

C(OC(=O)CCCCC/C=C\CCCCCCCC)C(OC(=O)CCCCC/C=C\CCCCCCCC)C(OC(=O)CCCCC/C=C\CCCCCCCC)

Triglyceride of palmitic acid

SMILES:

C(OC(=O)CCCCCCCCCCCCCCCC)C(OC(=O)CCCCCCCCCCCCCCCC)C(OC(=O)CCCCCCCCCCCCCCCC)

2 - Typical chemical structures present in biodiesel:

(cis, cis) linoleic acid, methyl ester

SMILES:

COC(=O)CCCCC/C=C\C/C=C\C\CCCC

(cis) oleic acid, methyl ester

SMILES:

COC(=O)CCCCC/C=C\CCCCCCC

palmitic acid, methyl ester

SMILES: COC(=O)CCCCCCCCCCCCCCCC

3 - ETBE

ETBE

SMILES: C(C)(C)(C)OCC

It is the degradability of these chemicals that was predicted by means of CATABOL and AOPWIN.

3 Results

3.1 Biodegradability

Triglyceride of (cis, cis) linoleic acid:

CATABOL predicts removal of one of the linoleic side-chains of the parent molecule, followed by splitting up of the degradation product thus formed in two parts. The linoleic side-chain and the metabolite thus formed are predicted to be fully mineralised in subsequent degradation steps.

AOPWIN allows to calculate an overall degradation rate constant of $3.91 \cdot 10^{-10}$ cm³/molecul-sec. Given annually averaged OH-radical concentrations of $1.5 \cdot 10^6$ cm⁻³ that are typical for the Northern hemisphere and a length of day light of 12 hours, this implies a half-life value for this chemical of 19.7 minutes (i.e. 50 % of the chemical will on average be degraded in the atmosphere within about 20 minutes). A similar value for the half-life is predicted for removal of this triglyceride by the action of ozone.

Triglyceride of (cis) oleic acid:

CATABOL predicts a somewhat different pathway for the biodegradation of the triglyceride of (cis) oleic acid. The triglyceride-moiety remains intact and instead of stepwise removal of this moiety, oxidation of the primary C-atoms takes place, followed by splitting off of a molecule of either acetic acid or oxalic acid. Acetic acid and oxalic acid are subsequently fully mineralized.

AOPWIN:

Predicted half-life for reaction with OH radicals: 33.2 minutes

Predicted half-life for reaction with ozone: 42.3 minutes

Triglyceride of palmitic acid:

A similar degradation pathway is predicted as for the triglyceride of (cis) palmitic acid as for the triglyceride of cis-oleic acid.

AOPWIN:

Predicted half-life for reaction with OH radicals: 2 hours

No reaction with ozone is predicted to take place due to the lack of unsaturated carbon bonds in the triglyceride of (cis) palmitic acid.

Methylester of (cis, cis) linoleic acid:

CATABOL predicts splitting off of methanol, followed by dehydrogenation and oxidation of the remaining acid moiety. The latter biotransformation yields acetic acid. All metabolites formed are fully mineralized.

AOPWIN:

Predicted half-life for reaction with OH radicals: 60.2 minutes

Predicted half-life for reaction with ozone: 63.5 minutes

Methylester of (cis) oleic acid:

CATABOL predicts dehydrogenation and oxidation of the carbon side chains to take place, followed by formation of acetic acid. Full mineralization of all intermediate products is predicted to take place.

AOPWIN:

Predicted half-life for reaction with OH radicals: 1.7 hours

Predicted half-life for reaction with ozone: 2.1 hours

Methylester of palmitic acid:

Similar to the methyl ester of (cis) oleic acid, CATABOL predicts dehydrogenation and oxidation of the carbon side chains to take place. This is followed by formation of acetic acid. Full mineralization of all intermediate products is predicted to take place.

AOPWIN:

Predicted half-life for reaction with OH radicals: 6.8 hours

No reaction with ozone is predicted to take place.

ETBE:

CATABOL predicts that ETBE is finally mineralized following release in the environment. However, the likelihood or probability that this will indeed be the case, is predicted by CATABOL to be lower than for all chemicals dealt with above. It is difficult to reliably interpret the factual meaning of this prediction, but at least it should be noted that the prediction of full mineralization of ETBE is to be confirmed by experimental data.

AOPWIN:

Predicted half-life for reaction with OH radicals: 1.4 days

No reaction with ozone is predicted to take place.

This too indicates that ETBE is less reactive than the other chemicals dealt with above.

3.2 Ecotoxicity

The ecotoxicity of ethanol, the triglycerides and the methyl esters of fatty acids is limited. This is in general also the case for the metabolites formed after biotic or abiotic degradation. As an example: the concentration at which there is an effect on 50 percent of the species tested is on average 390 mg/L for oleic acid. Further information on ecotoxicity testing was reported by Willing (4).

Hardly any information is reported in literature regarding the toxicity of either ETBE or MTBE for aquatic species, but it may be assumed that the toxicity of MTBE and ETBE is comparable. Acute toxicity endpoints range in between 472 to 1742 mg MTBE/L, while chronic endpoints were 57 to 308 mg MTBE/L. Aquatic invertebrates are in general more sensitive than fish to MTBE in acute and chronic exposure. Reported environmental concentrations of MTBE and ETBE are (several orders of magnitude) lower than concentrations observed to cause effects in freshwater organisms (5); Arp et al. (6) reported for instance typical concentrations of MTBE in Europe up till a maximum of in between 2 and 3 µg/L.

Laboratory tests have shown that LD50 values of ETBE for rats are > 5 g/kg, whereas LD50 values of > 4 g/kg were found for the effect of MTBE on mice (7). This too points to limited toxicity. No effects

on humans have been investigated, although problems associated with the odour of water containing ETBE or MTBE are commonly reported.

4 Conclusions

1 - Triglycerides and methyl esters of fatty acid:

It may be concluded that all model compounds used in this study will be relatively quickly degraded by a variety of biotic and abiotic pathways. Formation of persistent metabolites is not expected to take place, and complete mineralization is likely to take place. Whereas biodegradation is predicted to take place via a limited number of common degradation pathways, it is not known which metabolites are being formed following abiotic degradation. However, atmospheric transformation by definition yields more polar (oxygenated) transformation products which in term will be degradable as well. Indirect evidence for this statement is obtained from the observation that despite the long-time use of large volumes of large varieties of fats and oils, no accumulation of any degradation product has ever been reported.

The results reported here also show that abiotic transformation by means of reaction with OH-radicals is faster for chemicals containing larger number of unsaturated carbon bonds. Unsaturated hydrocarbons are thereupon also more susceptible for atmospheric degradation by ozone.

Although toxicity of the triglycerides and their degradation products is limited and, apart from contaminated sites, in general no adverse effects are expected to take place.

2 - ETBE:

Very limited literature reports are available regarding the biodegradation of ETBE. However, more information is available for its structural analogue methyl t-butyl ether degradation of the ethers ETBE and MTBE has been reported (8), and although biological degradation pathways exist, both chemicals in principle are to be considered as being non-easily degradable. Both chemicals may persist especially in groundwater. The lack of readily degradability is related to the presence of an ether linkage in the molecule in combination with a “bulky” t-butyl moiety. On top of the relative difficulty of breaking ether-linkages, it is the bulky t-butyl-moiety that provides steric hindrance against microbial or chemical attack. These structural functionalities thus shield the chemical from degradation. Biodegradation under aerobic conditions may nevertheless occur, but it should be noted that when other pollutants are present that may serve as a carbon source for micro-organisms, degradation of ETBE will be slowed down considerably (7). This actually is the rule in case of (soil) pollution by MTBE/ETBE-containing fuels. In view of the very high water solubility (approximately 40 gram MTBE/L and 12 gram ETBE/L) and the negligible tendency of these chemicals to adsorb to soil particles, there is a serious threat of contamination of deeper anaerobic groundwater. Both chemicals are virtually non-degradable under anaerobic conditions.

The general conclusion of this research is that biofuels are relatively easily degradable in the environment, and also their toxicity is limited. Problems are however expected with regard to the additive ETBE. This chemical is less prone to degradation and especially it is virtually non-degradable in anaerobic environmental compartments. Thereupon, ETBE is highly water soluble, allowing the chemical to migrate freely in the environment.

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