The PO production chain and possibilities for energy saving

Public Summary

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

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1 Introduction

1.1 General background

The Dutch Industry and the Dutch government have made long term agreements on energy efficiency (LEE) for companies that are under the European Trading Scheme (ETS). These companies have to report frequently on their possibilities and achievements on energy efficiency.
These reports describe the current state of energy use, the possible measures that can be taken and the measures already taken and their results.

LyondellBasell is one of the companies that take part in LEE. Lyondell Chemie Nederland B.V., as part of LyondellBasell, produces Propylene Oxide (PO) on two different production sites and in two different processes.
In the Maasvlakte site PO is produced with the POSM process where Styrene is a co-product. In the Botlek site PO is produced with the PO/TBA process where tert-butyl alcohol (TBA) is the co-product.

Energy efficiency can be found on the sites and in the product chain of PO, TBA and Styrene, both upstream and downstream. The LEE agreement gives companies the opportunity to assess measures both on site and in the product chain.

1.2 The project

Based on the agreements of LEE linked to ETS, companies make an effort to realise a significant energy saving within their business community, and the government supports them by means of process coordination and financing additional studies. Agentschap NL coordinates the governmental support. LyondellBasell asked Agentschap NL for support in assessing their energy efficiency on site and through the chain of its products.
CE Delft has been commissioned by Agentschap NL and LyondellBasell to determine the carbon footprint and cumulative energy demand of the two production sites of LyondellBasell in the Rotterdam area.

Purpose of the project is to identify energy saving potential within the PO, Styrene and tert-butyl alcohol production chains. This study also focuses on those options that require cooperation with other companies or yield savings for more than one company within the PO production chains.
The project was carried out in close cooperation with LyondellBasell. At all meetings Agentschap NL was represented.

The project consisted of two pathways.
The first assessed the possibilities of energy saving in the supply chain.
Both the Maasvlakte and the Botlek site of LyondellBasell were addressed.
The second pathway focused on three product chains: Styrene, Polyols and ETBE/MTBE.
This report presents the results of the projects second pathway: the product chains.

1.3 Approach

Each assessment started with the drawing of energy charts. An energy chart is an instrument to get insight in the combined energy and mass flows in the production chain. These energy charts give an overview of the energy content of each process step as well of the energy content of the feedstock and the products.

Using information from open source literature and data provided by LyondellBasell, each process step was worked out in more detail resulting in a map of the major mass and energy flows involved. These flows are presented as energy charts. The charts give an indication of the mass and energy flows involved and the level of detail allowed for by this approach.

In total two brainstorm sessions have been conducted and one special paper was produced. The brainstorm sessions focused on the possibilities of energy saving in the chain. The paper was on ETBE, MTBE and ethanol comparison.

After the brainstorms, possible measures were drawn up based on the suggestions made during these sessions, targeting both the energy saving potential and the technical and economic feasibility of the measure. The measures were reported to LyondellBasell.

1.4 Reading guide

This public summary is one of the six products that have been produced for Lyondell Chemie Nederland B.V.. The other five are confidential reports on the energy charts, the energy saving possibilities on site and in the production chains. The confidentiality concerns the site and production specific information.
The public summary explains the chosen approach for this study in Section 1.3, the energy saving possibilities in the production chain in Section 2.2 to 2.4. Chapter 3 gives the conclusions and recommendations.

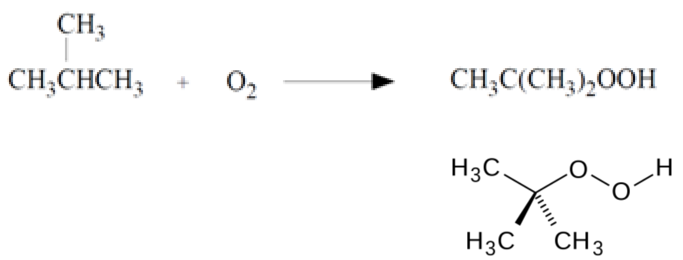
2 The production chains

2.1 The two processes

The general route to propylene oxide involves co-oxidation of the organic chemicals isobutylene or ethyl benzene. These processes are known as PO/TBA and POSM processes.

2.1.1 PO/TBA process

In the PO/TBA process applied at LyondellBasell's Botlek location isobutane is oxidised with industrial oxygen to tert-butyl hydroperoxide (TBHP).

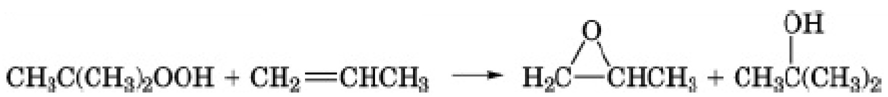


(TBHP)

The applied raw materials are supplied by third parties:

- The oxygen is produced by an over the fence conventional cryogenic air separation plant and supplied by pipeline.
- Propylene is purchased from steam cracking installations and supplied by pipeline and by ship.
- The isobutane is primarily purchased from natural gas processing plants and refineries and is supplied by ship and pipeline.

The produced tert-butyl hydroperoxide is next mixed with a catalyst solution to react with propylene, giving propylene oxide and TBA during this process step:



The produced propylene oxide and tert-butyl alcohol (TBA) are separated by distillation after which:

- The TBA is dehydrated into iso-butylene, which is subsequently converted into ETBE by addition of ethanol or to MTBE by addition of methanol. The ETBE or MTBE is supplied to oil companies for blending into gasoline.
- The propylene oxide is partly supplied to external consumers and partly processed on site into a range of chemicals, including ethers and glycols.

Undesired by-products are isolated as liquid and gaseous fuels. These are either:

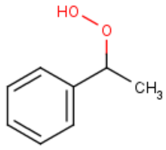
- applied on site for firing furnaces;
- sold to nearby CHP units which supply steam and power to LyondellBasell Botlek;
- or sold to cement industry as a secondary fuel.

Process steam and power for the different processes are supplied by nearby gas fired STAG-CHP plants and a natural gas and residual fired CHP steam boiler with back pressure steam turbine.

2.1.2 POSM process

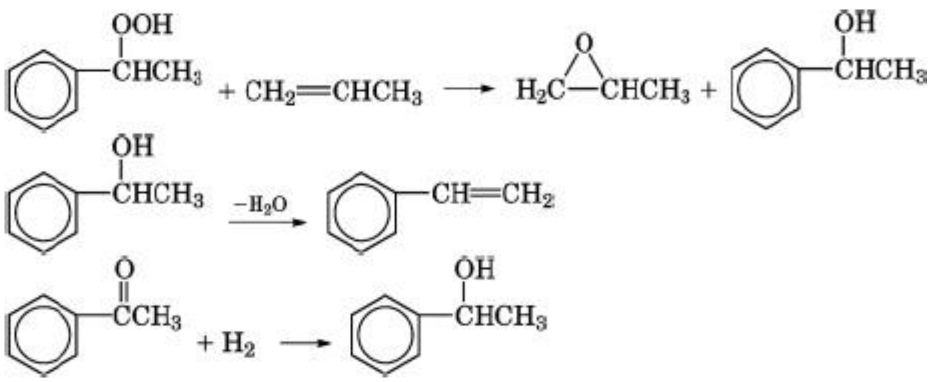
At LyondellBasell's Maasvlakte site, the ethylbenzene feedstock required for the applied POSM[1] process is first produced by reaction of ethylene and benzene. Both feedstocks are primarily purchased from steam cracking plants in the region and are supplied by ship and pipeline (ethylene).

The produced ethylbenzene is next oxidised with air into ethylbenzene hydroperoxide (EBHP).



EBHP

The produced EBHP is next mixed with propylene. Propylene is purchased from steam cracking installations and supplied by pipeline and by ship.
The two chemicals react, forming propylene oxide and 1-phenylalcohol. After the epoxidation reaction between propylene and EBHP, propylene oxide, excess propylene, and propane by-product are distilled overhead. Propane is purged from the process and sold as a fuel and propylene is recycled to the epoxidation reaction.
The 1-phenylethanol co-product, along with acetophenone from the hydroperoxide reactor, are converted into styrene by respectively dehydration and hydrogenation.



1 POSM = propylene oxide, styrene monomer.

A propane by-product is supplied as a fuel to the regular fuel market. Gaseous by-products and condensable organic by-products are supplied to a nearby CHP-plant, supplying steam and power to the LyondellBasell site. The POSM process also produces a large amount of waste water loaded with water soluble organic by-products and salts. The waste water is supplied to AVR together with a part of the condensable organic by-products and is burned as chemical waste. AVR claims that the burning of the waste water requires additional natural gas for achieving complete evaporation and raising the temperature of the flue gases to a required level of 1,200°C.

2.2 Expanded polystyrene

2.2.1 Production

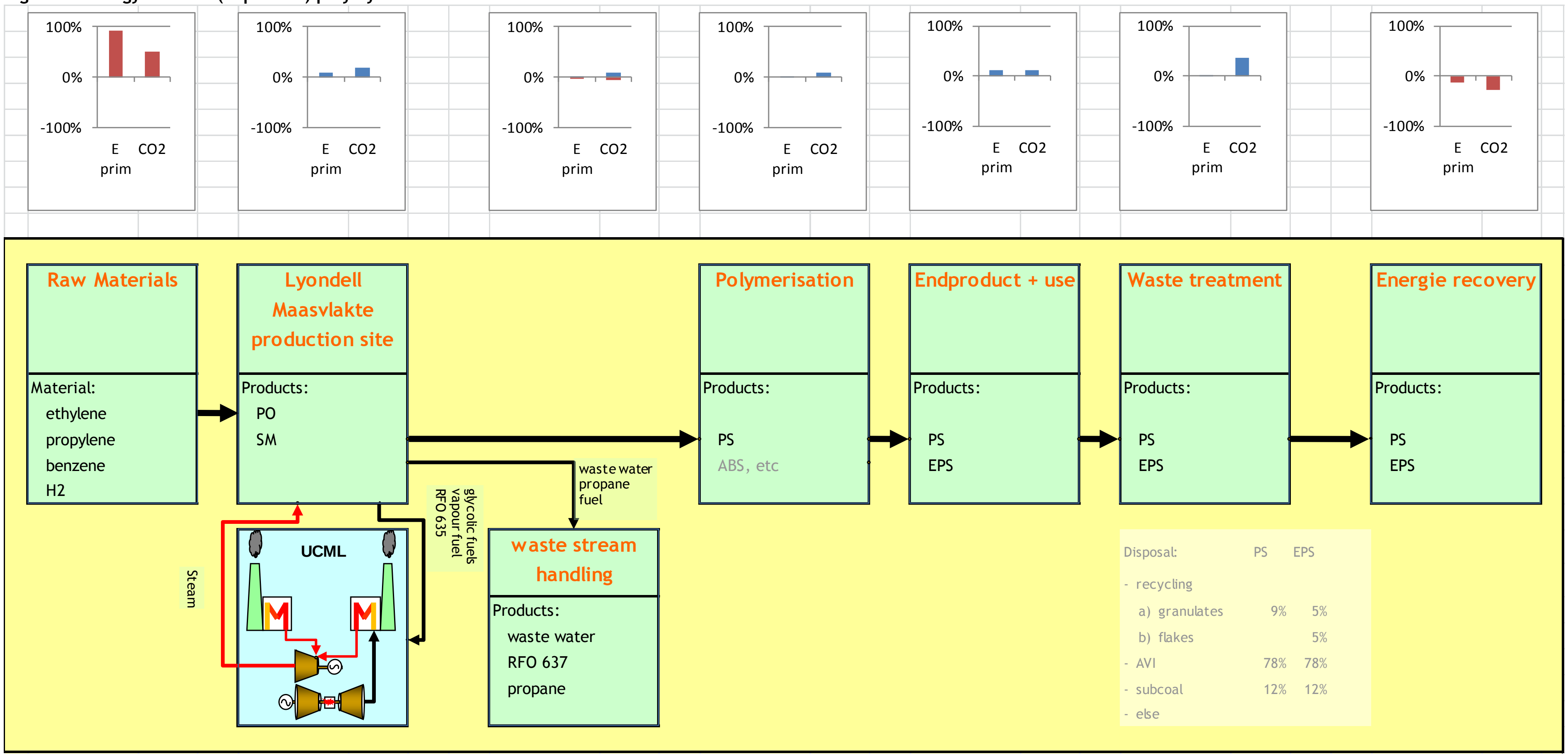
Styrene is used to produce polystyrene and in this case the expanded polystyrene (EPS) is assessed.
The production process follows the following steps.

1. Styrene, Pentane and water, with the supply of energy cause the polymerisation to Polystyrene.
2. Polystyrene is expanded to EPS pearls which are the basis for various products.

Production loss is recycled in the process.

2.2.2 Energy chart

Figure 1 Energy chart of (expanded) polystyrene



2.2.3 Brainstorm

The energy chart shows that the energy content of raw materials, products and waste streams, as well as the energy use of the main processes at RMO and downstream the chain. The largest use of energy is in the production of the raw materials, approximately 70% of total energy consumption in the chain. Opportunities that reduce the use of raw materials have a large impact in the total chain efficiency.

The brainstorm served to think ‘out of the box’ and come up with possible options for energy savings and optimisations in the chain. These are divided in one of three categories:

– raw materials and transport;
– energy usage onsite at Unipol;
– other ideas incl. products and rest streams.

The brainstorm resulted in a large number of suggestions. These were clustered to four categories.

2.2.4 Measures

The measures that have come up during the brainstorm are the following:

Chain Step	Options
Raw materials	Replace by bio-materials, Use less pure RMs
Transport and Logistics	Use different modalities
Energy on location	Heat integration
Other ideas	Recycling Change product specifications

2.2.5 Conclusions

The brainstorm on possible energy saving measures produced a large number of ideas.
LyondellBasell and Unipol will elaborate further possibilities, either together or alone.
The outcome of those elaborations is beyond the scope of this assessment.

2.3 Polyols

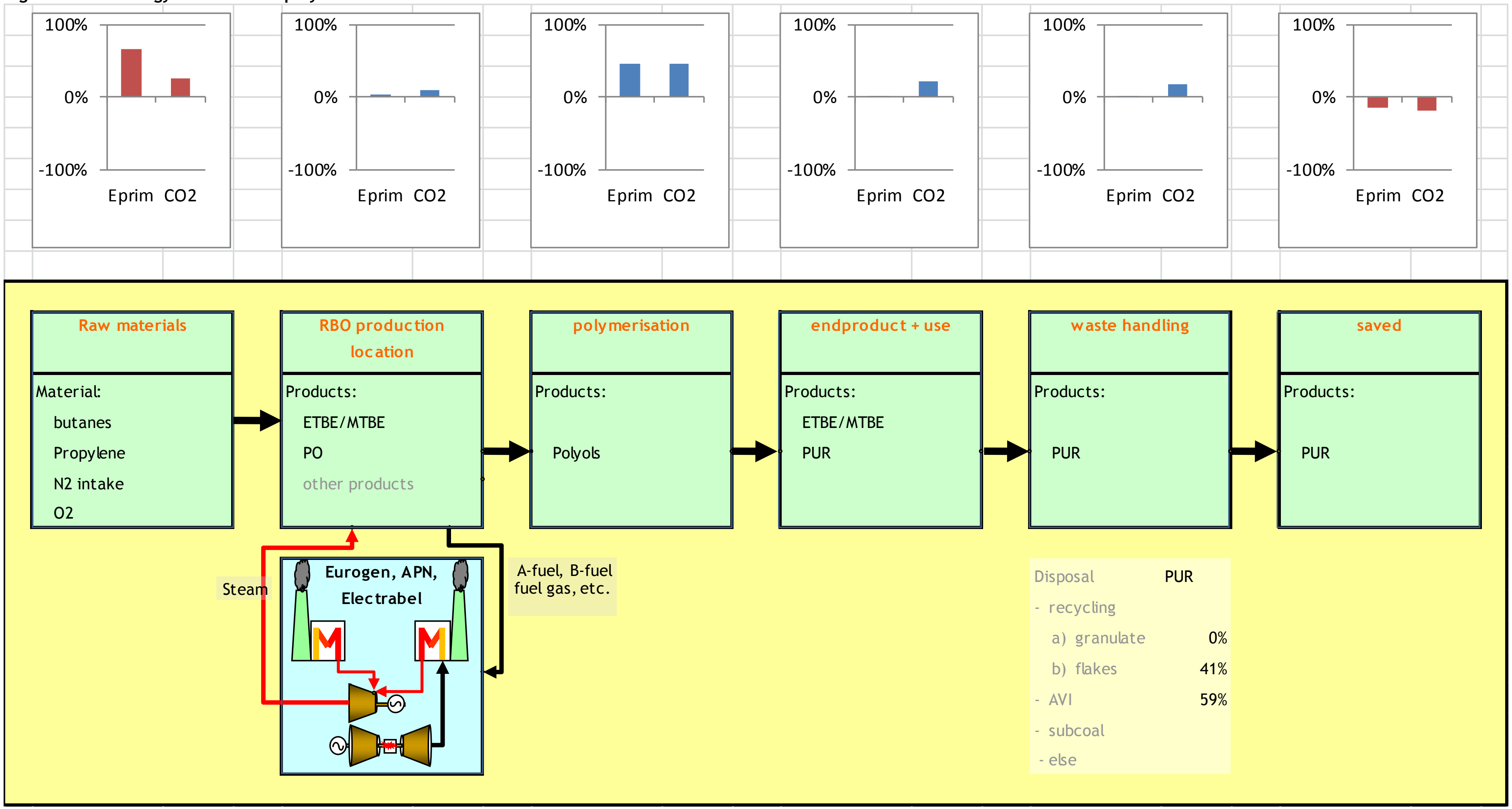
2.3.1 Production

Polyols are produced at the Huntsman plant from PO. In polymer chemistry, polyols are compounds with multiple hydroxyl functional groups available for organic reactions. A molecule with two hydroxyl groups is a diol, one with three is a triol, one with four is a tetrol and so on.

The main use of polymeric polyols is as reactants to make other polymers. They can be reacted with isocyanates to make polyurethanes, and this use consumes most polyether polyols.

2.3.2 Energy chart

Figure 2 The energy chart for the polyols



2.3.3 Brainstorm

The meeting was held in the context of a project to improve the energy efficiency of LyondellBasell's production chains, which at the request of Agentschap NL is being supported by CE Delft. The aim of the meeting was to identify options for improving the energy efficiency of the PO/polyol/PU production chain. Commercial aspects were beyond the scope of the meeting, which was confidential in nature.

Within the PU production chain the following key issues are identified:
- Much of overall energy consumption derives from the energy content of the feedstocks; this is the case for both the PO/polyol feedstocks and for the MDI feedstocks.
- The energy consumption of polyol production is low, but the CO_2 content of other products in the chain is high.
- Production of the PO feedstock does involve substantial energy use.

The brainstorm focused on potential improvements in production and supply of the PO used in polyol production.

2.3.4 Conclusions

Several promising measures have been identified.
LyondellBasell and Huntsman will continue to elaborate the most promising measures.

1. Research on alternative PO purification methods.
2. Use of low-grade PO stream to produce low-grade polyols.
3. Logistics of PO supply to Huntsman.
4. Bio-polyols.

2.4 TBA/iso-butylene applications

2.4.1 Compared applications for gasoline blending components

In this paragraph the energy and GHG content of ETBE, MTBE and bio ethanol are compared. As indicated in Section 2.1 the TBA co-product of the PO/TBA process at LyondellBasell's Botlek plant is dehydrogenated and the produced isobutylene is combined with ethanol produced from biomass to form ETBE or with methanol to produce MTBE.
ETBE with its bio ethanol component is next sold to the automotive fuel market as a biofuel applicable for meeting the Renewable Energy Directory (RED) targets for biofuels as well as the Fuel Quality Directive (FQD).

In CE (2007) the difference in energy requirements and climate impact between these applications of iso-butylene was determined.
Besides the production of raw materials (methanol, bio-ethanol) and the process itself, the indirect impact on the refining of gasoline is also visualised. It is an important part of the overall greenhouse gas emission.

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.

In accordance with the ISO 14040 guidelines, following limiting conditions were defined:

- In all chains the same functional unit should be considered.
- Specifications of the resulting gasoline mixture supplied to the market should be the same for all chains compared and should meet relevant legal standards and common market specifications.
- Changes in market demands for automotive fuels due to utilisation of different blending components (MTBE, ETBE, ethanol/iso-octene) are ignored.

The basic assumption for the comparison concerns the amount of biofuels blended into the gasoline pool. In our analysis a 5 vol% bio-ethanol blend with gasoline or equivalent blends of ETBE or MTBE and gasoline was considered. A 5 vol% blend of ethanol currently represents the most common application of ethanol.

Addition of ethanol or ETBE requires changes in operational parameters of refinery processes and in base fuel component specifications, compared with the reference case. The high vapour pressure of ethanol (compared to that of MTBE) requires a reduction of the vapour pressure of the petroleum base fuels compared to the reference system. All these changes have an effect on the environmental impact related to crude oil production and refinery operations. ETBE specification differ from MTBE and gasoline. Vapour pressure of the petroleum base fuels can be higher than in the reference system and octane numbers can be lower.

2.4.2 Considered chains for gasoline blending components

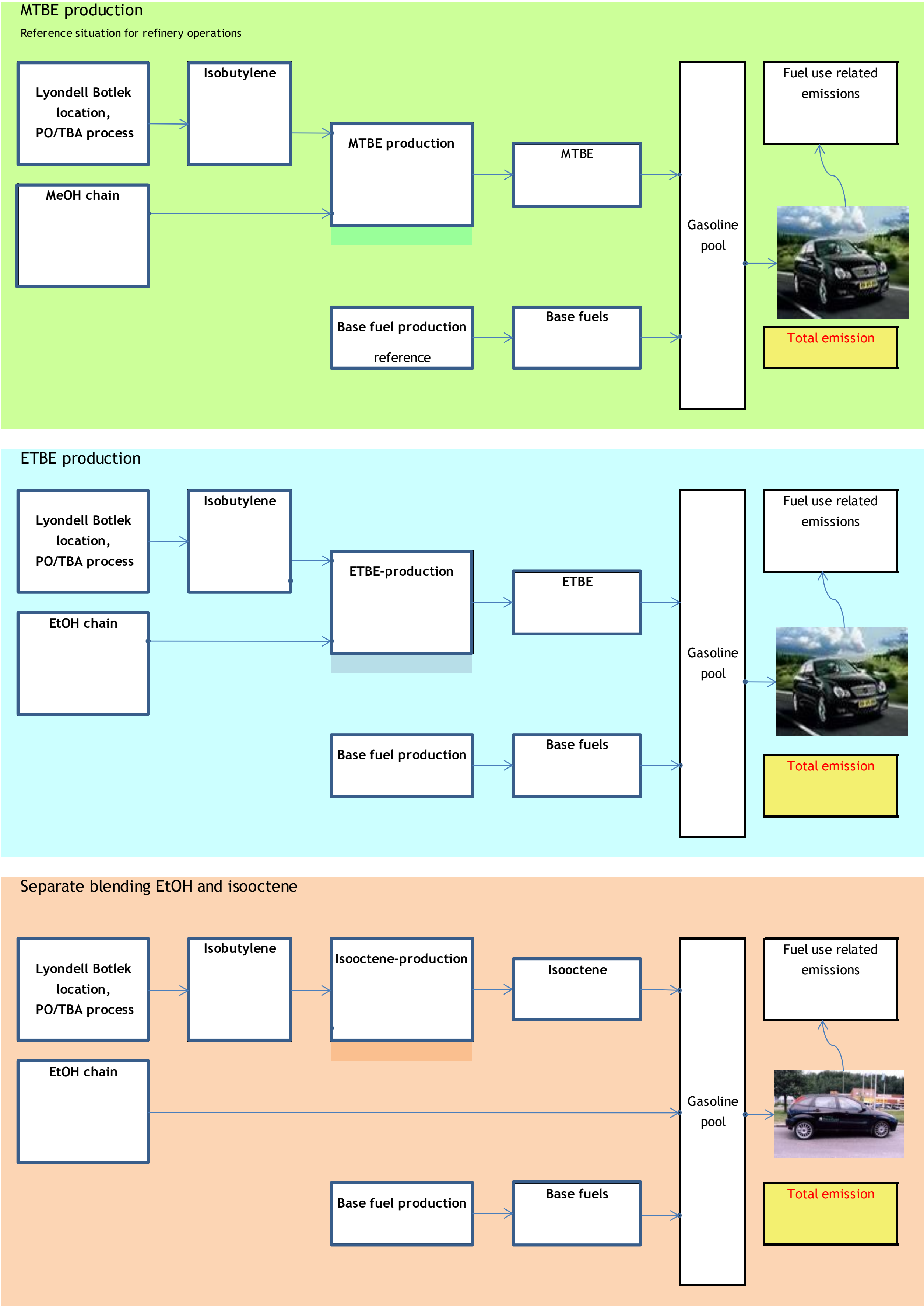
The considered chains are illustrated in **Fout! Verwijzingsbron niet evonden.**.

Current production capacity at LyondellBasell's Botlek plant was the basis for determining the amount of ETBE, MTBE and ethanol. For iso-octene production a 100% conversion efficiency was assumed.

A 50:50% mix of summer blend and winter blend Euro 95 with average specifications in terms of vapour pressure, MON and RON was considered. This to take into account effects of blending different blending components into the gasoline pool on oil refinery operations and production of an identical amount of final gasoline blend.

In the refinery 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).

Figure 3 Flowsheets of considered chains



2.4.3 Conclusions

Application of bio-ethanol as ETBE will result in significant reduction of greenhouse gas emissions compared to the alternatives.
Due to the fact that methanol is produced from natural gas (a fossil fuel) the CO_2 content of methanol is much higher compared to ethanol.
The overall CO_2 emission in the ETBE chain is lower than in the alternatives using either MTBE or bio-ethanol for the same gasoline blend. This is due to significant reduction of energy consumption associated with refinery operations and fuel-in-use effects (e.g. vapour pressure).

3 Conclusions, recommendations

3.1 Conclusions

The joint study showed the possibilities for LyondellBasell to save energy, both on site and through the complete chain.

The CO_2 emission and energy use related to the production of raw materials is the highest in the considered footprint. So the most leveraging ideas are related to finding raw materials with a reduced carbon footprint.
Second best is to improve CO_2 emission related to waste handling, for example increase recycling opportunities.
Polymerisations also have a significant contribution, due to the energy content of the different chemicals used.

The study approach which is based on two pathways using energy charts and the collaboration of other companies in the product chain results in promising measures and better insight for all parties involved.

Separately, blending of MTBE, ETBE and bio-ethanol in the gasoline pool was investigated. The study shows clear CO_2 emission reduction of blending ETBE in the gasoline pool compared to bio-ethanol or MTBE.

3.2 Recommendations

LyondellBasell is advised to further elaborate the most promising measures within the framework of the energy efficiency plans. For measures within the chain the cooperation of other companies is required and recommended.

4 Background of the Long-term Agreement Energy Efficiency ETS enterprises (LEE)

In the EU Climate and Energy Package of January 23rd, 2008 the European Member States concluded that the industrialised countries should make a joint commitment to reduce their greenhouse gas emissions by 30% in 2020 compared to 1990 within the framework of a meaningful global climate treaty. As long as that treaty has not been established, the EU unilaterally commits itself to a reduction of at least 20% in 2020 compared to 1990.
Furthermore, the package includes the objective to improve energy efficiency by 20% in 2020 (compared to 2005) and to achieve a share of 20% renewable energy in 2020. On December 12th, 2008 the European Member States reached an agreement about the EU Climate and Energy Package. The European Parliament approved the package on December 17th, 2008.

In the Sustainability Accord (*Duurzaamheidsakkoord*) between the national government and the business community of November 1st, 2007, VNONCW, MKB Nederland and LTO Nederland endorsed the need to pursue an active and progressive climate policy in the Netherlands and in Europe. The government undertook to ensure to the best of its ability that enterprises will be able to continue to operate on a level European and global playing field.
The Sustainability Accord gives direction to additional concrete agreements for the sectors: built environment, energy, industry, traffic and transport, agriculture and horticulture, and for medium-sized and small businesses. The Sustainability Accord provides for an evaluation of the progress of the programme Clean and Economical (*Schoon en Zuinig*) in 2010, which will include an evaluation of the progress of the sector accords, including this sector accord. The Sector Accord Energy 2008-2020 of October 28th, 2008 contains agreements between the national government and the energy sector. One of the agreements in that accord is that the national government may in the long term implement an obligatory share of sustainably generated energy, in principle in an European context.
The Sector Accord Industry contains various components. On July 1st, 2008 the Long-term Agreement 3 (LTA3) was entered into with the industries that had not participated in the Benchmarking Covenant. An intensification of the energy savings in the small and medium-sized businesses sector was also initiated through the Energy Centre for Small and Medium sized Enterprise.
For companies, in so far as they and their facilities are obliged to take part in the European system of trade in greenhouse gas emission rights (ETS enterprises), the Sector Accord Industry is implemented in two ways.
In the first place all participating ETS enterprises must comply with a CO_2 reduction obligation because they are part of the system of CO_2 emission trade. In that way they make an important contribution to the performance of the EU Climate and Energy Package and the Sustainability Accord.

In the second place the Benchmarking Covenant of July 6th, 1999 is amended with this sector accord as referred to in Article 20 of that covenant. That means that the participating ETS enterprises assume a commitment obligation in the field of energy efficiency, aimed at achieving a substantial improvement of the energy efficiency in the period up to 2020. At the time of signing of this sector accord the Ministers do not intend to impose obligations regarding renewable energy on ETS enterprises that participate in the sector accord. Because the sector accord focuses on ETS enterprises, participation by non-ETS enterprises that have joined the Benchmarking Covenant is not continued in this sector accord. Those enterprises are encouraged to take part in LTA3. Added value may, however, be generated if a non-ETS enterprise that will only become an ETS enterprise after 2012, or that is part of a group, continues to participate in the LEE after notifying the Competent Authority.

Parties are aware that improving the energy efficiency for ETS enterprises will require considerable effort and commitment. In the first place this concerns ETS enterprises that have to participate in the European system of trade in CO_2 emission rights, which entails considerable obligations with respect to the reduction of their CO_2 emission. In the second place a number of the ETS enterprises are already among the world's best in terms of energy efficiency. That limits the possibilities for further efficiency improvement. In the third place efficiency improvements are also included in the chain in this sector accord. That is a new element compared to the Benchmarking Covenant. Implementing and working out the chain approach in detail may involve a great deal of time and effort for realising concrete projects and results. The impact on efficiency improvement is difficult to assess beforehand. Finally, the Trade Associations, Commodity Boards or participating ETS enterprises will set up a preliminary study to find out if and to what extent a roadmap will provide new insights into possible energy efficiency improvements in the long term. Based on the results of this study, the efforts already made by the ETS enterprises and the relation with ETS, it will become clear what efficiency improvements are feasible for the participating ETS enterprises in the medium and long term.
Partly as a result of this sector accord, ETS enterprises will have to make substantial investments in CO_2 reduction and energy efficiency improvement. Both objectives may influence each other in either a positive or a negative way, in which case avoidance of the emission of CO_2 and other greenhouse gases will remain the primary goal. It is up to the parties themselves to create the necessary preconditions to realise the ambitions formulated in the sector accord. In any case the agreements in the EU Climate and Energy Package will be worked out in more detail during the coming period, including the possibility of compensating those ETS enterprises that are confronted by higher electricity rates as a result of the trade in emission in the electricity sector.

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