

CE Delft

**Solutions for
environment,
economy and
technology**

Oude Delft 180

2611 HH Delft

The Netherlands

tel: +31 15 2 150 150

fax: +31 15 2 150 151

e-mail: ce@ce.nl

website: www.ce.nl

KvK 27251086

ETBE and Ethanol: A Comparison of CO₂ Savings

Report

Delft, October 2007

Author(s): Harry Croezen
Bettina Kampman
Gerdien van de Vreede
Maartje Sevenster



Publication Data

Bibliographical data:

H.J. (Harry) Croezen, B.E. (Bettina) Kampman, G. (Gerdien) van de Vreede,
M.N. (Maartje) Sevenster
ETBE and Ethanol: A Comparison of CO₂-Savings
Delft, CE, 2007

LCA / Bio-ethanol / Refineries / Refining / Greenhouse Gasses / Effects

Publication number: 07.4226.42

CE-publications are available from www.ce.nl

Commissioned by: the European Fuel Oxygenates Association (EFOA)
Further information on this study can be obtained from the contact person, Harry Croezen.

© copyright, CE, Delft

CE Delft

Solutions for environment, economy and technology

CE Delft is an independent research and consultancy organisation specialised in developing structural and innovative solutions to environmental problems. CE Delfts solutions are characterised in being politically feasible, technologically sound, economically prudent and socially equitable.

For the latest information on CE check out our website: www.ce.nl.

This report is printed on 100% recycled paper

Preface

The greenhouse gas (GHG) reduction that is achieved by using biofuels is receiving increased regulatory and public attention. The production chain for the various biofuels is often complex and highly variable making correct “field-to-wheel” assessment difficult. The bio-ether ethyl tertiary butyl ether (ETBE) has established itself as an important route for channeling ethanol into petrol. However the GHG impact of the additional processing step in going from alcohol to ether is not well understood. The purpose of this study was to evaluate to what extent the GHG savings arising from the ability for a refiner to exploit the high octane delivered by ETBE counterbalanced the extra processing step.

Graeme Wallace
Director General - EFOA

Contents

Summary	1
1 Introduction	5
1.1 Background	5
1.2 Applied methodology	6
1.3 Point of departure	7
1.4 Report structure	8
2 Systems Considered	9
2.1 Introduction	9
2.2 Reference case	11
2.3 Ethanol case	11
2.4 ETBE case	13
3 Refinery Analysis	15
3.1 Refinery configurations considered	15
3.2 Refinery model	15
3.3 The main features of the refinery calculations	20
3.3.1 Constant HSR specifications	23
3.4 Results: required amounts and specifications of reformat and HSR	24
3.5 Effects on refinery fuel consumption	26
3.6 Net greenhouse gas emissions	27
4 Greenhouse gas emissions in the links outside the refineries	29
4.1 Introduction	29
4.2 Reference system	29
4.3 Ethanol system	31
4.4 The case of ETBE	32
4.5 Net greenhouse gas emissions	33
5 Overall effects	35
5.1 Results	35
5.2 Sensitivity analysis	35
6 Conclusions and Recommendations	37
6.1 Conclusions	37
6.2 Recommendations	39
References	41
A Process descriptions	47
B Crude TBP curves	51
C Alberta Envirofuels, Edmonton	53
D Detailed results of the sensitivity analysis	55

Summary

Introduction

More and more attention is given to the sustainability of biofuels. Especially the greenhouse gas (GHG) reduction that is achieved with different biofuels is getting increased attention. GHG savings may vary significantly for different biofuels, and several EU Member States are looking for options to differentiate between biofuels according to their actual GHG savings.

In this debate on GHG savings of biofuels and CO₂ tool development, the European Fuel Oxygenates Association (EFOA) wants to draw attention to an omission of current life cycle analyses (LCAs) that has a negative effect on the calculated GHG savings of ETBE and ethanol. EFOA has therefore asked CE Delft to conduct a study to investigate this issue.

LCA studies, even detailed well-to-wheel analyses, assume that the bio-ethanol replaces MTBE and a small quantity of gasoline, and that the base gasoline is not changed. In reality, however, refiners will adjust their refinery operation when bio-ethanol or ETBE is added, because of the very different characteristics of these products. This study indicates that the net effect of these refinery modifications on the GHG emissions is positive, i.e. GHG emissions reduce in both cases. The emission reduction is highest in the case of ETBE.

Aim and approach

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

- by 5 vol% ethanol, or
- by an equivalent amount of ETBE¹.

The GHG emissions of these two scenarios were compared with each other, and with the emissions of the reference situation in which no ethanol is used.

The calculation model

An average catcracker refinery configuration in the EU 25 was modelled. Consequently, the study is not a detailed analysis of the entire EU refinery sector with its over one hundred refineries. Point of departure in the study has been a 50:50% mix of summer and winter blend Euro 95, and ethanol produced from wheat and sugar beet, also in a 50%:50% (wt) ratio.

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

Addition of 5 vol% of ethanol will have the following impact on refinery operations.

- All MTBE is replaced, and a small part of the gasoline base fuels. The latter results in reduced crude intake.
- Ethanol has significantly different specifications, compared to MTBE and gasoline. 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 base fuel component specifications and in operational parameters of refinery processes.

Addition of the same volume of ethanol as ETBE means that

- All MTBE is replaced, and some gasoline base fuel.
- As ETBE, too, has different specifications than MTBE and gasoline, refinery operations will have to be adapted.
- Next to this, the amount of isobutylene required for ETBE production is far larger than the amount consumed in European MTBE production. This has to be accounted for in the LCA analysis as well.

These changes were all modeled, since they have an effect on the environmental impact related to crude oil production and refinery operations.

The calculation model set up for this study was based on data and information from literature. Because of the nature of the study - an abridged LCA - a number of simplifications and assumptions had to be made. In both the ethanol and ETBE cases analysed here, the base fuel amounts and specifications were attained by starting from the reference case, and changing:

- The added amounts of butanes.
- The added amounts of reformate and the RON specification of the added reformate fractions.

The results of this refinery model were then combined with results from an analysis of the emissions in the various (bio)fuel chains outside the refinery.

Results and conclusions

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 reformate and butanes, and to lower octane numbers for the reformate. Both effects reduce the CO₂-emissions of the refinery, and are more pronounced in the ETBE case than in the ethanol case. However, less severe catalytic reforming also yields less LPG, H₂ and refinery gases, which have to be compensated. This increases CO₂ emissions.

Combining these results with GHG emissions outside the refinery yields the net GHG effect of ethanol and ETBE blending to gasoline. These overall results are shown in Table 1, per GJ gasoline blend (top) and per GJ ethanol (bottom). The calculations yield a net reduction of 37 kg CO₂-eq/GJ ethanol when 5 vol% ethanol is added in pure form and 61 kg CO₂-eq/GJ ethanol in case the ethanol is converted into ETBE before blending. Compared to an LCA in which the ethanol and ETBE simply replace MBTE, the modifications in the refinery operations



cause an additional 3% GHG emission reduction in the ethanol case, and about 20% in the ETBE case².

Table 1 The net GHG reduction of the ethanol and ETBE systems, per GJ gasoline and per GJ ethanol

Net effect (kg CO ₂ /GJ gasoline blend)	Ethanol system	ETBE system
• outside the refinery	1.10	3.89
• in the refinery	-2.30	-5.83
Total	-1.20	-1.94
Net effect (kg CO ₂ /GJ ethanol)		
• outside the refinery	34	121
• in the refinery	-72	-182
Total	-37	-61

The results thus show that converting ethanol into ETBE improves the GHG balance of the ethanol. This is mainly caused by the lower RON of the reformat added in case of ETBE blending. This advantage for ETBE is to some extent undone by the higher GHG emissions related to production of ETBE and the production of extra isobutylene. The specific GHG reduction calculated for the ethanol case is comparable with the reduction from other LCA analyses³.

In order to assess the sensitivity of the results to some of the assumptions, results were also calculated for two different scenarios.

- Firstly, the assumption relating to the origin of the required extra isobutylene was varied. In the standard case, it is subtracted from surplus volumes normally applied as fuel and is substituted by natural gas. If it is assumed that the required extra isobutylene is produced from field butanes produced in the Middle East, the ETBE case is less positive, but still more favourable with a net GHG reduction of 43 kg CO₂-eq/GJ ethanol.
- Secondly, a gasoline summer blend was assumed, in stead of the yearly average gasoline blend. In this case we find that the net GHG reductions hardly change.

Recommendations

- The results from this study indicate that the changes to refinery operations lead to significant GHG reductions in the case of ETBE. We thus recommend to consider including this effect in the biofuel CO₂-tools currently being developed, and to include an estimate of effects on refinery operations in future LCAs on ethanol and ETBE.
- 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 were modelled with reasonable accuracy, it would be advisable to also perform these calculations with a more detailed and elaborate EU refinery model.

² Note that this percentage varies with the GHG emissions of the ethanol production, see chapter 6.

³ For example, the WTW study of Concawe/JRC/Eucar of 2007 gives a reduction of 40 kg CO₂-eq/GJ ethanol, using somewhat different assumptions.



1 Introduction

1.1 Background

In discussions on biofuels policies in the EU, the greenhouse gas (GHG) reduction that is achieved over the biofuels chain is getting increased attention. Studies have shown that GHG savings may vary significantly between various biofuels, and several EU Member States, such as the Netherlands and the UK, are looking for options to differentiate between biofuels according to their actual GHG savings.

To enable implementation of policy incentives for better performing biofuels (from a GHG savings point of view), both the Netherlands, Germany and the UK are currently developing a so-called CO₂-tool. This tool estimates the greenhouse gas emissions of specific biofuel chains, using LCA-methodology⁴. Biofuel producers may choose to either use default values given in the tool, or provide more accurate, real input data. The Dutch government commissioned CE Delft and Ecofys to develop this tool for the Dutch market. This is done in close cooperation with the UK and Germany, where governments are following a very similar route. The project of CE Delft and Ecofys includes both the development of the tool and a stakeholder consultation. However, the project does not allow in-depth analysis of new issues such as the one brought forward by the European Fuel Oxygenates Association (EFOA) and its members.

In this debate on GHG savings of biofuels and CO₂ tool development, EFOA wants to draw attention to an omission of current LCA's, that has a negative effect on the calculated GHG savings of ETBE, in comparison with ethanol. LCA studies, even the detailed well-to-wheel analysis of Concawe/JRC/Eucar (Concawe, 2007), assume that the bio-ethanol replaces MTBE and a small quantity of gasoline. In reality, however, refiners will adjust their refinery operation when bio-ethanol or ETBE is added, because of the very different characteristics of these products. These changes to the refineries may have an effect on GHG emissions that should be incorporated in the GHG calculations of biofuels, if significant.

EFOA has therefore asked CE Delft to conduct a study on the greenhouse gas effects of adding ETBE or ethanol to gasoline that takes into account the changes to refinery operations.

⁴ LCA = Life Cycle Analysis

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

- by 5 vol% ethanol or
- by an equivalent amount of ETBE⁵.

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 CO₂-tools.

1.2 Applied methodology

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

A spreadsheet model of refinery operations was set up to model the changes in the refineries, and their effects on GHG emissions. This model focussed on the main features and processes. Consequently, the study is not a detailed analysis of the entire EU refinery sector with its over one hundred refineries.

A basic assumption for this analysis has been the assumption that current EU 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 ratio's and specifications of refinery products supply to the EU market. This applied basic assumption also means that changes in export/import of refinery products have been ignored although changes in these transactions are perhaps more logical from an economic point of view than changes in refinery operations.

We have the following arguments for this basic assumption:

- The approach is required to fulfill ISO 14040 guidelines, which requires the same functional unit for all systems that are compared.
- Specifications of petroleum products have been defined and laid down in legal standards, which define the minimum quality of the refinery products. Production of products with significantly higher quality than required is an unlikely and economically less attractive scenario.
- Market demands may change due to changes in oil products prices as a result of ethanol and ETBE blending. A sharp price increase may result in reduced consumption. However, the amounts of ETBE and ethanol considered here are marginal compared to the entire crude slate processed, making it less likely that prices and production costs will change that much that these will influence market demand.

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



- At a stable and fixed global market demand, changes in import/export will cause indirect changes in refinery operations, i.e. at refineries outside the EU. These changes are very hard to predict. It seems more logical to consider changes within the EU25 only.
- The fact that in practice the EU refinery sector produces more than enough gasoline to supply the European market and approximately 40% of production is exported, is sidestepped by assuming that certain refineries produce primarily for export and certain refineries primarily for the EU home market.

The study has been performed for a catcracker refinery configuration. This configuration represents approximately 50% of the total EU 25 refinery capacity. The 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 stressed by Concawe, each refinery is unique and an analysis for one refinery will not be representative for any other refinery within the EU 25. So the analysis in this study is not translatable to a specific refinery.

In relation to the application of LCA methodology it has been assumed that market demands are covered by one artificial refinery.

1.3 Point of departure

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, MON⁶ and RON⁷ was considered. This product is a mixture of crude oil derived 'base fuel' components and an average MTBE content of 5% (vol).

A 50:50% mix of summer blend and winter blend was considered because it was anticipated that blending ETBE or ethanol in the summer blend pool would have the most pronounced effects in terms of composition requirements because of the limitations for vapor pressure. The limited vapor pressure reduces the amount of butane that can be added. Fuel specifications are given in Table 2.

Table 2 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

Composition of the blend in terms of percentages of lower heating value contributions are given in Table 3.

⁶ Motor Oxygen Number.

⁷ Research Octane Number.

Table 3 Current average blend composition of Euro 95 summer blend (GJ/GJ gasoline blend)

MTBE	4%
ETBE	
Ethanol	
Isooctene	
Petroleum base fuel	96%

1.4 Report structure

This report is structured as follows. The different systems compared in this study are described in the next chapter. The description covers both the structure of the systems in terms of processes and products as well as the specifications of the gasoline and its components in terms of RVP, RON and MON numbers. All systems considered of course include a refinery. Because of the complexity of the refinery this part of the different systems is analyzed separately in chapter 3. The other parts of the systems are considered in more detail in chapter 4, where the emphasis is on the greenhouse gas emissions in the different processes outside the refinery. The overall results are given in chapter 5, conclusions and recommendations can be found in chapter 6.



2 Systems Considered

2.1 Introduction

Blending in ETBE or ethanol effectively boils down to blending in two different shapes of ethanol:

- direct addition of ethanol to gasoline;
- ETBE, produced from using bio-ethanol and isobutylene.

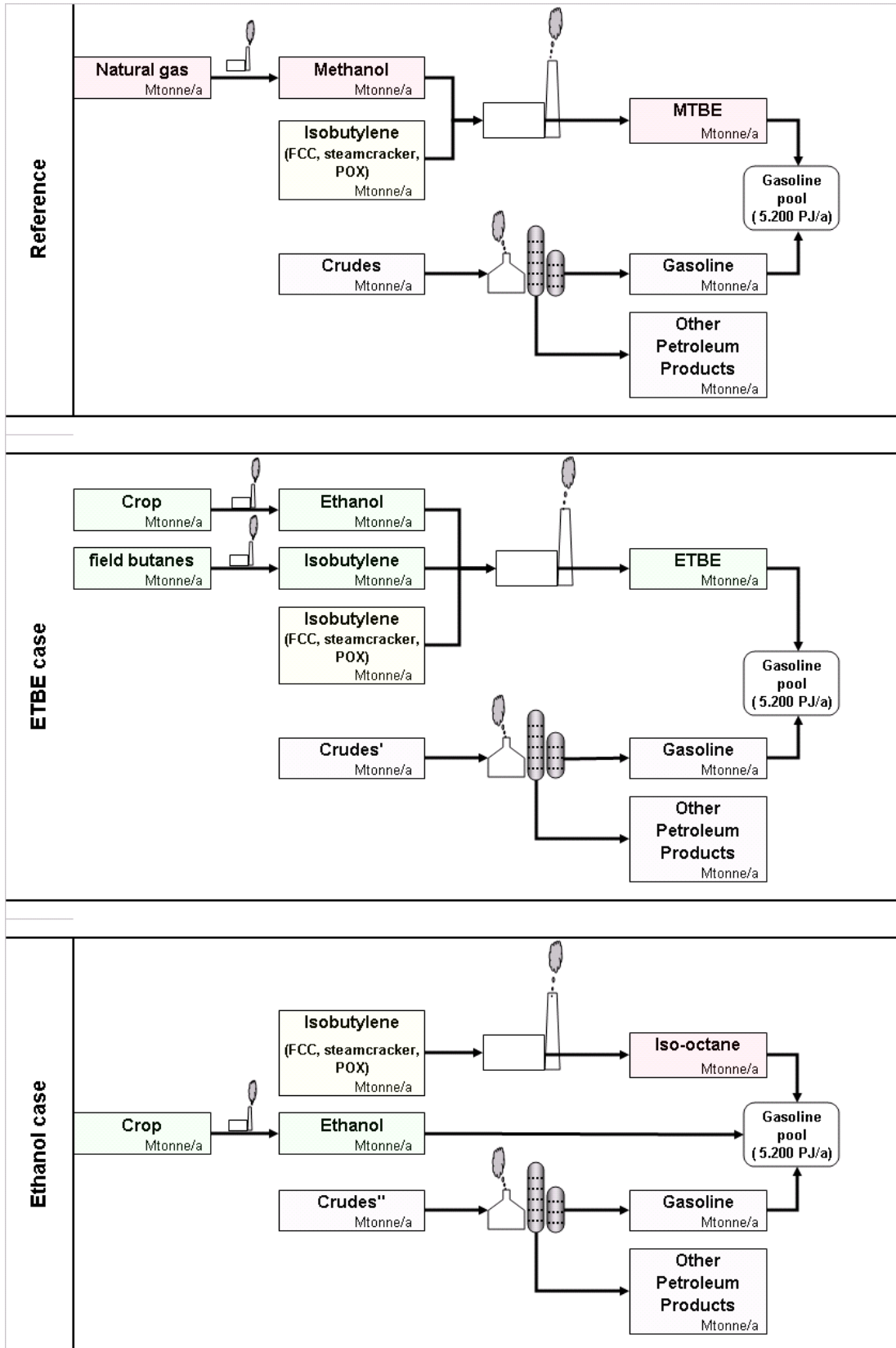
In this study, the greenhouse gas emissions of these two cases are to be compared with each other, and with the emissions of the reference situation in which no ethanol is used. In that (reference) case, a combination of base fuels and MTBE is offered at the gasoline stations.

It has been assumed that both ETBE and ethanol will first of all substitute MTBE as oxygenate and octane improver. Blending in higher amounts of ethanol and ETBE – more than the amount of MTBE that is normally blended in - will then result in substitution of other components of the petroleum base fuel.

Figure 1 illustrates the production chains for the three cases. A brief description of each of these cases is given in the paragraphs below.

Replacing MTBE by ETBE or ethanol means that the specifications and volume of the petroleum base fuels will have to be adapted in order to meet RVP, MON and RON specification requirements for the entire gasoline blend sold at refilling stations. This in turn has an effect on the composition and on other specifications of the petroleum base fuels. For example, petroleum base fuels density and lower heating value differ slightly from case to case. These specifications have been adapted iteratively on the basis of the calculated required RVP, RON and MON specifications of the petroleum base fuels fraction in the gasoline and the subsequent required petroleum base fuels fraction composition.

Figure 1 The three systems analysed in this report



2.2 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 is taken from (IEA, 2005).

The petroleum base fuels are combined or blended with a modest amount of 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. Feedstocks for MTBE production are natural gas based methanol imported from outside the EU and isobutylene that is produced as a byproduct, primarily at steam crackers during the cracking of naphta into petrochemical feedstock. Other, less significant sources of isobutylene are propylene oxide (POX) production and refinery FCCs⁸.

Giving the blend composition and the specifications of the blend and of MTBE, the gasoline base fuel specifications can be determined (see Table 4).

Table 4 Specifications of gasoline, MTBE and reference case gasoline base fuels

	RVP ^{1.25} (in kPa ^{1.25})	MON	RON	Density (kg/l)	LHV (MJ/kg)	Energy content (PJ/year)	vol%
Gasoline blend	220.7	85.5	96.5				
MTBE	7.3	5.0	5.8	0.75	34.80	200	4.9%
Petroleum base fuels	213.4	84.65	95.40	0.76	43.77	5.000	95.1%

2.3 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.

Addition of ethanol will have the following impact on refinery operations.

- First of all, adding 5 vol% of ethanol means that all MTBE is replaced.
- Since more ethanol is added in terms of energy content as is currently added in the shape of MTBE, this means that not only MTBE is substituted, but also a small part of the gasoline base fuels. This results in reduced crude intake.

⁸ FCC = Fluidized Catalytic Cracking Unit

- Next to this, the significantly different specifications of ethanol, compared to MTBE and gasoline have to be taken into account. This means that 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, the base fuel specifications have to change. This in turn 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 byproduct at steam crackers and POX. Based on the current developments on the Californian automotive fuels market, where MTBE has been phased out as a gasoline additive recently, it has been assumed that the surplus isobutylene is processed into isooctene. According to both market analysts and technology suppliers this is the most profitable alternative. This product is sold to refineries as a low vapor, high octane gasoline additive and blended in with the gasoline pool.

Assuming that the average specific weight per unit of volume of the gasoline does not change significantly as a result of blending ethanol and isooctene instead of MTBE, the blend will have the composition with respect to its lower heating value given in Table 5. The assumption that the average density of the gasoline blend will not change (significantly) is justified by the fact that ethanol has a somewhat higher density compared to the average gasoline sold at refueling stations, but isooctene has a somewhat lower density. The effects of both blending agents therefore more or less counterbalance each other.

Table 5 Blend composition for the ethanol system

	RVP ^{1.25} (in kPa ^{1.25})	MON	RON	Density (kg/l)	LHV (MJ/kg)	Energy content (PJ/year)	vol%
Gasoline blend	220.7	85.5	96.5				
Ethanol	31.8	8.2	10.1	0.79	26.40	167	5.0%
Isooctene	70.9	84.2	94.1	0.71	45.05	164	3.2%
Petroleum base fuels	188.9	84.21	94.12	0.76	43.80	4.869	91.8%

As a comparison of Table 5 with Table 4 shows, the amount of petroleum base fuels (in GJ) is somewhat lower here than in the reference case, meaning that less petroleum base fuels have to be produced and – assuming a constant consumption pattern for the other petroleum products – somewhat less crude is required.

The high 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.

2.4 ETBE case

In this case, too, adding an amount of ETBE that equals 5 vol% of ethanol means that all MTBE is replaced, and some gasoline base fuel. And ETBE, too, has different specifications than MTBE and gasoline. As discussed in the previous paragraph, these aspects will have an impact on refinery operations and subsequent environmental impact related to refinery operations and crude oil production and transportation.

Next to this, the amount of isobutylene required for ETBE production is far larger than the amount consumed in European MTBE production. The 5 vol% ethanol considered in the ethanol system corresponds to a weight fraction of 5.2% of the total gasoline blend. The equivalent amount of isobutylene required for converting the ethanol into ETBE amounts to 6.6% (wt). For MTBE production only 3% (wt) isobutylene. This leaves a deficit of 3.60% of isobutylene that has to be accounted for in the LCA 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.

Note that this approach differs from the one taken in Concawe (2007). In (Concawe, 2007) it is assumed that the gap between available and required amounts of isobutylene is filled by import of isobutylene from the Middle East. There seems to be an abundance of isobutanes and n-butanes - the mixture of these being called field butanes - in the Middle East. The abundantly available field butanes are a byproduct of regional natural gas production and are converted into isobutylene in the country of origin before being shipped to the EU. In this study, that scenario has been considered as part of a sensitivity analysis (see chapter 5).

The resulting composition of the blend and the specifications of the petroleum base fuels are given in Table 6.

Table 6 Blend composition for the ETBE system

	RVP ^{1.25} (in kPa ^{1.25})	MON	RON	Density (kg/l)	LHV (MJ/kg)	Energy content (PJ/year)	vol%
Gasoline blend	220.7	85.5	96.5				
ETBE	7.4	11.8	14.0	0.75	36.20	510	11.7%
Petroleum base fuels	213.3	83.44	93.51	0.75	43.88	4.690	88.3%

The amount of petroleum base fuels is somewhat lower than in the ethanol system. Vapour pressure of the petroleum base fuels can be higher than in the reference system and octane numbers can be lower.



3 Refinery Analysis

3.1 Refinery configurations considered

In general, four to six specific refinery configurations are distinguished, ranging from fairly uniform definitions for hydroskimming refineries to a broad range of definitions of what a complex refinery looks like. Most common definitions are given in Table 7.

Table 7 Refinery configurations

	Percentage of capacity in EU	Atmospheric distillation	Vacuum distillation	Catcracker	Hydrocracker	Coker	Residu gasification	Visbreaker
Hydroskimming	11%	X	(X)			(X)		(X)
FCC ^a	55%	X	X	X		(X)		(X)
Hydrocracking	11%	X	X		X	(X)		(X)
Complex	25%	X	X	X	X	(X)	(X)	(X)

^a FCC = Fluidized Catalytic Cracking Unit

In this report the FCC configuration was considered. This configuration represents 50% of total EU refinery capacity.

In the next paragraphs the refinery calculation model is first briefly discussed (paragraph 3.2) after which the main assumptions and features applied in the calculations are shown in paragraph 3.3. The results of the calculations are given in remaining paragraphs of this section.

3.2 Refinery model

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 for the configurations considered were taken from a study of the International Energy Agency, 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.

For a correct estimation of the effects of blending ethanol and ETBE a spreadsheet model was developed that was subsequently used for reproducing the product slate given in (IEA, 2005). This exercise gave additional information

about process operations for the configuration considered in the reference system, see e.g. Table 10.

Based on the mass balance produced by the model the impacts of ethanol and ETBE addition were estimated.

The calculation model for the FCC refinery configurations has been based mainly on two handbooks for petroleum refinery process economics, (Maples, 2000) and (Gary, 2001). Both handbooks give relationships for product yields and supplement each other. (Gary, 2001) contains more detailed relationships for several refinery processes but does not cover all processes. (Maples, 2000) gives more detailed relationships for product specifications, including e.g. octane numbers, where information concerning products specifications in (Gary, 2001) is often limited to product density.

The information in both sources has been supplemented on specific issues with information from various other sources:

- FCC naphtha splitter operations simulations have been based on (IFP, 2000) and the software included in Petroplan, version 3, available on a private internet website.
- Hydrodesulphurization operational parameters and products slate were largely based on (Purvin, 2000) (TU, 2003) and (EIA, 2001)
- For FCC naphtha HDS information concerning RON and MON loss was taken from (Axens, 2006) and (IFP, 2000).
- Additional information for RON, MON and RVP of different gasoline components was taken from (ECN, 1989) and (Schremp, 1999).
- Additional information concerning the refinery layout were derived from (Bechtel, 2000 and Purvin, 2000).

The model has been developed to produce the mass balance over the refinery For MON, RON and RVP of the different refinery products added to the gasoline pool default values were used.

As stated above, the model was used to reproduce the mass balance for the refinery configurations considered in (IEA, 2005). The proper functioning of the models was also checked by calculating the mass balance and products specifications for cases discussed in literature and comparing the model results with the results given in these literature sources, such as (IFP, 1995) and (IFP, 2001).

More background information on how distillation and reforming was modelled is given in Appendix A .

The crude slate and the product slate used in the model were taken from the FCC configuration data provided in (IEA, 2005). These are given in Table 8 and Table 9. The slate composition differs somewhat between the North-Western part of Europe – where relative more light and sweet North Sea oil is processed – and the Southern part of Europe, where relative more heavier and sour Middle



Eastern crudes are processed. In this study an average slate has been considered. Other sources, such as (Bechtel, 2000), (Purvin & Gertz, 2000) and various Concawe reports give comparable slate compositions for the crude slate consumed by the EU refinery sector.

Table 9 also shows the product slates calculated with the refinery model developed for this study. Products slates are given with and without HFO consumption. Part of the HFO is consumed within the refinery and products slate is given for both taking this consumption into account and not taking it into account.

The resulting mass balance for the reference cases is given in Figure 2.

Table 8 Crude slate composition

Composition	By volume	By weight
- Arab light	4.8%	4.8%
- Arab heavy	4.4%	4.5%
- Iran light	4.8%	4.8%
- Iran heavy	4.7%	4.8%
- Oseberg	25.0%	24.5%
- Brent/Fourties	7.7%	7.5%
- Bonny	10.2%	10.3%
- Urals	28.7%	29.3%
- Sahara	9.9%	9.4%
Specific weight (kg/m ³)	0.85	
S-content (kg/m ³)	7.41	
LHV (GJ/tonne)	42.53	

Table 9 Comparison of products slates

	This study		IEA, 2005
	HFO consumption included	HFO consumption excluded	
Naphta	7.608%	7.608%	7.608%
Gasoline blend, butane included	29.201%	29.201%	29.201%
Kerosine	6.021%	6.021%	6.020%
Diesel	25.813%	25.813%	25.813%
IGO pool	7.695%	7.695%	7.695%
HFO pool	18.425%	14.184%	18.425%
	94.763%	90.523%	94.762%

Figure 2 Mass balance for reference case

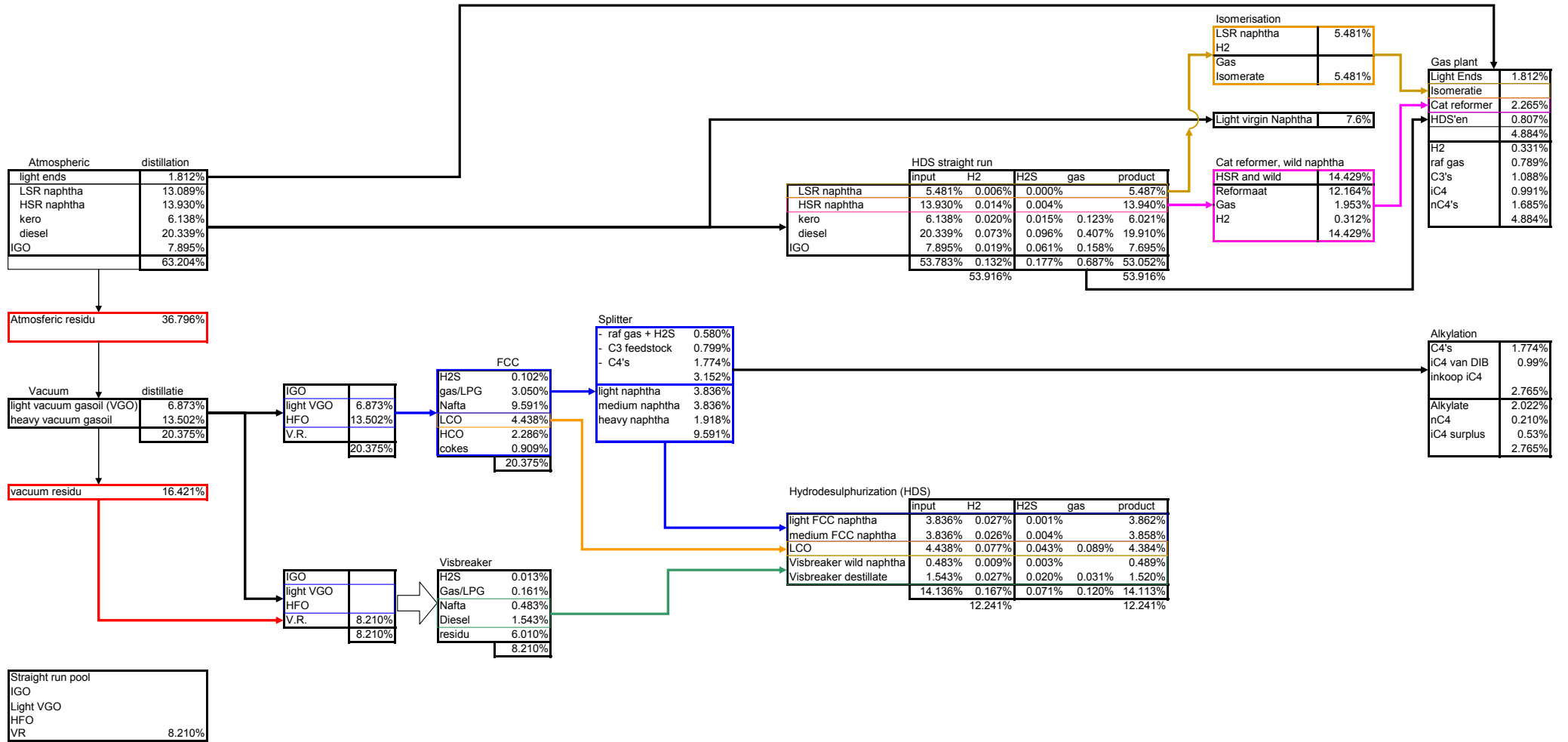


Table 10 Operational parameters

Operational parameters of conversion processes		Cut points		
• Conversion		• Light ends	20	
a FCC	67%	• LSR and MSR naphta	134	
b Visbreaker	8%	• HSR naphta	209	
• Cat reformer		• Kerosene	240	
a Type	semi continuous	• Diesel	350	
b Pressure (bar) =	20	• IGO	400	
• Isomerase type	once through	• LVGO	450	
		• HFO	558	
Residual sulphur content after HDS		Gas plant separation efficiencies		
Light naphtha	8	C ₃ =	90%	
Heavy naphtha	8	C ₃	90%	
Kerosene	250	C ₄ =	100%	
Diesel	8	IC ₄	100%	95%
FCC light naphta	8	NC ₄	100%	
FCC medium naphta	8			
Visbreaker naphta and distillate	8			
IGO treater	1,000			
LCO	8			

The results of the model have been compared with the energy consumption and associated greenhouse gas emissions given in (IEA, 2005), see Table 11. Calculated consumptions for steam generation and furnace fuel requirement are comparable, but in (IEA, 2005) estimated fuel requirement for electricity generation are ten times higher than estimations in this study. However, since the electricity consumption in (IEA, 2005) is also ten times higher than the values from practice (see e.g. (ECN, 2003), (Duyvestein, 2004)), the IEA data seem not entirely correct and have therefore been ignored in this study⁹.

Table 11 Comparison of fuel consumptions

	This study	IEA, 2005
Furnace fuel	1.65	1.53
Steam		
• HP-steam generation fuel	0.26	
• LP-steam generation fuel	0.11	
	0.37	0.53
Electricity		
• GJ electricity	0.10	
• GJ fuel for generation	0.29	3.38
Total fuel consumption (GJ/tonne crude)	2.31	5.45

⁹ The 300 - 350 kWh/tonne crude electricity consumption given in (IEA, 2005) would require a 400 MWe power plant next to every average (10 Mton nameplate) catcracker refinery.

3.3 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.

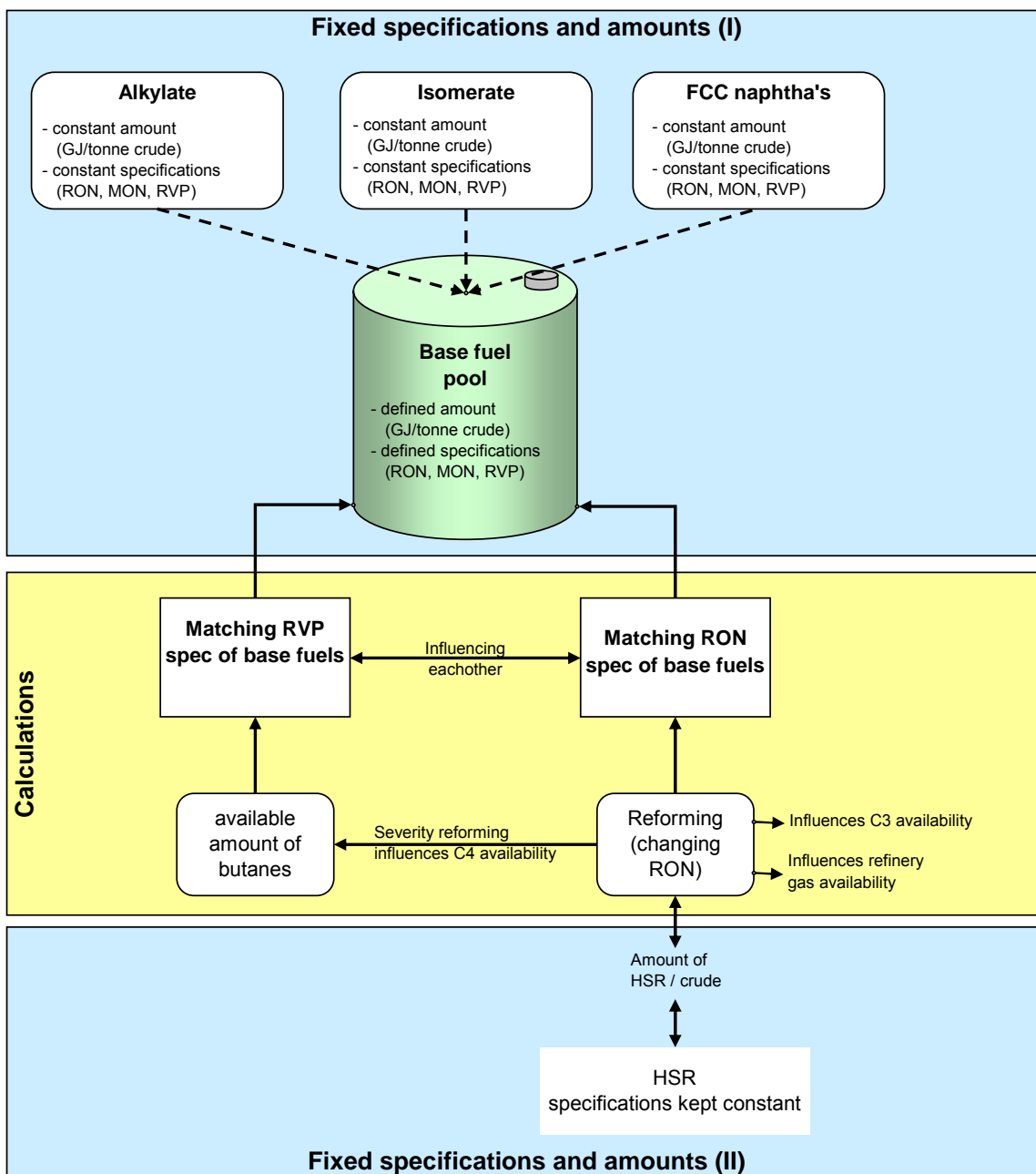
- First of all, in consultation with the customer it was decided that with respect to changes in crude consumption we would only consider reduction of the average crude slate, not a reduction in the consumption of one or a few individual crudes.
- Next to this we did not consider changes in operational parameters of conversion process (FCC, Visbreaker) and in the production volumes of both processes. Both installations are the most expensive ones in the entire refinery (together with the catalytic reformer) and produce the cheapest components for the gasoline and diesel pools. It is therefore reasonable to assume these processes are operated at maximum capacity. We also assumed that the applied operational parameters represent the economic optimum equilibrium for operation of both processes.
- We assumed that the produced amount of light and medium naphtha would not change and the specifications of the medium naphtha would not change. The latter would result in different products slate at steam crackers, which would have to be taken into account. These assumptions imply that the amount and quality of the light straight run naphtha does not change either.

The above assumptions implicate that the amounts and the specifications of the alkylate, FCC naphtha's 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/isooctene or ETBE by changes in the amounts of reformate and butane and the quality of the reformate in terms of octane numbers.

The essence of the refinery related calculations is illustrated in Figure 3.



Figure 3 Illustration of the type of calculations performed in this project and the applied boundary conditions



As can be seen in the figure, the base fuel pool is composed of alkylate, isomerate, FCC naphthas and products produced by the reformer. The amounts of isomerate, alkylate and FCC naphtha's are assumed to be fixed, as are their specifications (see Table 12). The specifications and the required amounts of the total blend of crude oil derived base fuels (alkylate, isomerate, FCC naphtha's and reformate) are known, since these can be determined by:

- The specifications of the gasoline sold at refilling stations.
- The specifications and the added amounts of ethanol/isooctene and of ETBE.

The latter are given in Table 13 and Table 14.

Table 12 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 13 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 14 Required specifications of petroleum base fuel pool blend

	RVP (kPa)	MON	RON
Gasoline at refueling station	75.0	85.5	96.5
Base fuels			
Base case	76.0	84.7	95.4
Ethanol case	70.9	84.2	94.1
ETBE case	80,6	83.4	93.5

The RVP of the added reformat fractions was assumed to be constant, too. In practice, the RVP of the reformat decreases slightly with increasing RON. However, the reformat RON specifications of the reformat fractions added in the different scenarios c.q. cases differs relatively little so that changes in RVP will be small, presumably neglectable¹⁰.

In the ethanol and ETBE cases analysed here, the base fuel amounts and specifications were thus attained by starting from the reference case, and changing:.

- The added amounts of butanes.
- The added amounts of reformat and the RON specification of the added reformat fractions.

The amounts of butanes and reformat that can be added and the RON of the added reformat fractions are restricted by the amounts and specifications of the base fuels blends in the different scenarios and by the considered amounts and specifications of isomerate, FCC naphtha's and alkylate.

¹⁰ This approach of keeping reformat RVP constant is also applied in the Petroplan flowsheeting program.



Determining added amounts of butanes and reformat and determining reformat RON is an iterative process in which each of the three parameters influences the other. For example, adding more butanes means less reformat can be added. The RON of the blend will lower slightly, too, when adding more butanes and this has to be compensated by an increased RON specification of the added reformat.

Iteration was done by hand applying a loop. The first step was iteratively adapting the added amount of butanes until the RVP of the entire base fuels blend was correct. After that the other parameters were adjusted. Then the sequence of iterative steps was carried on through again until all boundary conditions were satisfied.

However, changing the RON specification of the reformat also influences the mass balance over the reformer and fuel, steam and electricity requirement of the reforming process. The mass balance over the reformer has an impact on both the required amount of heavy straight run (HSR) naphtha and on the availability of butanes, propane, refinery gas and hydrogen.

In order to simplify the calculations somewhat, HSR naphtha specifications were assumed to be constant. This issue is further discussed in Appendix next paragraph, while calculation results are given in the two following paragraphs.

3.3.1 Constant HSR specifications

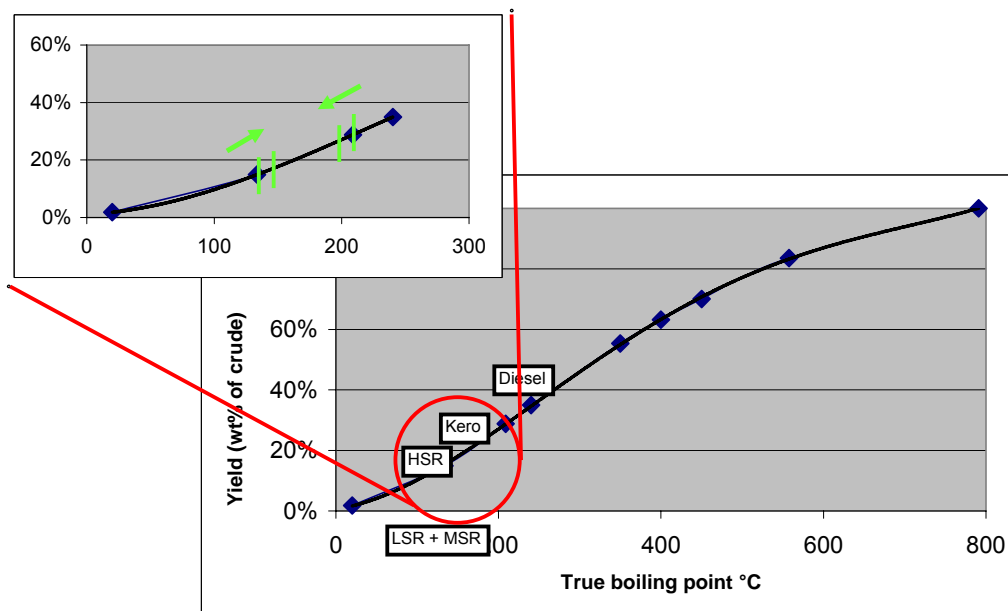
As indicated in the previous paragraph, blending in ethanol/isooctene or ETBE will reduce the required amount of base fuels derived from crude oil. Assuming that this reduction in base fuels is translated in a reduction of the amount of reformat (see previous paragraph), less heavy straight run naphtha (HSR) is required. Reduction of HSR means reduction in crude consumption.

Reduction in HSR is established by changing the cut points such that the produced amount of HSR decreases while the fraction specifications are kept constant. The produced amounts of other distillates is kept constant. This approach is illustrated in Figure 4.

We assumed that the distillation cut points are shifted such that the resulting HSR has the same specifications in every scenario c.q. case. This gives the advantage of having known input specifications for reforming related calculations.

Kerosine specifications will change somewhat as a result of the adjustment in cut points. The effects of this change on refinery operations is assumed to be negligible, since the only following processing the crude kerosene goes through is hydrodesulphurization (HDS). The change in cut points has a small to very small effect on sulphur content and naphthalenes and aromates content.

Figure 4 Change in cut points yielding constant HSR naphtha specifications



Changes in the specifications of the LSR/MSR naphtha fraction and the diesel fraction will be small and presumably negligible because of the large volume of these fractions. Specifications of heavier distillates are assumed to firmly remain constant.

3.4 Results: required amounts and specifications of reformate and HSR

The added amounts of butanes and reformate and the RON specification of the different reformate fractions yields the base fuels blend compositions given in Table 15.

Table 15 Base fuel pool compositions (weight% per tonne crude processed in reference case)

	Reference		Ethanol case		ETBE case	
	weight %	vol %	weight %	vol %	weight %	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 ₄ 's	1.2%	6%	1.0%	4.7%	1.4%	6.8%
	28.6%	100.0%	27.9%	100.0%	26.8%	100.0%

As indicated in chapter 2, 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 naphtha's 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 produced by distillation, and needs to be hydrodesulphurized and processed in the reformer.
- Lower octane numbers means catalytic reforming can be less severe and therefore less energy is required for reforming.

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.

Less severe catalytic reforming on the other hand yields less LPG (butanes, propane), H₂ and refinery gases.

The resulting reformer mass balance and the changes in crude requirement, fuel consumption and availability of butanes, refinery gas, H₂ and C₃ are given in Table 16 and Table 17.

Table 16 Mass balance for catalytic reformer (all percentages per tonne of crude processed in reference case)

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

Table 17 Results for H₂ and C₃ 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 ₂ availability	0.31%	0.27%	0.24%
• C ₃ availability	0.57%	0.46%	0.39%
• HSR required	13.93%	12.96%	11.20%
Net fuel required (GJ/tonne crude)			
a reformer	0.44	0.39	0.33
b gas plant requirement	0.03	0.03	0.02
c HSR production and HDS	0.20	0.18	0.16
Net requirement	0.67	0.60	0.51

3.5 Effects on refinery fuel consumption

Net fuel consumption and fuel composition

The reduction in fuel requirement calculated in the previous paragraph 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. This is explained below.

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 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 makes it logical 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 H₂ - 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. This is, for example, the case at the Rotterdam Botlek ExxonMobil refinery.

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.

C3 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).

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.



3.6 Net greenhouse gas emissions

The net effects of reduced HSR requirement, reduced C₃ availability and changes in natural gas export/import, and the resulting effects on greenhouse gas emissions are depicted in Figure 5.

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 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 made undone by fact that the C₃ supply by the refinery is reduced.

These results clearly indicate that addition of ETBE leads to 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 additive 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. So in the ethanol case more reformat per unit of ethanol has to be produced compared to the ETBE case. Next to this, the reformat 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 reformat has to be produced against a higher fuel consumption per unit of reformat.

Figure 5 Calculation of net greenhouse gas emissions

Consumptions and productions (GJ/GJ gasoline)

	Reference case	ethanol	ETBE
Reduced HSR input in reforming	0.466	0.434	0.375
natural gas supplied to refinery	-0.007	-0.007	0.007
C3 produced in refinery	0.020	0.016	0.014

Net effect in consumptions and productions (GJ/GJ gasoline)

	Reference case	ethanol	ETBE
Change in HSR consumption		-3.3%	-9.1%
Change in natural gas consumption		0.0%	1.5%
Change in C3 supply		0.4%	0.6%

Spec. GHG emissions

kg CO2/GJ
79.0
64.8
69.8

X

=

Resulting greenhouse gas emissions (kg CO2-eq/GJ gasoline)

	ethanol	ETBE
Crude consumption	-2.58	-7.23
Natural gas consumption	0.00	0.95
C3 supply	0.27	0.45

Net difference with reference

	ethanol	ETBE
In kg CO2/GJ gasoline	-2.30	-5.83
In kg CO2/GJ ethanol	-72	-182

4 Greenhouse gas emissions in the links outside the refineries

4.1 Introduction

The refinery is, 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. As in the previous chapter, we first discuss the reference system (without any ethanol or ETBE), then the ethanol and ETBE cases.

4.2 Reference system

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 (5,000 mile) to EU;
- MTBE production and MTBE transportation to refinery (250 kilometers by rail).

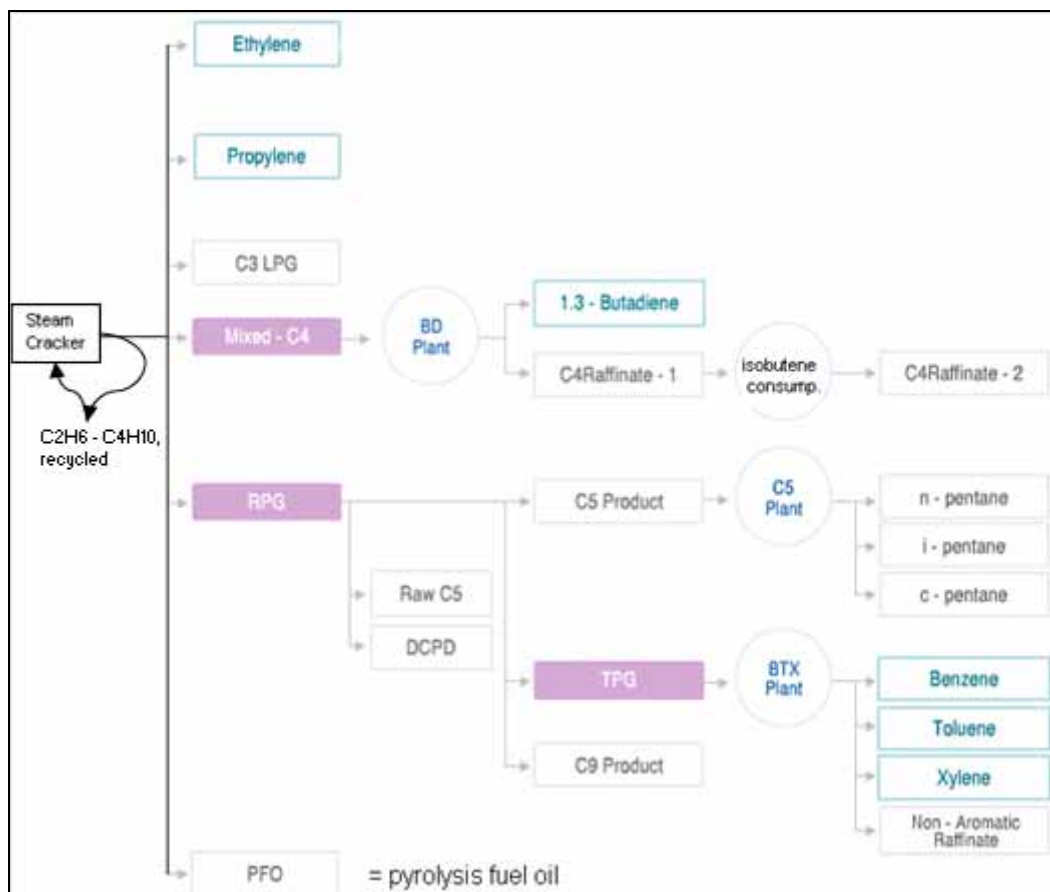
The last three links have been aggregated into 'the MTBE chain'. Energy consumption and greenhouse gas emissions related to this 'chain' are discussed below.

As was derived in §2.2, Table 4, MTBE currently makes up 5 vol% of the gasoline blend sold at petrol stations in the EU, which amounts to 4% in terms of energy content. The majority of MTBE consumed in the EU is produced within the EU from isobutylene by-product from steam crackers, refinery FCC's and production of propylene oxide (POX). 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), a mixture of isobutylene, 1-butenes and 2-butenes. C4raffinate1 from steam crackers contains 20% - 45% by weight of isobutylene¹¹.

The methanol is produced from natural gas from remote gas fields without pipeline connection to consumer markets in e.g. Northern Norway and Latin America. It is then shipped in dedicated tankers to the EU.

¹¹ <http://www.freshpatents.com/Isobutylene-dt20070510ptan20070106102.php>. Isobutylene is actually separated from mixed C4's by reaction with methanol to MTBE, then cracking the separated MTBE again in isobutylene and methanol http://nexant.ecnext.com/coms2/summary_0255-2972_ITM

Figure 6 Origins of the majority of isobutylene (source: <http://www.lgpetro.com/eng/petroinfo/product/product.html>)



The methanol is produced from natural gas from remote gas fields without pipeline connection to consumer markets in e.g. Northern Norway and Latin America and is 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 (REFBREF, 2003)¹². Electricity consumption amounts to 16 kWh/tonne MTBE.

Resulting greenhouse gas emissions per GJ product are given in Table 18. Data for processes concerning methanol production and transportation - 'methanol chain' – and MTBE transportation were taken from (Concawe, 2006).

¹² 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.



Table 18 Greenhouse gas emissions in MTBE production chain

	kg CO ₂ /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

4.3 Ethanol system

The main processes yielding greenhouse gas emissions in the reference 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 the ethanol system the ethanol represents 3.3% of the final gasoline blend sold at petrol stations in terms of energy content (which equals 5 vol%).

In this case all of the MTBE is substituted. As indicated in chapter 2 this means that another market will be needed for the isobutylene that is 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 units¹³. The resulting contribution to the gasoline pool amounts to 3.2% in terms of its energy content (see Table 5, paragraph 0).

Information concerning greenhouse gas emissions related to ethanol production from wheat and sugar beet have been taken from (Concawe, 2006).

In (Concawe, 2006) the assumed application of the by-products from sugar beet and wheat based ethanol production (beet pulp and distiller's dried grains with solubles – DDGS) has a significant impact on the net greenhouse gas emission related to ethanol production¹⁴. Assuming application as fodder ingredients gives a 10 - 30 kg CO₂-eq/GJ ethanol higher contribution to climate change than assuming application as a fuel.

In accordance with current market situation it has been assumed in this study that the by-products are sold as fodder ingredients. The corresponding average greenhouse gas emission amounts to 58.4 ± 0.9 kg CO₂-eq/GJ ethanol. This figure includes wheat and sugar beet cultivation.

Note that the assumption for ethanol GHG emissions used here is conservative and influences the total GHG emissions of the ethanol and ETBE systems considered. However, it does not influence the comparison between ethanol and ETBE since the comparison concerns two equal amounts of ethanol.

¹³ 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.

¹⁴ In Concawe, 2006 several illustrative, but not common configurations for the ethanol plant are also considered, including natural gas and lignite based CHP. These configurations have been ignored in this study because of their limited representativeness.

The ethanol produced is transported by road to regional distribution centres for ‘splash blending’ into tailor made gasoline base fuel blend produced by the refineries. Data for this link have been adapted from (Concawe, 2006).

For the production of isooctene from isobutylene a greenhouse gas emission of 8.0 kg CO₂-eq/GJ isooctene or 0.3 tonne CO₂-eq/tonne isooctene is assumed. This estimate is based on contractor data stating a steam consumption of 2 tonnes/tonne isooctene¹⁵ and a lower heating value of 45 MJ/kg isooctene.

The contractor data based greenhouse gas emission was found to be comparable to published data for the Alberta Envirofuels plant in Edmonton (see Appendix C).

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 CO₂-eq/GJ product.

The relevant figures extracted in this paragraph are summarized in Table 19 and Table 20.

Table 19 Greenhouse gas emissions for the ethanol chain

	kg CO ₂ /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 20 Greenhouse gas emissions for the isooctene chain

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

4.4 The case of ETBE

As stated in paragraph 2.4 conversion of the 5 vol% of ethanol into ETBE requires an additional amount of 3.6% of isobutylene in terms of the lower heating value, compared to the 3.0% required for MTBE production. The total amount of ETBE makes up 10.0% of the blend eventually sold at petrol stations.

The greenhouse gas emissions related to

- Production and shipping of this extra isobutylene,
- production of ETBE
- transportation of ETBE to the refinery

have been adapted from (Concawe, 2006), see Table 21.

The GHG emissions related to the ethanol were taken from the previous paragraph.

¹⁵ Two tonnes of steam $\approx 2 \times 2,75 \approx 5,5$ GJ steam. Assuming a boiler efficiency of 90%, 6,1 GJ of natural gas is required. Greenhouse gas emission per GJ of natural gas amounts to 59 kg/GJ, including gas transport and treatment.



In the analysis, the required extra isobutylene is derived from surplus volumes, normally applied as a fuel. We assume that the derived amount is substituted by extra natural gas. The total greenhouse gas emissions per GJ natural gas amounts to 65 kg CO₂-eq/GJ, precombustion contribution included. The combustion of isobutylene on the other hand gives a greenhouse gas emission of approximately 70 kg CO₂/GJ. This means that applying surplus isobutylene in ETBE production will result in a net greenhouse gas emission reduction of 65 - 70 = -5 kg CO₂-eq/GJ.

As part of the sensitivity analysis we also considered the approach applied in (Concawe, 2007) for the production of the required extra isobutylene. In this study the applied assumption is that the extra isobutylene is produced from field butanes from natural gas liquids (NGL's) 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 artificially correct for it by assuming natural gas based hydrogen production is avoided¹⁶.

For combustion of ETBE only the CO₂-emissions related to the carbon atoms originating from isobutylene are taken into account.

The other figures were adopted directly from (Concawe, 2006).

The results are shown in Table 21.

Table 21 Greenhouse gas emissions per GJ ETBE

	kg CO ₂ /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

4.5 Net greenhouse gas emissions

With these data, the resulting GHG emissions outside of the refinery can be 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 22.

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

¹⁶ In fact this utilization of hydrogen as a fuel is exactly what happens at Alberta Envirofuels.

ETBE case are much higher than in the ethanol case because more ETBE is added compared to the added volume of ethanol and isooctene.

Table 22 Calculation of the greenhouse gas emissions outside of the refinery

Amount (GJ/GJ gasoline blend)				X	Spec. GHG emissions		=	Resulting greenhouse gas emissions (kg CO ₂ -eq/GJ gasoline)			
	Reference case	ethanol	ETBE		kg CO ₂ /GJ			Reference case	ethanol	ETBE	
MTBE	3.8%			84.20		3.24					
ETBE			9.8%	72.75				7.13			
Ethanol		3.2%		58.90			1.89				
Isooctene		3.2%		77.90			2.45				
						3.24	4.34	7.13			

Net difference with reference		
In kg CO ₂ /GJ gasoline	1.10	3.89
In kg CO ₂ /GJ ethanol	34	121



5 Overall effects

5.1 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 23, per GJ gasoline blend (top) and per GJ ethanol (bottom). Combination and aggregation yields a net reduction of approximately 37 kg CO₂-eq/GJ ethanol when 5 vol% ethanol is added in pure form and approximately 61 kg CO₂-eq/GJ ethanol in case the ethanol is converted into ETBE before blending.

Table 23 The net GHG reduction of the ethanol and ETBE systems, per GJ gasoline and per GJ ethanol

Net effect (kg CO ₂ /GJ gasoline blend)	Ethanol system	ETBE system
• outside the refinery	1.10	3.89
• in the refinery	-2.30	-5.83
Total	-1.20	-1.94
Net effect (kg CO ₂ /GJ ethanol)		
• outside the refinery	34	121
• in the refinery	-72	-182
Total	-37	-61

The specific greenhouse gas reduction calculated for the ethanol case is comparable with the reduction given in (Concawe, 2007), a reduction of 40 kg CO₂-eq/GJ ethanol. The reduction calculated in this study is slightly lower because in (Concawe, 2007) it is assumed that the ethanol substitutes MTBE. In the present study a mix of ethanol and isooctene is assumed to substitute a mix of MTBE and petroleum base fuels. MTBE has a higher specific greenhouse gas emission compared with the substituted petroleum base fuels.

The results show that converting ethanol into ETBE improves the GHG balance of the ethanol. This is mainly caused by the the lower RON of the reformat added in case of ETBE blending. This advantage for ETBE is to some extent undone by the higher greenhouse gas emissions related to production of ETBE and the production of extra isobutylene.

5.2 Sensitivity analysis

As discussed throughout the report, various assumptions were made in the various modelling 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 subtracted 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 CO₂-eq/GJ ethanol. This value matches very well with the greenhouse gas reduction calculated in (Concawe, 2007), a value of 44 kg CO₂-eq/GJ. The net GHG emissions reduction calculated for this situation are shown in Table 24.

Table 24 The net GHG reduction per GJ ethanol for the case in which isobutylene is produced from field butanes from the Middle East

Net effect (kg CO ₂ /GJ gasoline blend)	Ethanol system	ETBE system
• outside the refinery	1.10	4.44
• in the refinery	-2.30	-5.83
Total	-1.20	-1.39
Net effect (kg CO ₂ /GJ ethanol)		
• outside the refinery	34	138
• in the refinery	-72	-182
Total	-37	-43

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

As is shown in Table 25, we find that the net greenhouse gas reductions hardly change compared to the yearly average gasoline blend case.

Table 25 The net GHG reduction per GJ ethanol for the gasoline summer blend case

Net effect (kg CO ₂ /GJ gasoline blend)	Ethanol system	ETBE system
• outside the refinery	1.10	3.85
• in the refinery	-2.35	-5.84
Total	-1.26	-1.99
Net effect (kg CO ₂ /GJ ethanol)		
• outside the refinery	34	121
• in the refinery	-74	-183
Total	-39	-62



6 Conclusions and Recommendations

6.1 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 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 biofuel (well-to-wheel) chain.

From this analysis, we conclude the following.

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 blended into gasoline. Since these modifications lead to changes in refinery fuel consumption and composition, GHG emissions of the gasoline base fuels are affected.
- 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 reformate and butanes, and also lower octane numbers for the reformate. Both effects reduce the CO₂-emissions of the refinery: less HSR naphta has to be produced and processed, and catalytic reforming can be less severe.
- These effects are more pronounced in the ETBE case.
- However, less severe catalytic reforming also yields less LPG, H₂ and refinery gases, which have to be compensated according to LCA methodology. This increases CO₂ emissions.
- Despite this effect, 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.

GHG emission effects outside the refineries.

- The refinery is, of course, only part of the biofuel chains. The emissions in the rest of the chain also need to be included in the analysis. We have based the calculation of these emissions on literature. With some exceptions, the Concawe/JRC/Eucar study was used as a data source for these calculations.
- The results show that GHG emissions outside of the refinery are higher in the ethanol and ETBE cases, compared to the reference. The emissions are highest in the ETBE case, because more ETBE is added compared to the added volume of ethanol and isooctene..

Total GHG emission effects

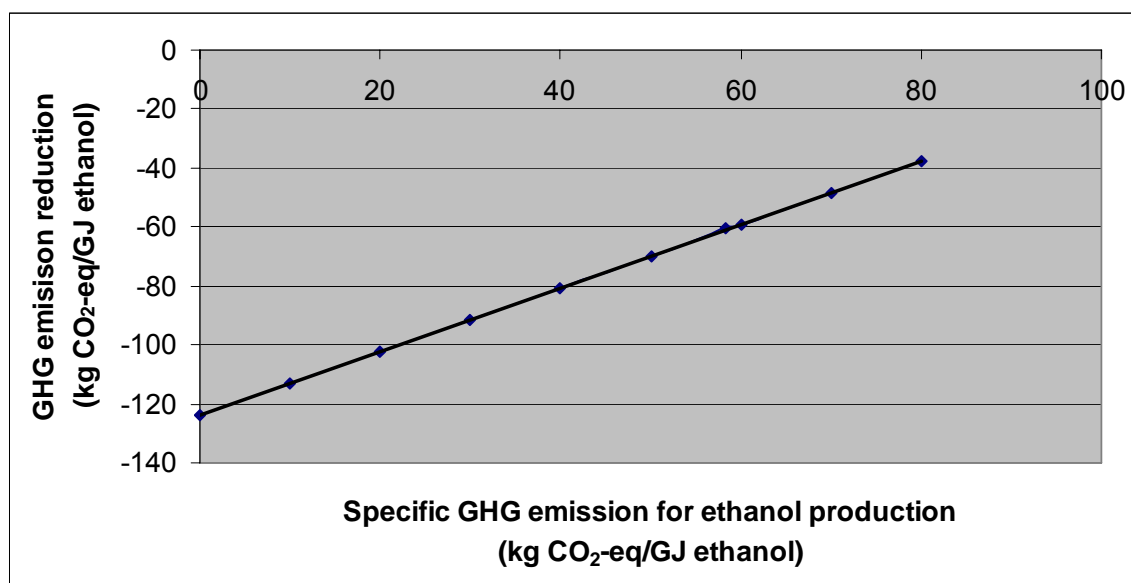
- Combining these results, the net effects of ethanol and ETBE blending to gasoline on the GHG emissions can be calculated. The results are shown in Table 26, per GJ gasoline sold at gasoline stations are shown. Combination and aggregation yields a net reduction of approximately 37kg CO₂-eq/GJ ethanol when 5 vol% ethanol is added in pure form and approximately 61kg CO₂-eq/GJ in case the ethanol is converted into ETBE before blending.

Table 26 The net GHG reduction of the ethanol and ETBE systems, per GJ gasoline and per GJ ethanol

Net effect (kg CO ₂ /GJ gasoline blend)	Ethanol system	ETBE system
• outside the refinery	1.10	3.89
• in the refinery	-2.30	-5.83
Total	-1.20	-1.94
Net effect (kg CO ₂ /GJ ethanol)		
• outside the refinery	34	121
• in the refinery	-72	-182
Total	-37	-61

- The GHG reduction calculated for the ethanol case is comparable with the reduction given in (Concawe, 2007), a reduction of 40 kg CO₂-eq/GJ ethanol. The reduction calculated in this study is slightly lower because in (Concawe, 2007) it is assumed that the ethanol substitutes MTBE, whereas in the present study a mix of ethanol and isooctene is assumed to substitute a mix of MTBE and petroleum base fuels.
- The results show that converting ethanol into ETBE improves the GHG balance of the ethanol. This is mainly caused by the lower RON of the reformat added in case of ETBE blending. This advantage for ETBE is to some extent undone by the higher greenhouse gas emissions related to production of ETBE and the production of extra isobutylene.
- These results are for ethanol made from wheat and sugar beet, using Concawe/JRC-Eucar data for emissions of feedstock cultivation and ethanol production (58.9 kg CO₂-eq/GJ ethanol, see §4.3). If other feedstocks are used, the emission reductions will change. In Figure 7 the net GHG reductions of both systems analysed here are shown for a range of ethanol GHG emissions.

Figure 7 Relationship between specific greenhouse gas (GHG) emission for ethanol production and net saved GHG emissions by application of ethanol in ETBE production (all figures in kg CO₂-eq/GJ ethanol)



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 isooctene will have on refinery operations at refineries with catcracker configuration. In the project we assumed an average lay out of the refinery, but many individual catcracker refineries will no doubt have a deviating lay out and results will subsequently also differ for these refineries.

Next to this we also assumed certain averaged parameters for efficiencies of furnaces, boilers and inplant electricity generation. We also took into account a certain level of heat integration within the refinery (see Appendix A). All these aspects may differ for individual refineries, again, also giving different results on individual refinery level.

6.2 Recommendations

The results from this study indicate that the changes to refinery operations lead to significant GHG reductions, especially in the case of ETBE. These reductions are large enough to significantly improve the GHG balance of the ETBE, an important criterion in future biofuels policies. We thus recommend to consider including this effect in the biofuel CO₂-tools currently being developed. In addition, we recommend to include an estimate of effects on refinery operations in future LCAs on ethanol and ETBE.

As explained in chapter 3, it should be realised that 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, it would be advisable to also perform these calculations with a more detailed and elaborate EU refinery model.

Some of the assumptions made in this study are quite significant, i.e. 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.



References

Axens, 2006

Jean-Claude Plumail

Two Routes to Residue Upgrading via Hydroconversion : Presentation at 7th Annual Middle East Refining Conference - Dubai - 27/28 february 2006

S.I. : Axens, 2006

Bechtel, 2000

A Technical Study on Fuels Technology related to the Auto-Oil II Programme

S.I. : Bechtel Limited, 2000

CML, 2001

J. Guinée, ...[et al.]

Handbook on life cycle assessment : operational guide to the ISO Standards

Leiden : CML (Centrum voor Milieukunde Rijksuniversiteit Leiden) , 2001

CONCAWE, 2004

J.S. McArragher, ... [et al.]

Gasoline volatility and ethanol effects on hot and cold weather driveability of modern European vehicles

Brussels : CONCAWE, 2004

CONCAWE, 2005

M. Dastillung, ...[et al.]

The impact of reducing sulphur to 10 ppm max in European automotive fuels : an update

Brussels : CONCAWE, 2005

CONCAWE, 2007

R. Edwards

Well-to-wheels analysis of future automotive fuels and powertrains in the European context, version 2c

Brussels : CONCAWE/EUCAR/JRC, 2007

Duyvestein, 2004

C.P.T.M. Duyvestein

CO₂ / NO_x monitoringsprotocol Esso raffinaderij Rotterdam

Rotterdam : ExxonMobil, 2004

ECN, 1989

F. Van Oostvoorn, P. Kroon, A.V.M. de Lange

Serum : een model van de Nederlandse raffinage-industrie

Petten : ECN, 1989

ECN, 2003

M.L. Neelis, M.K. Patel, P.W. Bach, W.G. Haije
Analysis of energy use and carbon losses in the chemical and refinery industries
Petten : ECN, 2005

EIA, 2001

The transition to ultra-low sulphur diesel fuel: effects on prices and supply
Washington DC. : EIA (Environmental Investigation Agency), 2001

Energetics, 2006

Energy bandwidth for petroleum refining processes
S.I. : Energetics Incorporated, 2006

Gary, 2001

J.H. Gary, G.E. Handwerk
Petroleum Refining : Technology and Economics
New York : Marcel Dekker Inc, 2001

IEA, 2005

J.Reinaud
The European refinery industry under the EU emission trading scheme
Paris : IEA (International Energy Agency), 2005

IFP, 1995

J-P Wauquier
Crude oil, petroleum products, process flow sheets
Paris : IFP (Institut Français du Pétrole), 1995

IFP, 2000

The domino interaction of refinery processes for gasoline quality attainment
Response by Institut Français du Pétrole to a study of AEA
Paris : IFP (Institut Français du Pétrole), 2000
See: http://www.aeat-env.com/Sulphur_Review/

IFP, 2001

J-P Favennec
Refinery operation and management
Paris : IFP (Institut Français du Pétrole), 2001

IPTS, 2003

JRC Jint Research Centre, Technologies for Sustainable Development European IPPC
Bureau
Integrated Pollution Prevention and Control (IPPC) : Reference Document on Best
Available Techniques for Mineral Oil and Gas Refineries
Sevilla : IPTS (Institute for Prospective Technological Studies), 2003

Hedden, 1994

K. Hedden, A. Jess
IKARUS, bereich Raffinerien und Ölveredelung
Karlsruhe/Stuttgart : Universität Karlsruhe/Universität Stuttgart, 1994



Maples, 2000

R.E. Maples
Petroleum refinery process economics
Tulsa : PennWellBooks, 2000

Purvin, 2000

C. H. Birch. R. Ulivieri
ULS gasoline and diesel refining study
Houston : Purvin & Gertz, Houston, 2000

Schremp, 1999

Gordon Schremp, ...[et al.]
Supply and cost of alternatives to MTBE in gasoline
Sacramento (CA) : California Energy Commission, 1999

Slaback, 2004

D.D. Slaback
A surrogate model approach to refinery-wide optimization
Lubbock : Texas Tech University, 2004



ETBE and Ethanol: A Comparison of CO₂ Savings

ANNEXES

Report

Delft, October 2007

Author(s): Harry Croezen
Bettina Kampman
Gerdien van de Vreede
Maartje Sevenster





A Process descriptions

In this appendix an abridged overview of the refinery model applied in this project is presented. In the first paragraph the considered configuration is described. In the subsequent paragraphs the most important processes are considered.

A.1 Overall descriptions

In the catcracker refinery crude is separated into different so-called straight run fractions in two steps: atmospheric distillation and vacuum distillation.

Applied cut points for distillation are given in Table 28. The cut points have been determined iteratively until the mass balance over the refinery model matched that of the FCC configuration considered in (IEA, 2005).

Table 27 Applied cut points

Cut points distillation (°C)	
light ends	20
light gasoline	134
heavy gasoline	209
kerosine	240
diesel	350
IGO	400
light VGO	450
HFO	558

Atmospheric distillation

Fractions produced in atmospheric distillation are:

- Refinery gas, the methane and ethane that were dissolved in the crude.
- LPG, propane and butanes.
- Light, medium and heavy straight run naphtha or LSR, MSR and HSR naphtha.
- Kerosene (or kero).
- Atmospheric gasoil, applied as automotive diesel.
- Atmospheric gasoil, applied as industrial gasoil (IGO).

In accordance with (IEA, 2005) it is assumed that medium straight run naphtha is sold to steam crackers for production of chemical industry feedstock (ethane, propene, aromates, etc.). All light straight run naphtha is assumed to be desulphurized and subsequently isomerized.

All HSR is assumed to be desulphurized and reformed. Reforming yields reformate but also hydrogen and more refinery gas, propane (C₃) and butanes and isobutanes. These byproducts are treated and separated in the saturated gas plant.

Kero, diesel and IGO are all desulphurized. During desulphurization a small part of the straight run fractions will be converted into lighter products, refinery gas and LPG. These byproducts are circulated to the saturated gas plant.

In the saturated gas plant the gases from atmospheric distillation, reforming and hydrodesulphurization of heavier distillation fractions are separated into individual components. The isolated hydrogen is utilized in hydrodesulphurization processes. The surplus of hydrogen is applied as refinery fuel, as is the refinery gas (methane and ethane).

All propanes produced in atmospheric distillation or reforming are assumed to be sold as LPG. Isobutanes produced in reformer or distilled off in atmospheric distillation are isolated in the de-isobutanizer or DIB and are applied as feedstock in alkylation. Part of the n-butane not required as LPG is added to the gasoline pool. The surplus is applied as refinery fuel.

Vacuum distillation

In the vacuum distillation process the residu of atmospheric distillation is fractioned further in light vacuum gasoil, heavy vacuum gasoil and vacuum residu.

As far as we can deduct all produced light and heavy vacuum gasoils are processed in the catcracker. In this process the gasoils are primarily converted into gases, naphtha's and a diesellike product, light cycle oil. But part of the feed is converted into heavy fuel oil (heavy cycle oil) and coke.

In this project we assumed following outlets for the product fractions:

- FCC LPG is assumed to be consumed in alkylate production and is further sold as C₃ and C₄.
- Light and medium FCC naphtha's are desulphurized and added to the gasoline pool.
- Heavy FCC naphtha is added to the heavy fuel oil pool.
- LCO is assumed to be desulphurized and added to the diesel pool.
- Coke is burned to provide heat for the FCC process.

The vacuum distillation residu is partly sold or consumed internally as a fuel. The other part is visbroken. In the EU 25 about 50% of the vacuum residue is processed in the visbreaker. Visbreaking primarily results in lowering vacuum residu viscosity, but also yields limited volumes of gases, naphtha and diesel. The gases are burned as refinery fuel, the naphtha and diesel desulphurized and respectively reformed and added to the diesel pool.

A.2 Crude distillation

For crude distillation product yields were determined applying the distillation curves given in Appendix B. Distillation was assumed to be perfect with cut point being end point. For estimating the furnace fuel consumption following specifications for the produced fractions were assumed, based on (Energetics, 2006) and (Slaback, 2004) (see Table 28):



Table 28 Specifications of distillation products

	Light ends	Light gasoline	Heavy gasoline	Kerosine	Diesel	IGO	Light VGO	HFO	V.R.
MJ/tonne heat of vaporization	450	350	300	250	230	230	350	350	350
Specific heat (kJ/kg·°C)		1.26	1.14	1.22	1.23	1.23	1.17	1.17	1.17

Diesel and heavier products are assumed to exchange heat with crude. The pinch for heat exchange was assumed to be 20°C. The heat supplied for heating and vaporizing naphtha's and kerosene is cooled away and is lost. Furnace efficiency was estimated assuming an initial flue gas temperature of 750°C and a pinch with the ingoing crude was assumed to be 20°C. Due to the heat exchange between heavier products and ingoing crude the furnace has a suboptimal efficiency. Surplus heat was assumed to be applied for LP steam.

Steam consumption has been estimated assuming a 15 kg/m³ consumption for the vaporized fractions and a 45 kg/m³ consumption for the atmospheric residu (see ECN, 1989).

Resulting fuel and steam consumptions were compared with the ranges mentioned in (REFBREF, 2003), (ECN, 1988).

Electricity consumption was assumed to be a fixed value of 5 kWhe/tonne crude (REFBREF, 2003).

A.3 Vacuum distillation

For vacuum distillation products yields were also determined on the basis of the assumed distillation curves given in Table 28. It was assumed that the atmospheric residue is heated to approximately 400°C and that heavy vacuum gas oil and short residue exchange heat with atmospheric residue. The pinch for heat exchange was assumed to be 20°C. Heat supplied to light vacuum gas oil is assumed to be lost. Furnace efficiency was estimated assuming an initial flue gas temperature of 750°C and a pinch with the ingoing crude was assumed to be 20°C

Steam consumption for maintaining a vacuum in the distillation tower was assumed to be a fixed value of 50 kg HP steam/tonne atmospheric residue for creation of vacuum and 30 kg LP steam/tonne atmospheric residue for stripping.

A.4 Catalytic reforming

In the estimation of the energy consumption for catalytic reforming following aspects are taken into account:

- Providing heat for reactions in the catalytic reformer, calculated as the difference of the LHV of ingoing HSR and the LHV of the products. A furnace efficiency of 75% is assumed.
- Steam consumption, assumed proportional to the fuel consumption and being 65 kg HP steam per 2.4 GJ/tonne of furnace fuel
- Electricity consumption, assumed proportional to the fuel consumption and being 13kg HP steam per 2.4 GJ/tonne of furnace fuel

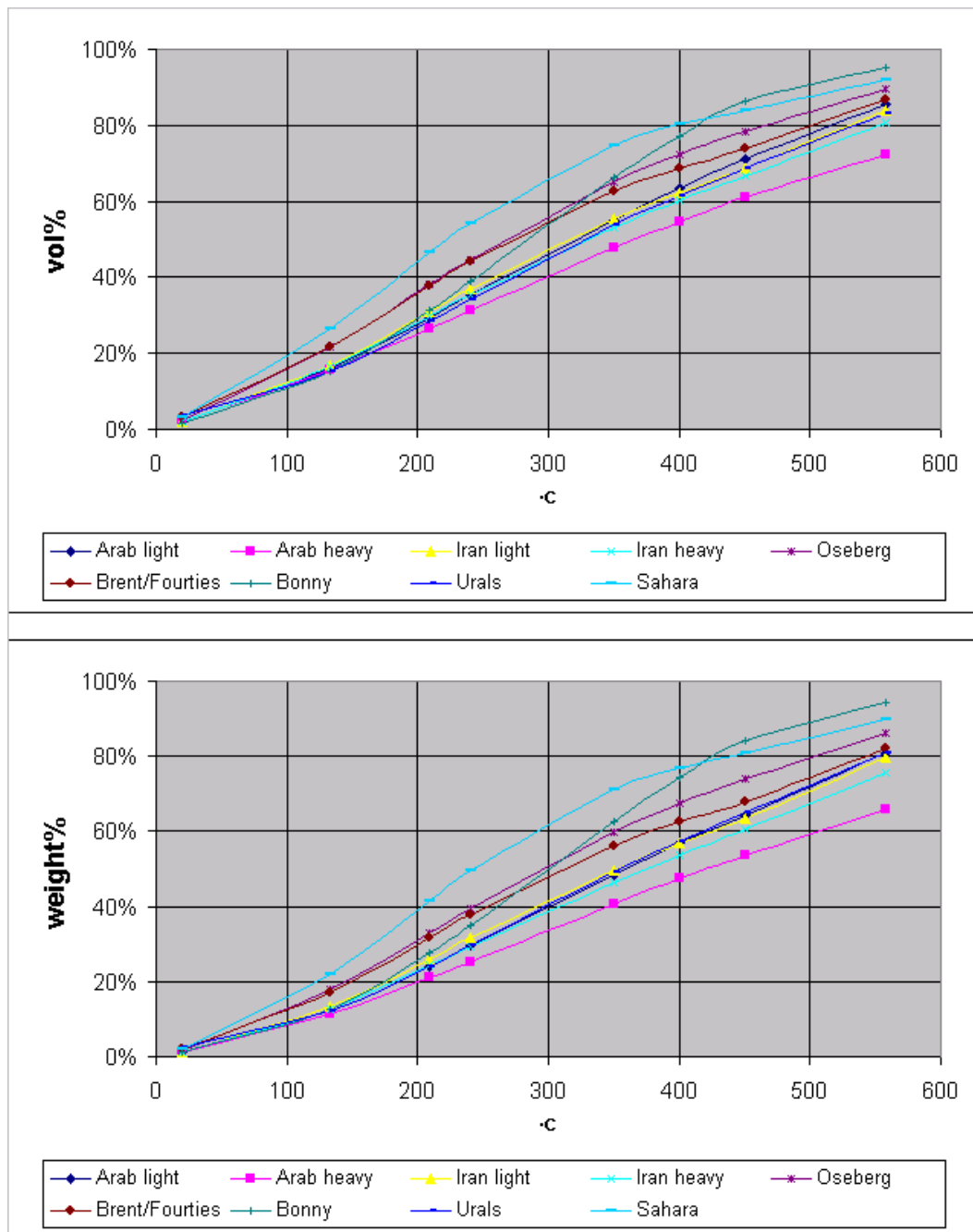


B Crude TBP curves

In the following graphs, the true boiling point (TBP) curves are depicted for various types of crude.

- Data were derived from Total website for Bonny, Urals, Sahara, Oseberg.
- Data for Brent/Fourties was taken from Chevron-Exxon website.
- Data for the four considered crudes were taken from a background study about MTBE phase out in California (Schremp, 1999).

Figure 8 Crude TBP curves



The boiling curves of the individual crudes were used to produce a fourth grade polynome for weight and volume yield as a function of temperature. These polynomes were used to determine atmospheric and vacuum distillation products slates.

Lower heating value and hydrogen and carbon content of the different distillation fractions were estimated based on the specific weight of the fractions, which was determined from the boiling curves for weight and volume.

Hydrogen content was estimated with following relation: $26\% - 15\% \cdot \rho$ (kg/l) - see Perry's. LHV (MJ/kg) was assumed to obey following relation: $-0,82143 \cdot \rho^2 + 2,2607 \cdot \rho + 46,838 - 0,32 \cdot S$ (% wt).



C Alberta Envirofuels, Edmonton

This facility which produces approximately 500 ktonnes of isooctane annually from isobutylene generates an average annual greenhouse gas emission of 350 ktonnes CO₂-eq¹⁷.

The emission for this specific facility includes CO₂ emissions related to conversion of field butanes into isobutylene¹⁸ and may also include CO₂ emissions related to the production of the hydrogen consumed in the last step of the process, the hydrogenation of the produced isooctene into isooctane.

Utilizing greenhouse gas emissions from (Concawe, 2006) for butane isomerisation of field butanes and production of isobutylene from iso-butanes (10,3 kg CO₂-eq/GJ isobutylene) and assuming:

- a Complete conversion at 100% selectivity for both isobutylene production from field butanes and isooctene production.
- b Application of the hydrogen by-product from isobutylene production in isooctane.

the greenhouse gas emission related to isobutylene production alone would amount to $500 \times 0,045 \times 10,3 \approx 230$ ktonnes/a. This would leave a greenhouse gas emission related to isooctene production of 120 ktonnes/a, 0,24 tonne/tonne isooctene or 5,3 kg CO₂-eq/GJ isooctene.

Given the uncertainties in the estimation for Alberta Envirofuels and the fact that the isobutylene source considered in this study is not the pure stream produced at Alberta Envirofuels the similarity between the applied estimation and the specific emission of the considered plant is evaluated as being close enough.

¹⁷ <http://www.ec.gc.ca/pdb/ghg/onlinedata/staticxls/pdf/2004T3English.pdf>,

http://www3.gov.ab.ca/env/air/documents/2005_GHG_Report.pdf

¹⁸ http://industrialheartland.com/pdf/j_wright_presentation.pdf



D Detailed results of the sensitivity analysis

In the following tables, the detailed results are provided for the two cases discussed in paragraph 5.2.

Table 29 Results for the case in which it is assumed that the extra isobutylene required in the ETBE is produced from field butanes from the Middle East

Outside the refinery				Amount (GJ/GJ gasoline blend)			X	Spec. GHG emissions	=	Resulting greenhouse gas emissions (kg CO ₂ -eq/GJ gasoline)		
			Reference case	ethanol	ETBE	kg CO ₂ /GJ				Reference case	ethanol	ETBE
MTBE			3.8%				84.2		MTBE	3.24		
ETBE					9.8%		78.3		ETBE			7.68
Ethanol				3.2%			58.9		Ethanol		1.89	
Isooctene				3.2%			77.9		Isooctene		2.45	
										3.24	4.34	7.68
Net difference with reference												
										In kg CO ₂ /GJ gasoline	1.10	4.44
										In kg CO ₂ /GJ ethanol	34	138
Effects of changes to refinery processes												
Consumptions and productions (GJ/GJ gasoline)				Net effect in consumptions and productions (GJ/GJ gasoline)			X	Spec. GHG emissions	=	Resulting greenhouse gas emissions (kg CO ₂ -eq/GJ gasoline)		
Reduced HSR input in reforming	0.466	0.434	0.375	Change in HSR consumption		-3.3%		-9.1%		79.0	Crude consumption	-2.58
natural gas supplied to refinery	-0.007	-0.007	0.007	Change in natural gas consumption		0.0%	1.5%	64.8	Natural gas consumption	0.00	0.95	
C3 produced in refinery	0.020	0.016	0.014	Change in C3 supply		0.4%	0.6%	69.8	C3 supply	0.27	0.45	
Net difference with reference												
										In kg CO ₂ /GJ gasoline	-2.30	-5.83
										In kg CO ₂ /GJ ethanol	-72	-182
Total results												
Net effect kg CO₂/GJ gasoline blend												
										- refinery excluded	1.10	4.44
										- refinery related	-2.30	-5.83
											-1.20	-1.39
Net effect kg CO₂/GJ ethanol												
										- refinery excluded	34	138
										- refinery related	-72	-182
											-37	-43

