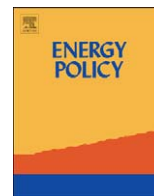




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# The impact of ethanol and ETBE blending on refinery operations and GHG-emissions

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## ARTICLE INFO

### Article history:

Received 11 December 2008

Accepted 23 July 2009

### Keywords:

LCA

Biofuels

Refining

## ABSTRACT

The sustainability of biofuels, including the greenhouse gas (GHG) reduction that they achieve, is getting increased attention. Life cycle analyses (LCAs) of biofuels production routes show that the GHG savings may vary significantly for different biofuels. An increasing number of governments are therefore looking for options to differentiate between biofuels according to their actual GHG savings. Accurate calculations of GHG savings thus become increasingly important. This paper deals with an omission of current LCAs for ethanol and ETBE blends, which leads to an underestimation of their calculated GHG savings. Current studies do not take into account that refiners will adjust their refinery operation when bioethanol or ETBE is added, because of the different characteristics of these products. The analysis indicates that the net effect of these refinery modifications on the GHG savings is positive, i.e. GHG-emissions reduce in both cases. The emission reduction is highest in the case of ETBE. We recommend to include this effect in future LCA calculations for ethanol and ETBE. As the calculation model used for this study is only a simplified representation of the EU refinery sector, we also advise to perform a more detailed analysis of these effects using more elaborate refinery models.

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## 1. Introduction

In discussions on biofuels policies, the greenhouse gas (GHG) reduction that is achieved with biofuels is getting increased attention. Studies have shown that GHG savings may vary significantly between different biofuels, and may even be negative in cases with high energy and fertiliser input, or if emissions due to land use change are large. Several EU Member States, such as the Netherlands, the UK and Germany, have therefore developed methodologies to calculate and monitor the GHG savings of the biofuels sold. These countries are also aiming to differentiate between biofuels according to their actual GHG savings. Early in 2008, the European Commission published a proposal along the same lines (European Commission, 2008). In this proposal, a GHG emission calculation methodology was presented, and a minimum GHG saving requirement was proposed for biofuels in order to count towards a biofuel obligation that would come into force after 2010. Previously, the European Commission proposed to oblige oil companies to gradually reduce the life cycle GHG-emissions of the transport fuels they sell in the EU, by 1% a year between 2011 and 2020 (European Commission, 2007).

These developments can improve the environmental impact of the biofuels policies, and add business value to biofuels with good GHG emission performance. A minimum GHG saving requirement would mean that biofuels with a low GHG savings score will lose their market, unless improvements are made to the production chain to improve the score. If the GHG savings of biofuels count towards the life cycle GHG savings of transport fuels, higher savings of the biofuels may mean less investments in emission reductions elsewhere. However, these policies can only achieve the desired environmental effects and result in a fair treatment of the various biofuel producers if the GHG savings achieved with specific biofuels routes are calculated accurately.

To enable implementation of policy incentives for better performing biofuels (from a GHG savings point of view), both the Netherlands, Germany and the UK have developed so-called CO<sub>2</sub>-tools, and the European Commission proposed a calculation methodology for GHG-emissions of specific biofuels. The methodologies used for these tools are all based on standard LCA-methodology and are roughly similar in their design, but vary in some aspects. It is expected that the EU will decide on a common calculation methodology in the coming year.

In this debate on GHG savings of biofuels and CO<sub>2</sub> tool development, the European Fuel Oxygenates Association (EFOA) wanted to draw attention to an omission of current LCAs, which leads to an underestimation of the GHG savings of ETBE. Both the CO<sub>2</sub>-tools and the more detailed well-to-wheel analysis such as, for example, that of Concawe/JRC/Eucar (Concawe, 2007) or

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GHGenius, assume that the bioethanol and ETBE simply replaces MTBE and a small quantity of gasoline. In reality, however, refiners will adjust their refinery operation when bioethanol or ETBE is added, because of the very different characteristics of these products, such as high octane. In order to generate a blend that satisfies gasoline standards, base fuel component specifications can be quite different from the reference case without biofuel. This effect can be expected to occur for both ethanol and ETBE. As these changes to the refineries may have an effect on GHG-emissions they should be incorporated in the GHG calculations of biofuels.

The following paper describes a study CE Delft has conducted to estimate the greenhouse gas effects of adding ETBE or ethanol to gasoline, taking into account the changes to refinery operations. We first describe the aim and scope of the study, the methodology used and systems considered. We then describe the effects that can be expected in the refineries when ethanol or ETBE is added to the fuel, both in terms of changes to the processes and in CO<sub>2</sub> emissions. Then, these results are added to the rest of the well-to-wheel fuel chains, i.e. to the process steps outside the refinery. The paper then concludes with results, conclusions and recommendations.

## 2. Aim and scope of the study

The objective of the study is to derive an estimate of the net effects on greenhouse gas emissions that result from blending ethanol and ETBE in gasoline, at current blending percentages used in the EU-25. The analysis focuses on the modifications to the refinery processes that can be expected to accommodate the different characteristics of ethanol and ETBE, and on the resulting effects of the GHG-emissions of the refineries. The focus is on the EU-25 refinery sector.

The study looks at two scenarios: substitution of MTBE and gasoline components:

- by 5 vol% ethanol or
- by an equivalent amount of ETBE.<sup>1</sup>

Addition of 5 vol% was chosen as a representative basic assumption for legislative and market related considerations. At the time the study was initiated (late 2006) the maximum allowed ethanol concentration in EU petrol was 5% v/v. Allowance for higher concentrations as included in the new EU Fuel Quality Directive (10% v/v) will not be officially issued until the summer of 2009 with an implementation period for EU Member States until the end of 2010 to implement it. Moreover, even then, a large fraction of the EU vehicles will still use the current fuels with a 5% ethanol maximum.

The effect on greenhouse gas emissions has been expressed in kg per tonne ethanol, so that the result can be combined with greenhouse gas emission estimates for the production of ethanol and can be integrated in aforementioned CO<sub>2</sub>-tools.

In general, four to six specific refinery configurations are distinguished, ranging from fairly uniform definitions for hydro-skimming refineries to a broad range of definitions of what a complex refinery looks like (Bechtel, 2000; ECN, 1989; EIPPCB, 2003, etc.). For the refinery impacts of one refinery type, which most likely would be subject to process modifications when commencing ethanol or ETBE blending, was considered.

In order to simplify the calculations, the study has been performed for a catcracker refinery configuration only (a Fluidized Catalytic Cracking Unit, FCC). This configuration represents approximately 50% of the total EU-25 refinery capacity (IEA, 2005), (EIPPCB, 2003). All refineries using captive produced MTBE belong to this category. A calculation model was set up to represent the average lay-out of the catcracker refineries within the EU-25, without detailed analysis of one specific refinery. As each refinery is unique and an analysis for one refinery will not be representative for any other refinery within the EU-25 (Concawe, 2005), the analysis in this study is not translatable to a specific refinery.<sup>2</sup>

## 3. Methodology

The study has been conducted as an abridged LCA, in accordance with ISO 14040 guidelines and following CML methodology for LCAs (Guinée et al., 2001). Project results can thus be compared with existing LCA studies.

A basic assumption for this analysis has been the assumption that current EU gasoline market demands and the EU refinery structure supplying this market are a firm boundary condition. This means that blending in of ethanol or ETBE will not result in alteration of the amounts, relative ratios and specifications of refinery products supply to the EU market. Current gasoline consumption in the EU-25 amounts to 5200 PJ/a (IEA, 2005), (Concawe, 2005). This assumption also means that changes in export/import of refinery products, or any possible changes in specifications of petroleum products have been ignored.

The approach is required to fulfill ISO 14040 guidelines, which requires the same functional unit for all systems that are compared. It also seems to be justified from a technical and commercial point of view, as it is unlikely that the amounts of ETBE and ethanol considered here are marginally compared to the entire crude slate processed.

Point of departure in the study has been current gasoline quality as sold at gasoline stations across Europe. A 50:50% mix of summer blend and winter blend Euro 95 with average specifications in terms of vapor pressure, MON<sup>3</sup> and RON<sup>4</sup> was considered. This product is a mixture of crude oil derived 'base fuel' components and an average MTBE content of 5 vol%, i.e. 4% based on lower heating value contributions. Fuel specifications are given in Table 1.

Three systems are considered and compared in this paper (see Figs. 1–3):

1. The reference system, in which no ethanol is used, a combination of base fuels and MTBE is offered at the gasoline stations.
2. Direct addition of 5 vol% ethanol to gasoline.
3. Addition of an equivalent amount of ETBE, produced from using bioethanol (the same amount as in the second scenario) and isobutylene.

In this study, the greenhouse gas emissions of the latter two cases are compared with each other, and with the emissions of the reference situation.

<sup>2</sup> References used for model development: (Bechtel, 2000), (Energetics, 2006), (IEA, 2005), (Gary, 2001), (Maples, 2000), (Purvin, 2000), (Slaback, 2004).

<sup>3</sup> Motor oxygen number.

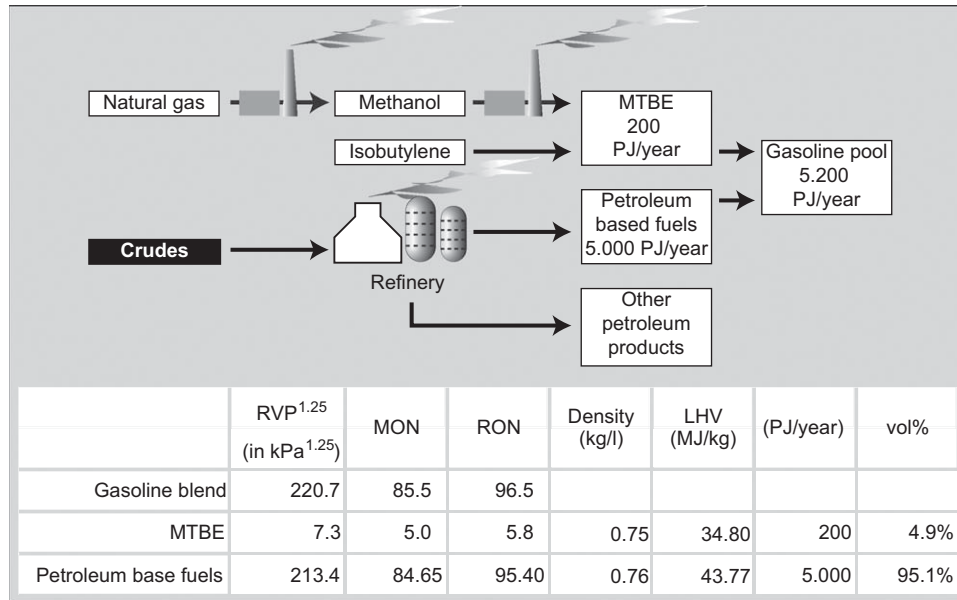
<sup>4</sup> Research octane number.

<sup>1</sup> This means that the amount of ethanol equalling 5 vol% of total gasoline blend is assumed to be processed into ETBE.

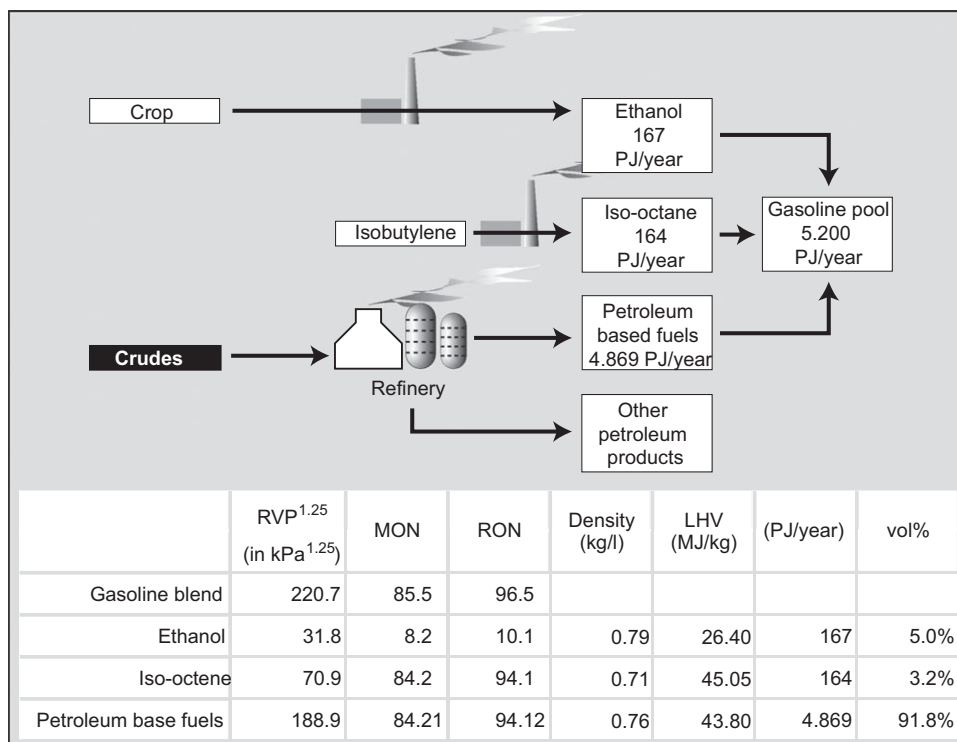
**Table 1**  
Fuel specifications for Euro 95 blend (figures refer to practice).

	RVP (kPa)	MON	RON	Density (kg/l)	LHV MJ/kg	LHV MJ/l
Gasoline at gasoline station	75.0	85.5	96.5	0.73	43.5	31.7

NB. RVP = Reid vapor pressure, LHV = Lower heating value.



**Fig. 1.** Reference system structure with associated amounts and specifications of gasoline pool components.



**Fig. 2.** Ethanol system structure with associated amounts and specifications of gasoline pool components.

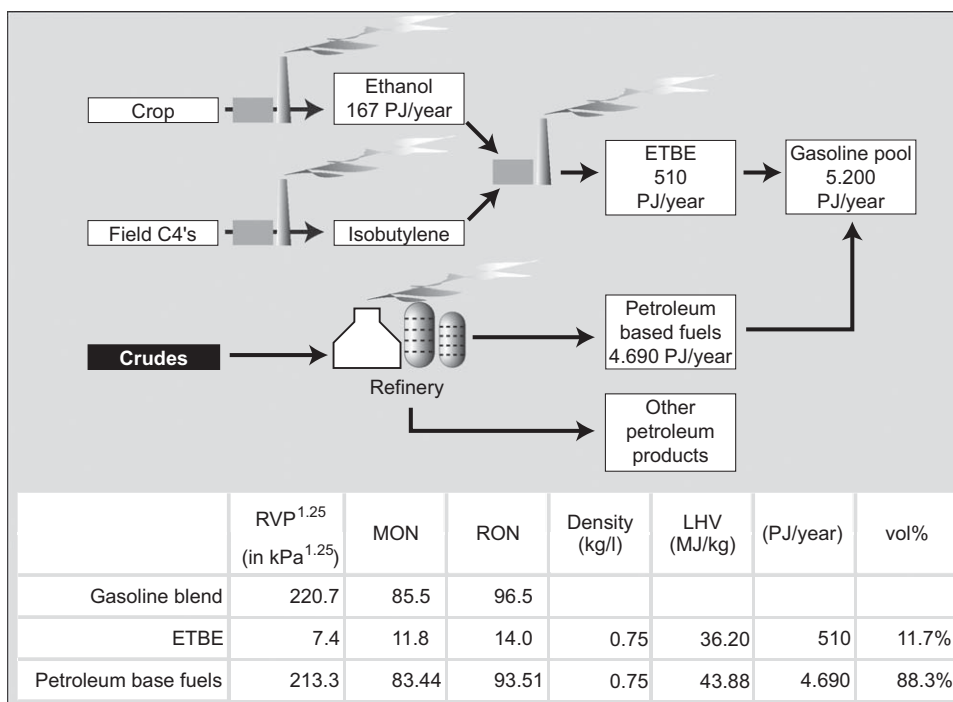


Fig. 3. ETBE system structure with associated amounts and specifications of gasoline pool components.

### 3.1. Reference case

In the reference case a mixture of crudes from the Middle East, North Sea and various regions in Africa is processed to gasoline base fuels and other oil products. Data on this mixture are taken from (IEA, 2005). The petroleum base fuels are combined or blended with MTBE in order to increase octane numbers and to add oxygen to the gasoline for better combustion.

The MTBE consumed within the EU is largely (80%) produced within the EU (EFOA, 2007). Feedstocks for MTBE production are natural gas based methanol imported from outside the EU and isobutylene that is produced as a by-product or co product. In Europe, almost equal volumes of isobutylene to the etherification units come from three different sources: from steam crackers during the cracking of naphtha into petrochemical feedstock, propylene oxide (PO) production and refinery FCCs.<sup>5</sup> There is no fuel ether production based on isobutane dehydrogenation in the EU (EFOA, 2007).

Giving the blend composition and the specifications of the blend and of MTBE, the specifications of the refinery produced petroleum base fuel can be determined. Resulting annual consumption of base fuels and MTBE are given in Fig. 1.

### 3.2. Ethanol case

In this case a 5 vol% of ethanol is added to the crude oil derived base fuels. The net energy content of the ethanol/petroleum base fuel blend remains the same as in the reference system, covering gasoline demand within the EU. RON, MON and RVP of the ethanol/petroleum base fuel blend are also equal to those in

the reference system. The ethanol is assumed to be produced in the EU from sugar beet and wheat.

In the calculations, it is assumed that addition of 5 vol% ethanol will have the following impact on refinery operations.

- First of all, all MTBE is replaced.
- Since more ethanol is added in terms of energy content as is currently added in the shape of MTBE, a small part of the gasoline base fuels is substituted as well. This results in reduced crude intake.
- Since the specifications of ethanol are significantly different from those of MTBE and gasoline, the base fuel specifications have to change in order to generate a base fuel/ethanol blend that satisfies gasoline standards and has specifications comparable to the gasoline produced in the reference case. This requires changes in operational parameters of refinery processes and in base fuel component specifications.

All these changes have an effect on the environmental impact related to crude oil production and refinery operations.

Blending in ethanol instead of MTBE will make MTBE production obsolete, meaning that another outlet is required for the isobutylene produced as a by-product at steam crackers and PO. Based on the current developments on the Californian automotive fuels market (see Croezen et al., 2007 for references), it has been assumed that the surplus isobutylene is processed into isooctene. This product is sold to refineries as a low vapor, high octane gasoline component and blended in with the gasoline pool.

The high blending vapor pressure of ethanol (compared to that of MTBE) requires a reduction of the vapor pressure of the petroleum base fuels compared to the reference system. On the other hand, the octane numbers of the petroleum base fuels can also be lower due to the high octane numbers of ethanol. Resulting annual consumption of base fuels, ethanol and isooctene are given in Fig. 2.

<sup>5</sup> FCC = Fluidized Catalytic Cracking Unit.

### 3.3. ETBE case

Adding an amount of ETBE that equals 5 vol% of ethanol again means that all MTBE is replaced, and some gasoline base fuel. And ETBE, too, has different properties than MTBE and gasoline.

Next to this, the amount of isobutylene required for ETBE production is far larger than the amount consumed in European MTBE production. The amount of isobutylene required for converting the 5 vol% ethanol into ETBE amounts to 6.6% (wt), whereas for MTBE production only 3.1% (wt) isobutylene is required. This leaves a deficit of 3.60% of isobutylene that has to be accounted for in the analysis.

In this study we assumed that the required extra isobutylene can be subtracted from excess volumes of isobutylene now applied as a fuel. Excess volumes are available e.g. at naphtha cracker plants (EFOA, 2007). An alternative approach was considered as part of a sensitivity analysis: would be assumed that the gap between available and required amounts of isobutylene is filled by import of isobutylene from the Middle East (see, for example, Concauwe, 2007).

The amount of petroleum base fuels is somewhat lower than in the ethanol system. Vapor pressure of the petroleum base fuels can be higher than in the reference system and octane numbers can be lower. Resulting annual consumption of base fuels and ETBE are given in Fig. 3.

## 4. Refinery analysis

### 4.1. Considered refinery and applied simulation model

As stated above, in our study a FCC refinery configuration was considered.

In such a configuration both atmospheric and vacuum distillation are included and the vacuum gas oils and vacuum residue are cracked into lighter products in respectively fluidized catcracker (FCC) and visbreaker. The gasoline base fuel pool is made up of a mixture of:

- Hydrotreated straight run naphthas.
- Catalytically converted light straight run naphtha (C5/C6 isomerate).
- Catalytically converted heavy straight run naphtha (reformate).
- Catalytically converted butanes (alkylate).
- Hydrotreated naphthas from FCC and visbreaker.
- Butanes, as far as allowed by base fuel vapor pressure specification limits.

Refinery processes are tuned for maximum gasoline and diesel production (the products with the highest market price), with tuning possibilities confined by-product specifications.

For estimating the effects of blending in ETBE or ethanol instead of MTBE a spreadsheet model for this configuration was developed, producing the mass balance and consumption of fuels and hydrogen for the refinery.

The calculation model developed for this study was aimed at producing the mass balance over the refinery. Because the refinery model set up for this study does not include an economic optimization analysis for the refinery operations, information concerning processed crude slate composition, operational parameters and products slate composition were primarily taken from or tuned by comparing with a IEA model simulation for the EU refinery sector that did include an economic operational optimization analysis (IEA, 2005). It has been assumed that the

information in this study is an accurate representation of the EU refinery situation.

More detailed information on this model can be found in (Croezen et al., 2007).

Applied specifications for several refinery operations

Operational parameters of conversion processes		Cut points (°C)	°C
Conversion		Light ends	20
FCC	67%	LSR and MSR naphtha	134
Visbreaker	8%	HSR naphtha	209
Cat reformer		Kerosene	240
Type	Semi continuous	Diesel	350
Pressure (bar) =	20	IGO	400
Isomerate type	Once through	LVGO	450
Residual sulphur content after HDS	ppm	HFO	558
		Gas plant separation efficiencies	IDB
Light naphtha	8	C <sub>3</sub> =	90%
Heavy naphtha	8	C <sub>3</sub>	90%
Kerosene	250	C <sub>4</sub> =	100%
Diesel	8	IC <sub>4</sub>	100% 95%
FCC light naphtha	8	NC <sub>4</sub>	100%
FCC medium naphtha	8		
Visbreaker naphtha and distillate	8		
IGO treater	1000		
LCO	8		

### 4.2. The main features of the refinery calculations

Because of the nature of the study – an abridged LCA – a number of simplifications have been made in the refinery calculations.

- First of all, it was decided that with respect to changes in crude consumption we would only consider reduction of the average crude slate, not a reduction in the consumption of one or a few individual crudes.
- Next to this we did not consider changes in operational parameters of the conversion process (FCC and visbreaker) and in the production volumes of both processes. Both installations are among the most expensive ones in the refinery and produce the cheapest components for the gasoline and diesel pools (see e.g. Bechtel, 2000; Maples, 2000; IEA, 2005). It is therefore reasonable to assume these processes are operated at maximum capacity, and at the economic optimum equilibrium for operation.
- We assumed that the produced amount and specifications of light and medium naphtha would not change.

The above assumptions implicate that the amounts and the specifications of the alkylate, FCC naphthas and isomerate contributed to the gasoline pool remain constant for all considered systems. The base fuels specifications and volume must therefore be adapted to the requirements from blending in MTBE, ethanol/isoctene or ETBE by changes in the amounts of reformate and butane and the quality of the reformate in terms of octane numbers (Fig. 4).



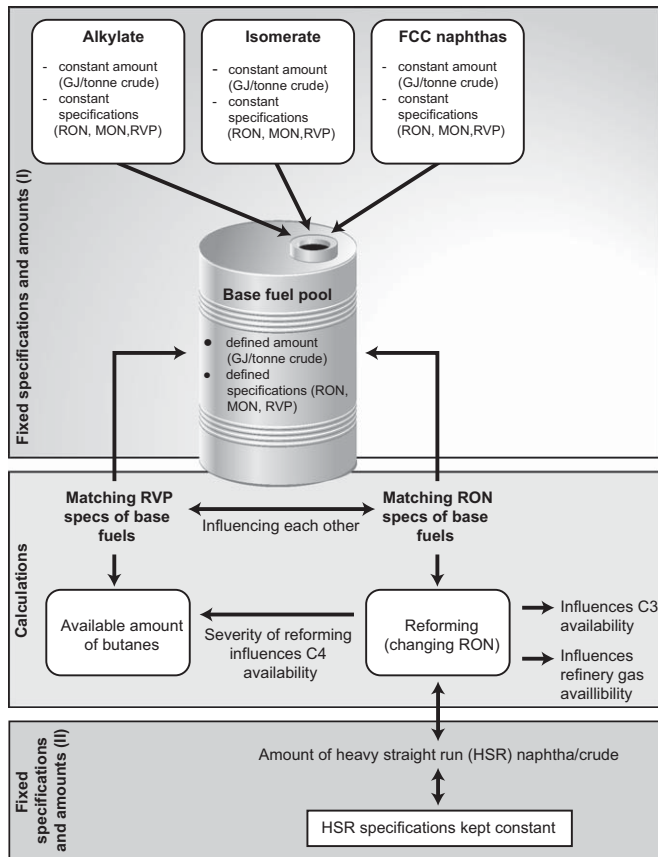


Fig. 5. Illustration of the type of calculations performed in this project and the applied boundary conditions.

Table 2 Specifications of fixed petroleum base fuel pool components.

	RVP (kPa)	MON	RON
Alkylate	37.8	92.2	94.7
Light FCC naphtha	69.0	80.7	91.9
Medium FCC naphtha	20.2	79.1	91.2
Isomerate	87.3	80.5	82.5

Table 3 Composition of gasoline blend sold at refilling stations, percentages in percentage of energy content.

	Reference (%)	Ethanol (%)	ETBE (%)
MTBE	3.8		
Isooctene		3.2	
Ethanol		3.2	
ETBE			9.8
Petroleum base fuels	96.2	93.6	90.2

Table 4 Required specifications of petroleum base fuel pool blend.

	RVP (kPa)	MON	RON
Gasoline at refueling station	75.0	85.5	96.5
Petroleum base fuels			
Reference case	76.0	84.7	95.4
Ethanol case	70.9	84.2	94.1
ETBE case	80.6	83.4	93.5

Table 5 Base fuel pool compositions (wt% per tonne crude processed in reference case).

	Reference		Ethanol case		ETBE case	
	wt%	vol%	wt%	vol%	wt%	vol%
Alkylate	2.0	8	2.0	7.8	2.0	8.0
Light FCC naphtha	3.9	15	3.9	14.9	3.9	15.4
Medium FCC naphtha	3.9	13	3.9	13.4	3.9	13.8
Isomerate	5.5	21	5.5	21.2	5.5	21.9
Reformate	12.2	38	11.6	38.0	10.1	34.2
C <sub>4</sub> 's	1.2	6	1.0	4.7	1.4	6.8
	28.6	100.0	27.9	100.0	26.8	100.0

Table 6 Mass balance for catalytic reformer (all percentages per tonne of crude processed in reference case).

	Reference (%)	Ethanol case (%)	ETBE case (%)
H <sub>2</sub>	0.31	0.27	0.24
C <sub>1</sub>	0.22	0.17	0.14
C <sub>2</sub>	0.41	0.33	0.28
C <sub>3</sub>	0.63	0.51	0.43
IC <sub>4</sub>	0.30	0.24	0.20
NC <sub>4</sub>	0.39	0.31	0.26
Reformate	12.16	11.62	10.14

scenarios considered, yields the base fuels blend compositions given in Table 5.

As indicated above, blending in ETBE or ethanol/isooctene reduces the petroleum base fuel requirement, which can also have lower octane numbers (RON/MON). Since we have fixed the amounts and specifications of alkylate, FCC naphthas and isomerate, this boils down to a lower requirement for reformate and butanes and also lower octane numbers for the reformate.

This gives a twofold decline in energy requirements for reforming, atmospheric distillation, gas separation and HSR naphtha hydrodesulphurization:

- Less reformate and butanes means less HSR naphtha has to be (a) produced by distillation and (b) needs to be hydrodesulphurized and processed in the reformer.
- Lower octane numbers means catalytic reforming can be less severe.

The effects are more pronounced in the ETBE case because required amounts of reformate and butanes and required reformate octane numbers are lower than in the ethanol/isooctene case.

In addition, the LCA analysis also has to take into account that less severe catalytic reforming yields less LPG (butanes, propane), H<sub>2</sub> and refinery gases.

The resulting reformer mass balance and the changes in crude requirement, fuel consumption and availability of butanes, refinery gas, H<sub>2</sub> and C<sub>3</sub> are given in Tables 6 and 7.

#### 4.3.2. Effects on refinery fuel consumption

4.3.2.1. Net fuel consumption and fuel composition. The reduction in fuel requirement is partly matched by reduced availability of refinery gas. Reduced fuel requirement, reduced availability of refinery gas and different amounts of butanes that can be added to the petroleum base fuels pool give different net effects on fuel composition and associated greenhouse gas emissions.

As mentioned earlier in this chapter, we based our analysis on the IEA analysis (IEA, 2005), which included an economic optimization for the refinery configurations considered in that

**Table 7**

Results for H<sub>2</sub> and C<sub>3</sub> production, HSR requirement and fuel consumption in the three cases analysed (all figures per tonne crude in reference case).

	Reference	Ethanol case	ETBE case
Mass balance consequences (per tonne crude)			
H <sub>2</sub> availability	0.31%	0.27%	0.24%
C <sub>3</sub> availability	0.57%	0.46%	0.39%
HSR required	13.93%	12.96%	11.20%
Net fuel required (GJ/tonne crude)			
Reformer	0.44	0.39	0.33
Gas plant requirement	0.03	0.03	0.02
HSR production and HDS	0.20	0.18	0.16
Net requirement	0.67	0.60	0.51

study. In the IEA study consumption of vacuum residue was estimated at 1.3 GJ/tonne crude. Since the IEA analysis was optimized economically, this obviously is the economically most attractive amount for refinery fuel application. For the other two scenarios we assumed the same amount being applied as refinery fuel. The low market value of vacuum residue compared to other refinery products justifies the assumption that vacuum residue is used as fuel preferably to other refinery fuels, in case there is an outlet for surpluses.

In both the reference situation and the ethanol case the aggregated amounts of vacuum residue and other fuel – refinery gas, surplus butanes and H<sub>2</sub> – exceed total refinery fuel requirements. We assumed that in that case refinery gas is exported and supplied to the regional natural gas network, substituting natural gas.

In the ETBE case however, more butanes can be added to the base fuels blending pool, due to the favourable RVP specifications of ETBE. As a result there is a significant reduction in the amount of butanes available for fuel applications. Next to this, the available amount of refinery gas is also reduced because of lower reformer operation severity. Both mechanisms result in the aggregated amount of vacuum residue, refinery gas, butanes and hydrogen being less than the fuel requirement of the refinery. In order to compensate this shortage it is assumed that (some) natural gas has to be imported by the refinery in this case.

**4.3.2.2. C<sub>3</sub> availability.** Reduced severity of reformer operations and a reduced production rate of reformate both result in reduced production of propane. This reduced availability means market demand cannot be satisfied by refinery propane deliveries.

In accordance with the ISO 14,000 guidelines for LCAs we assume that the reduced deliveries by the refinery are compensated by propane from another source. Our expectation is that this would be propane produced from natural gas liquids (NGL), as is also assumed in (Concawe, 2007).

**4.3.2.3. Reduced HSR.** Blending in more ethanol/isooctene or ETBE and butanes than the current amount of MTBE present in gasoline means that less HSR and crude oil are required. The net effects of reduced HSR requirement, reduced C<sub>3</sub> availability and changes in natural gas export/import are shown in Table 8.

#### 4.3.3. Effects on GHG-emissions

The resulting effects on greenhouse gas emissions are depicted in Table 9.

Greenhouse gas emission reduction related to the reduced HSR requirement are calculated on the basis of the carbon content of the crude: 86% (wt) at a LHV of 42.5 GJ/kg. Greenhouse gas

**Table 8**

Net effect in consumptions and productions (compared to the reference case, in terms of GJ/GJ gasoline).

	Ethanol (%)	ETBE (%)
Change in HSR consumption	–3.3	–9.1
Change in natural gas consumption	0.0	1.5
Change in C <sub>3</sub> supply	0.4	0.6

**Table 9**

Resulting effects on greenhouse gas emissions of the refinery (compared to the reference case, in kg CO<sub>2</sub>-eq/GJ gasoline).

	Ethanol	ETBE
Crude consumption	–2.58	–7.23
Natural gas consumption	0.00	0.95
C <sub>3</sub> supply	0.27	0.45
Total		
In kg CO <sub>2</sub> /GJ gasoline	–2.30	–5.83
In kg CO <sub>2</sub> /GJ ethanol	–72	–182

emissions related to production and transportation of the avoided crude oil (4.5 kg/GJ) were also taken into account.

As can be seen in the last column of the table, the reduced HSR requirement and fuel requirement in both the ethanol and ETBE cases leads to a GHG emission reduction. However, this is partly undone by fact that the C<sub>3</sub> supply by the refinery is reduced.

These results clearly indicate that both in the ethanol and ETBE scenarios, GHG-emissions of the refineries are reduced. Addition of ETBE leads to significantly higher GHG emission reductions in the refinery than the addition of ethanol.

The result is somewhat distorted by the fact that in the ETBE more alternative, not petroleum based fuel components are added to the gasoline pool as in the ethanol case: ETBE will make up approximately 10% of the gasoline blend by LHV while ethanol and isooctene will make up some 6.4% of the gasoline blend by LHV.

But next to this, ETBE also has the advantage of being a blending component with both a high RON and a low RVP. In the ethanol case the high ethanol vapor pressure reduces the possibilities of adding butanes to the gasoline pool. Therefore, when ethanol is blended, more reformate per unit of ethanol has to be produced compared to the ETBE case. Next to this, the reformate RON has to be somewhat higher which means that reforming severity must be higher and subsequently fuel requirements for reforming are higher. In short more reformate has to be produced against a higher fuel consumption per unit of reformate.

## 5. Greenhouse gas emissions outside the refineries

The refinery is the focus of this study, but, of course, only one part of the (bio)fuel chains. In this chapter the other components of the three systems considered are discussed, and the greenhouse gas emissions related to these components are estimated.

### 5.1. Reference case

The processes yielding greenhouse gas emissions in the reference system other than the refinery are:

- Production and treatment of natural gas outside the EU.
- Production of methanol and methanol shipping (5000 mile) to EU.

**Table 10**  
Greenhouse gas emissions in MTBE production chain.

	kg CO <sub>2</sub> /GJ MTBE
Methanol chain, from natural gas extraction to methanol delivered	4.3
MTBE production	7.9
MTBE transport to refinery	0.2
MTBE combustion	71.8
	84.2

- MTBE production and MTBE transportation to refinery (250 km by rail).

The majority of MTBE consumed in the EU is produced within the EU from isobutylene by-product from steam crackers, refinery FCCs and production of propylene oxide (PO).

In this study it has been assumed that the consumed isobutylene is a component in the mixed C4's product or the C4Raffinate1 fraction of steam crackers (see [http://nexant.ecnext.com/coms2/summary\\_0255-2972\\_ITM](http://nexant.ecnext.com/coms2/summary_0255-2972_ITM)), a mixture of isobutylene, 1- and 2-butenes. The methanol is produced from natural gas from remote gas fields without pipeline connection to consumer markets for e.g. Norway and Latin America. It is then shipped in dedicated tankers to the EU.

Inputs for production of 1 MJ of MTBE are 0.19 MJ of methanol and 0.81 MJ of isobutylene. The process requires approximately  $1.5 \pm 0.5$  tonnes or 4.6 GJ of medium pressure, saturated steam per tonne of MTBE produced for product distillation and methanol recovery (EIPPCB, 2003).<sup>6</sup> Electricity consumption amounts to 16 kWh/tonne MTBE.

Resulting greenhouse gas emissions per GJ product are given in Table 10.

Data for processes concerning methanol production and transportation and MTBE transportation were taken from (Concawe, 2007).

### 5.2. Ethanol case

The main processes yielding greenhouse gas emissions in the ethanol system other than the refinery and crude production and transportation are:

- Cultivation and harvesting of the feedstock (in this report taken to be 50:50% (wt) wheat and sugar beet).
- Production of ethanol from harvested crops.
- Isooctene production from isobutylene by-product.

In this case all of the MTBE is substituted, which means for the LCA analysis that another market will be needed for the isobutylene used for MTBE production in the reference system. We assume that the new outlet will be conversion by dimerization to isooctene and blending of the product in the gasoline pool. The process can be applied at retrofitted MTBE units.<sup>7</sup>

Greenhouse gas emissions related to ethanol production from wheat and sugar beet have been taken from (Concawe, 2007). In accordance with the current market situation it is assumed that the by-products from the ethanol production (beet pulp and

<sup>6</sup> For the steam a net energy content of 2.5 GJ/tonne was assumed. Corresponding energy consumption amounts to approximately  $1.5 \times 2.75 \approx 4.1$  GJ steam or  $\approx 4.6$  GJ natural gas per tonne of MTBE.

<sup>7</sup> An example of a commercial large scale MTBE production facility converted into a isooctene/isooctane production facility is the Alberta Envirofuels inc plant in Edmonton, Canada.

**Table 11**  
Greenhouse gas emissions for the ethanol chain.

	kg CO <sub>2</sub> /GJ ethanol
Ethanol chain, from field to factory gate	58.4
Ethanol transport to regional depot	0.5
Ethanol combustion	0.0
	58.9

**Table 12**  
Greenhouse gas emissions for the isooctene chain.

	kg CO <sub>2</sub> /GJ isooctene
Isooctene production	8.0
Isooctene transportation to refinery	0.2
Isooctene combustion	69.8
	77.9

distillers dried grains with solubles—DDGS) are sold as fodder ingredients. Note that the assumption for ethanol GHG-emissions used here does not include any indirect land use effects, as these were not included in the Concawe study. However, this does not influence the comparison between ethanol and ETBE since the comparison concerns two equal amounts of ethanol. The ethanol produced is transported by road to regional distribution centres for 'splash blending' into tailor made gasoline base fuel blends, data for this link have been adapted from (Concawe, 2007).

For the production of isooctene from isobutylene a greenhouse gas emission of 8.0 kg CO<sub>2</sub>-eq/GJ isooctene is assumed. This estimate is based on contractor data, and was found to be comparable to published data for the Alberta Envirofuels plant in Edmonton (Croezen et al., 2007). For transportation of isooctene to the refinery the same emission has been assumed as for gasoline and diesel transportation to regional depots by train: 0.2 kg CO<sub>2</sub>-eq/GJ product.

The relevant figures extracted in this paragraph are summarized in Tables 11 and 12.

### 5.3. ETBE case

Emissions of the following processes outside the refinery need to be included in the ETBE scenario.

- The production of ethanol.
- Production and shipping of additional isobutylene. As stated earlier, conversion of the 5 vol% of ethanol into ETBE requires more isobutylene than the MTBE production in the reference case.
- Production of ETBE.
- Transportation of ETBE to the refinery.

The GHG-emissions related to the ethanol were taken from the previous paragraph. The emissions related to the last three processes have been adapted from (Concawe, 2007).

In the analysis, the extra isobutylene is derived from surplus volumes. As these are normally applied as a fuel, we assume that it is substituted by extra natural gas. The total greenhouse gas emissions per GJ natural gas amounts to 65 kg CO<sub>2</sub>-eq/GJ, precombustion contribution included. The combustion of isobutylene on the other hand gives a greenhouse gas emission of approximately 70 kg CO<sub>2</sub>/GJ. This means that applying surplus isobutylene in ETBE production will result in a net greenhouse gas emission increase of 5 kg CO<sub>2</sub>-eq/GJ.

**Table 13**  
Greenhouse gas emissions per GJ ETBE.

	kg CO <sub>2</sub> /GJ ETBE	
	Standard analysis	Sensitivity analysis
Ethanol production chain, crop cultivation and ethanol transport included	19.7	19.7
Additional isobutylene production	–1.5	3.1
Additional isobutylene transportation	0.4	1.4
ETBE production	7.7	7.7
ETBE transportation to refinery	0.2	0.2
ETBE combustion	47.4	47.4
	72.7	79.5

**Table 14**  
Greenhouse gas emissions of the processes *outside* the refinery (compared to the reference case, in kg CO<sub>2</sub>-eq/GJ gasoline).

	Reference case	Ethanol	ETBE
MTBE	3.24		
ETBE			7.13
Ethanol		1.89	
Isooctene		2.45	
	3.24	4.34	7.13
<b>Total</b>			
In kg CO <sub>2</sub> /GJ gasoline		1.10	3.89
In kg CO <sub>2</sub> /GJ ethanol		34	121

As part of the sensitivity analysis we also considered the approach applied in (Concawe, 2007), in which the extra isobutylene is produced from field butanes from natural gas liquids (NGLs) or associated gas. For the production of isobutylene we utilized a somewhat different approach compared to (Concawe, 2007). In (Concawe, 2007) the hydrogen resulting from dehydrogenation is valued as a by-product. However, if the isobutylene is produced in the Middle East or some other remote region without much possibilities for hydrogen utilization we consider it to be more logical to assume that the hydrogen is consumed as a fuel rather than to correct for it by assuming natural gas based hydrogen production is avoided.<sup>8</sup>

For combustion of ETBE only the CO<sub>2</sub>-emissions related to the carbon atoms originating from isobutylene are taken into account. The other figures were adopted directly from (Concawe, 2007). The results are shown in Table 13.

#### 5.4. Results for greenhouse gas emissions outside the refinery

With these data, the resulting GHG-emissions outside of the refinery were calculated for the three cases under investigation. The results, including the net GHG effect of the ethanol and ETBE case compared to the reference, are shown in Table 14.

As can be expected, the GHG-emissions outside the refinery are higher in both the ethanol and ETBE case, compared to the reference. Note that the emissions in the ETBE case are much higher than in the ethanol case especially due to the incremental production of isobutylene and ETBE outside the refinery gate.

<sup>8</sup> In fact this utilization of hydrogen as a fuel is exactly what happens at Alberta Envirofuels.

**Table 15**  
The net GHG reduction of the ethanol and ETBE systems, per GJ gasoline and per GJ ethanol.

	Ethanol system	ETBE system
Net effect (kg CO <sub>2</sub> /GJ gasoline blend)		
Outside the refinery	1.10	3.89
In the refinery	–2.30	–5.83
<b>Total</b>	<b>–1.20</b>	<b>–1.94</b>
Net effect (kg CO <sub>2</sub> /GJ ethanol)		
Outside the refinery	34	121
In the refinery	–72	–182
<b>Total</b>	<b>–37</b>	<b>–61</b>

## 6. Overall results and conclusions

### 6.1. Results

The net effects of ethanol and ETBE blending to gasoline on the GHG-emissions per GJ gasoline sold at gasoline stations can now be determined by combining the information given in both previous chapters. Results are shown in Table 15, per GJ gasoline blend (top) and per GJ ethanol (bottom). Combination and aggregation yields a net reduction of approximately 37 kg CO<sub>2</sub>-eq/GJ ethanol when 5 vol% ethanol is added in pure form and approximately 61 kg CO<sub>2</sub>-eq/GJ ethanol in case the ethanol is converted into ETBE before blending.

The larger savings in the ETBE case are due to the energy savings that can be achieved in the refinery when adapting the processes to the higher octane of ETBE. This advantage for ETBE is only partly undone by the higher greenhouse gas emissions related to production of ETBE and the production of extra isobutylene. These results differ from the conventional LCAs published in literature, e.g. Concawe/JRC/Eucar (Concawe, 2007) or GHGenius (see <http://www.ghgenius.ca/>), as these do not take the impact on refineries into account.

A more detailed graphical overview of net GHG-emissions per GJ gasoline blend and the various contributions to the total net GHG-emissions are given in Fig. 6.

### 6.2. Sensitivity analysis

As discussed throughout the report, various assumptions were made in the various modeling steps. Some of these might have significant impact on the outcome of the study. In order to assess the sensitivity of the results to some of these assumptions, two of them were varied, and results were recalculated.

The first sensitivity analysis that was carried out relates to the assumption that the required extra isobutylene is taken from surplus volumes normally applied as fuel and is substituted by natural gas. This assumption significantly contributes to the advantage for the ETBE case.

However, if we assume that the required extra isobutylene is produced from field butanes produced in the Middle East, the ETBE case is still more favourable and gives a net greenhouse gas reduction of 43 kg CO<sub>2</sub>-eq/GJ ethanol. The net GHG-emissions reduction calculated for this situation is shown in Table 16.

The second sensitivity analysis concerns an analysis for a gasoline summer blend. Because of the lower RVP specification (60 kPa) for gasoline summer blends, addition of ETBE and ethanol will result in different adjustments in terms of the reformate quantity and RON and the amount of butane blended in.

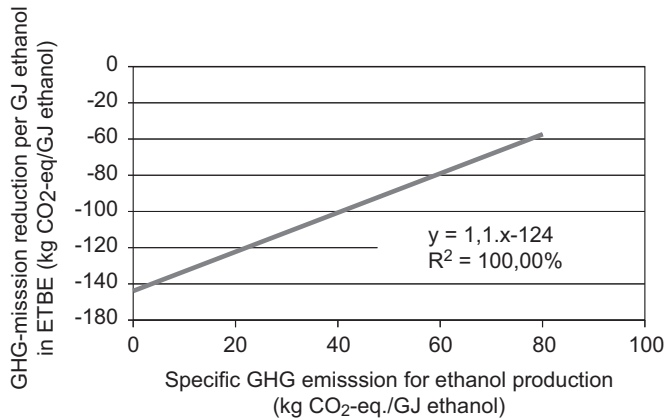


Fig. 6

Table 16

The net GHG reduction per GJ ethanol for the case in which isobutylene is produced from field butanes from the Middle East.

	Ethanol system	ETBE system
Net effect (kg CO <sub>2</sub> /GJ gasoline blend)		
Outside the refinery	1.10	4.44
In the refinery	-2.30	-5.83
<b>Total</b>	<b>-1.20</b>	<b>-1.39</b>
Net effect (kg CO <sub>2</sub> /GJ ethanol)		
Outside the refinery	34	138
In the refinery	-72	-182
<b>Total</b>	<b>-37</b>	<b>-43</b>

Table 17

The net GHG reduction per GJ ethanol for the gasoline summer blend case.

	Ethanol system	ETBE system
Net effect (kg CO <sub>2</sub> /GJ gasoline blend)		
Outside the refinery	1.10	3.85
In the refinery	-2.35	-5.84
<b>Total</b>	<b>-1.26</b>	<b>-1.99</b>
Net effect (kg CO <sub>2</sub> /GJ ethanol)		
Outside the refinery	34	121
In the refinery	-74	-183
<b>Total</b>	<b>-39</b>	<b>-62</b>

As is shown in Table 17, we find that the net greenhouse gas reductions hardly change compared to the yearly average gasoline blend case.

### 6.3. Conclusions

In this project, a simplified refinery model was set up to perform an analysis of the effects in the refineries of blending ethanol or ETBE into gasoline. Effects on fuel consumption by the refinery were calculated, as well as the effects on GHG-emissions of the refineries. The results of this model were then combined with the GHG-emissions of other parts of the fuel (well-to-wheel) chains.

From this analysis, we conclude the following.

#### 6.3.1. Effects on refinery operations and emissions

- Ethanol and ETBE have significantly different characteristics, compared to the fuel components they replace. This results in modifications to refinery operations when these products are

Table 18

The net GHG reduction per GJ ethanol for the gasoline summer blend case.

	Ethanol system	ETBE system
Net effect (kg CO <sub>2</sub> /GJ gasoline blend)		
Outside the refinery	1.10	3.89
In the refinery	-2.30	-5.83
<b>Total</b>	<b>-1.20</b>	<b>-1.94</b>
Net effect (kg CO <sub>2</sub> /GJ ethanol)		
Outside the refinery	34	121
In the refinery	-72	-182
<b>Total</b>	<b>-37</b>	<b>-61</b>

blended into gasoline. Since these modifications lead to changes in refinery fuel consumption and composition, GHG-emissions of the gasoline base fuels are affected. These effects should be considered in LCAs for biofuels.

- Blending in ethanol or ETBE reduces the petroleum base fuel requirement, which can also have lower octane numbers (RON/MON). In our model, this leads to a lower requirement for reformat and butanes, and also lower octane numbers for the reformat. Both effects reduce the CO<sub>2</sub>-emissions of the refinery. These effects are more pronounced in the ETBE case.
- However, less severe catalytic reforming also yields less LPG, H<sub>2</sub> and refinery gases, which have to be compensated according to the LCA-methodology. This increases CO<sub>2</sub> emissions.
- The net effect on GHG-emissions is positive, i.e. GHG-emissions reduce in both cases. The emission reduction is highest in the case of ETBE.

#### 6.3.2. GHG emission effects outside the refineries

- GHG-emissions outside of the refinery are higher in the ethanol and ETBE cases, compared to the reference case. The emissions are highest in the ETBE case, because more ETBE is added compared to the added volume of ethanol and isoctene.

#### 6.3.3. Total GHG emission effects

- Combining these results, the net effects of ethanol and ETBE blending to gasoline on the GHG-emissions can be calculated. The results are shown in Table 18, per GJ gasoline sold at gasoline stations. Combination and aggregation yields a net reduction of approximately 37 kg CO<sub>2</sub>-eq/GJ ethanol when 5 vol% ethanol is added in pure form and approximately 61 kg CO<sub>2</sub>-eq/GJ in case the ethanol is converted into ETBE before blending.
- The GHG reduction calculated for the ethanol case is comparable with the reduction given in (Concawe, 2007), in which a reduction of 40 kg CO<sub>2</sub>-eq/GJ ethanol is calculated. The reduction calculated in this study is slightly lower because in (Concawe, 2007) it is assumed that the ethanol substitutes only MTBE, whereas in the present study a mix of ethanol and isoctene is assumed to substitute a mix of MTBE and petroleum base fuels. Because the specific GHG emission per unit of substituted MTBE is higher as the specific GHG emission per unit of substituted base fuel our study assumes a smaller amount of GHG-emissions avoided.
- The results show that converting ethanol into ETBE improves the GHG balance of the ethanol. This is mainly caused by energy savings in the refineries due to the lower RON of the reformat added in case of ETBE blending. The higher greenhouse gas emissions related to production of ETBE and the

production of extra isobutylene are more than compensated by the savings at the refineries.

- The results presented in this study have been produced considering conventional wheat and sugar beet based ethanol production as considered in the Concauwe/JRC-Eucar report (see Concauwe, 2007). According to this report the fast majority of ethanol production plants in the EU use a conventional gas fired boiler for heat generation and sell by-products as feed. According to Concauwe GHG-emissions for feedstock cultivation and ethanol production amount to an average of approximately 59 kg CO<sub>2</sub>-eq/GJ ethanol.<sup>9</sup>

We have chosen this bioethanol chain described in this specific report because of the authoritativeness of the Concauwe/JRC-Eucar study and because – as stated in Concauwe, 2007 – this chain is representative for the fast majority of ethanol plants in the EU.

However it is of course possible to select another bioethanol chain with different GHG-emissions related to feedstock cultivation and ethanol production for estimating net GHG emission savings related to blending of ethanol as ETBE. Annex V of the Renewable Energy Directive for example (see European Commission, 2009) mentions some eleven different bioethanol chains varying from wheat based ethanol production with lignite fired boiler to wheat straw based ethanol production, these different chains having associated GHG-emissions ranging between 10 and 70 kg CO<sub>2</sub>-eq/GJ.

The results of this study can be used to estimate the net GHG reduction for blending 5 vol% of ethanol as ETBE for these other bioethanol chains too. Using our model we derived a linear relation between GHG-emissions for ethanol feedstock cultivation and ethanol production and the net GHG emission reduction achieved when blending 5 vol% of ethanol to gasoline as ETBE:

$$\text{net GHG (kgCO}_2\text{-eq/GJ}_{\text{ethanol}}) = 1.1 \times \text{gros GHG (kgCO}_2\text{-eq/GJ}_{\text{ethanol}}) - 124$$

In this formula the factor –124 kg CO<sub>2</sub>-eq/GJ ethanol represents the net GHG emission from processes outside the bioethanol chain and subsequent ETBE production, such as production of substituted MTBE, reduction in refinery emissions and avoiding of crude oil production and transportation. Because all these GHG emitting processes are independent of the considered bioethanol chain these emissions can be regarded as a constant. The 1.1 slope represents the relative contribution of GHG-emissions of ethanol production to total GHG-emissions related to ETBE production.

In Fig. 6 the net GHG emission per unit of ethanol applied in ETBE (vertical axis) plotted against the gros GHG-emissions per unit of ethanol consumed in ETBE production.

#### 6.3.4. Some comments about uncertainties in these results

The calculations performed in this project give an estimate of the effects that blending in ETBE or ethanol and isoctene will have on refinery operations at refineries with catcracker configuration. Averaged parameters for efficiencies of furnaces, boilers and in-plant electricity generation were used, and a certain level of heat integration within the refinery was assumed. Many individual catcracker refineries will no doubt have a deviating lay-out and results will subsequently also differ for these refineries. Other types of refineries may also lead to different effects.

<sup>9</sup> The gros GHG-emissions resulting from crop cultivation, crop processing and fermentation.

## 7. Recommendations

The results from this study indicate that the changes to refinery operations may lead to significant GHG reductions, especially in the case of ETBE. The reductions found here are large enough to significantly improve the GHG balance of the ETBE. From an LCA-methodology point of view, these effects on refinery operations should be included in future LCAs on ethanol and ETBE.

As the GHG balance is expected to be an important criterion in future biofuels policies in the EU and perhaps also elsewhere, we also recommend to consider including this effect in the biofuel CO<sub>2</sub>-tools and CO<sub>2</sub> calculation methodologies that are currently being developed or used by various governments.

The calculation model used for this study is only a simplified representation of the EU refinery sector. Even though we feel that the most important processes and effects could be modelled with reasonable accuracy, we would advise to also perform these calculations with a more detailed and elaborate EU refinery model.

Some of the assumptions made in this study are likely to have a significant impact on the results. We would therefore recommend to further look into some of these assumptions, and to assess what effects other choices might have on the outcome of the calculations.

## Acknowledgement

This research was funded by the European Fuel Oxygenates Association (EFOA).

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