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Summary

In this Conceptual Process Design, the feasibility and the profitability of an intensified membrane reactor for the hydro-isomerisation of C5/C6 alkanes are investigated.

This process is designed to process 1000 ton/day of straight run naphtha (mainly composed of C4, C5 and C6) in a continuous process. The normal alkanes from this feed are converted to branched alkanes that have higher Research Octane Numbers (RON) (Cf. Appendix A: Significance of MON and RON). This yields an improved product with a high RON that can be used in gasoline blending.

The core of this project is a reactor that combines the separation and reaction operations. The separation is achieved within tubular membrane units of zeolite 5A. The reactions occur in a packed bed of a recently developed platinum-based chlorinated alumina catalyst. Hydro-isomerisation reactions are reversible and usually cannot reach high conversions because of the limits imposed by thermodynamics (Appendix B: Thermodynamic Equilibrium). The membrane only supplies the reactants to the packed bed where the very active catalyst enables reaching the equilibrium conversion.

Two different processes are designed and compared from an economic point of view. The first is a once-through process while the second includes a recycle through a second membrane.

A RON of 90 is obtained for the second process alternative (a double-membrane reactor configuration). The yield achieved is 96 %. The purge can carry an important fuel value for other parts of the plant. The total investment for the project is k$ 6,643.4 for a plant economic life of 10 years.

The feasibility of the project is proved but further optimisation is needed in order to increase this RON and improve the profitability. In general, the expectation is that this process technology would be more and more appealing and more profitable in the future as the technology is mastered. This would reduce the costs associated with the manufacture of the membrane units. Another major advantage of this technology is the reduction in the size of the installation; this could be crucial in countries and areas where the space constitutes a problem for the proliferation of the hydrocarbon processing activities. The dimensions of the reactor are 3.92m in diameter and 3m high.

The economic appraisal of this project is carried out with cost correlations obtained in Coulson Volume 6 and the result may raise some concern. But only a rough estimate of the catalyst price was supplied by AkzoNobel as these data are usually not disclosed to public. The same applies for the prices of gasoline with different grades; the price estimates were supplied by Shell, but are subject to serious fluctuations as they strongly depend on the crude oil prices. These are areas for further improvement in the future studies.

A future investigation could consider substituting the zeolite 5A membrane with a silicalite-1 one as this should in principle improve the RON of the final product and therefore improve the overall profitability of the process.
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1. Introduction

Hydroisomerisation is a part of catalytic reforming, the most important industrial application of catalysis. Catalytic reforming was developed to produce gasoline of high anti-knock quality (high RON). The objective is to convert saturated alkanes in petroleum naphtha fraction (boiling point in the range 47°C-193°C). The market for isomerisation of petroleum fractions is still growing. The incentive for this growth is found in the increasing demand for high RON caused by the expanding market for unleaded gasoline and environmental regulations that limit more and more the content of olefins, benzene [5] and aromatics in gasoline.

Of the alternatives available to increase the RON, C5/C6 hydroisomerisation is the most effective regarding the environmental constraints. It aims at converting normal alkanes into monobranched or even dibranched alkanes that have usually higher RON ( Cf. Appendix E: Pure components properties). At present, the state-of-the-art process TIP (Total Isomerisation Package) uses two units, a reaction unit with Pt-H-Mordenite as a catalyst, and a separation unit using pellets of zeolite 5A to separate the branched molecules from the normal ones ( Cf. Appendix F: The TIP and UOP Penex processes). This process can be improved in terms of energy consumption, which is a highly popular concern at a time when energy conservation is finally established as one of the top priority for the industry.

In this conceptual process design, the integration and densification of the hydroisomerisation of straight run naphtha (mainly C5 and C6 molecules) is considered. The main improvement, compared to the TIP, is the use of zeolite 5A as a membrane that holds the potential of separating at a relatively low energy cost. This allows to supply only reactants to the catalyst in a continuous manner and therefore to operate in steady state unlike the TIP. Improvement can also be made with regards to the catalyst, by choosing a catalyst active at low temperature to reach the maximum conversion of normal alkanes.

The new reactor is designed to contain a bundle of tubular membranes of zeolite 5A that have not yet been built at this scale. They are filled with catalysts particles of a recent development of platinum based chlorinated alumina. The advantage of this configuration is that separation takes place before reaction thereby limiting cracking and deactivation of the catalyst through strong aromatic adsorption on metal sites.

From chapter 3 of this conceptual process design, two processes are studied to compare the performance of a product recycle through a second membrane with the product from a single pass. The capital investment of each process is presented in Appendix Y and the economic calculations are supplied in Appendices Z and AA.

No plant of this kind is built yet. The profit of such an installation is difficult to fix because the major cost is the raw material cost and it is subject to daily fluctuations (according to world oil prices).
2. Process definition

2.1. Process Options

Several processes exist for the hydro-isomerisation of C5/C6 paraffins. They can be classified according to the catalyst that is used to promote the reaction. Two types of catalysts are currently used industrially, i.e. Platinum based catalysts on chlorinated alumina and Platinum based zeolitic (mordenite) catalyst.

2.1.1. Processes using Pt base catalysts on chlorinated alumina

Paraffin isomerisation over amorphous catalysts has been practised for a long time and at present the amorphous catalysts based on Pt/Cl alumina remains the most active ones. In the current UOP Penex process (cf. Appendix F: The TIP and UOP Penex processes and ref. [3]) the catalyst can isomerise the C5/C6 stream at 115-150°C. This low temperature is advantageous from a thermodynamic point of view because it favours the branched alkanes that have higher Research Octane Numbers (RON) (see Appendix A: Significance of MON and RON). A once-through operation increases the RON from about 69 to 83 (See figure below)

*Figure 2.1. Effect of normal paraffins recycle and temperature on the octane numbers achievable in isomerisation [17].*

The high acidity of chlorinated alumina is responsible for the benefits of the low-temperature operation but also constitutes its weakness: in general chlorinated alumina catalysts are more susceptible to contaminants like water and sulphur than zeolite and are irreversibly deactivated. Although the units are equipped with dryers to remove water, it is inevitable that some moisture will enter the reactor.

2.1.2. Processes using Pt base zeolitic catalysts

Zeolitic paraffin isomerisation catalysts are less active than amorphous ones and in consequence have to operate at higher temperature i.e. about 250°C, with the inherent disadvantage that the conversion per pass is lower and the content in dibranched
species is lower. Processes based on this type of catalyst (ex: Hysomer by Shell) are still widely used because of their robustness to water and other poisons. In the Total Isomerisation Package (TIP) [3], the Hysomer process, which is the reaction unit, is combined with the Isosiv separation unit (from Union Carbide) [5]. In the latter, normal alkanes are separated from branched alkanes by selectively adsorbing the normals on pellets of zeolite A. Because the normals need to desorp to be recycled, the separation unit runs in a cyclic mode: adsorption / desorption. A scheme of this process is presented in Appendix F: The TIP and UOP Penex Processes.

2.2. Process Structure Chosen

The aim of this design is to better integrate and densify the reaction and separation operations into a single unit, i.e. a membrane reactor. The following considers the several possible catalysts and membranes in order to select the appropriate combination that is suited to the designed task.

Five different alternatives are considered in this part. All of them are constituted of a membrane reactor that combines the separation (membrane) and the reaction (catalyst), unlike the TIP process. Process intensification offers many advantages on many grounds: energy savings, process safety, better controllability, reduction in the installation size and better operation.

2.2.1. Catalyst chosen

A platinum based chlorinated alumina is chosen. Utilising a high activity super-acidic catalyst such as chlorinated alumina allows working at a lower temperature and operating at a low $\text{H}_2 : \text{hydrocarbons}$ ratio. It also allows the decrease in the recycle volume to the reactor and therefore the size of the installation. But presence in feedstock of water is more dramatic than for a zeolitic catalyst as explained above. In this design, the feed is assumed to be dried enough to allow the use of this catalyst.

2.2.2. Choice of membrane

Two types of membranes appeared to be interesting to selectively separate the molecules in the process. The first is silicalite-1 zeolite with a pore size of 0.55 nm that allows normal and monobranched alkanes to go through. With such a membrane, it is possible to isomerise these two kinds of alkanes and hence, to have a product with the maximum of double branched alkanes, which yields the highest RON (with some exceptions: 2,2-DimethylPropane). The other membrane of interest is a zeolite 5A with a pore size of 0.45 nm that only allows normal alkanes from a feed. The branched alkanes cannot pass through the pores of this membrane.

It is obviously interesting to have a membrane that allows normal and monobranched alkanes to reach the catalyst, like silicalite-1. On the other hand, it is not of interest to isomerise isopentane that has a RON of 93 to 2,2-DimethylPropane, which has a RON of 83. Since normal pentane and isopentane are the main components of our feed (36.5 and 22 molar % respectively), it was decided to develop processes using zeolite 5A that will prevent isomerisation of isopentane. Hereafter, five options are presented with zeolite 5A or silicalite-1 or both and with or without recycle of the product.
2.2.3. Five processes

1. **First option: zeolite 5A with recycle**

2. **Second option: zeolite 5A without recycle**

3. **Second process: silicalite-1 without recycle**

4. **Fourth process: silicalite-1 and recycle through zeolite 5A**
Figure 2.5: Fourth option

5. Fifth process: Zeolite 5A and recycle through zeolite 5A

Material balances performed in Excel for each processes showed that the best increase in RON are achieved with options 4 and 5, both including a recycle through a zeolite 5A.

Table 2.1: RON of the five processes

<table>
<thead>
<tr>
<th>Process</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>RON</td>
<td>88.73</td>
<td>87.91</td>
<td>87.89</td>
<td>90.03</td>
<td>89.90</td>
</tr>
</tbody>
</table>

According to the fact that isomerisation of isopentane is not wanted, the two options retained from these five are therefore 2 instead of 4 and 5, where silicalite-1 is not used. Option 2 makes use of a smaller zeolite 5A membrane after the flash unit that reduces the cost.

In the remaining chapters of this report, alternative 2 (use of a zeolite 5A without recycle) is referred as option 1 and alternative 5 (use of a zeolite 5A with recycle through another zeolite 5A) is named option 2.
3. **Basis of design**

3.1. **Description of the design**

One of the important tasks in oil refineries is to upgrade suitable intermediate product streams to automotive gasoline of better quality. The gasoline octane number can be improved by addition of lead or MTBE (methyl tertiary butyl ether) or by isomerisation of normal alkanes (C5 and C6). Recent developments of this latter technology have been primarily prompted by environmental factors:

- Elimination of lead alkyl additives,
- Limitation in the content of olefins, benzene and total aromatics,
- Recent legislation to phase-out MTBE because of environmental and health concerns.

As opposed to normal paraffins, iso-alkanes (monobranched and dibranched molecules) have a higher octane number (table 3.2). Based on this, it is possible to boost the octane number of gasoline by skeletal hydro-isomerisation.

The state of the art process TIP (Total Isomerisation Package) from UOP (formerly known as Union Carbide) comprises two units: a catalytic reactor with Pt-H-mordenite and a separation unit based on zeolite 5A pellets (Cf. Appendix F: The TIP process). This process aims at improving the performance of the catalytic reactor (to approach equilibrium conversion) as well as the replacement of the ubiquitous distillation units by a zeolitic separation unit.

The performance of the TIP process cannot be optimised beyond the bottlenecks. Also, the state of the art process makes use of a pressure swing adsorption unit to accomplish the separation. This means that the process operates in the transient regime. A novel process, making use of membrane technology, can overcome the bottlenecks and controllability constraints by operation on a steady-state continuous basis.

The main objective of this conceptual process design is to develop a process that allows the complete integration of reaction and separation units by using a catalytic reactor with membrane technology, thereby saving energy and reducing the size of the installations. The reactor will consist of tubular membrane units loaded with catalyst pellets. The advantage of such a configuration resides in the fact that separation takes place just before the reaction. The membrane only sends selected reactants to the catalyst and therefore facilitates the approach of thermodynamic equilibrium conversions (See figure 3.1.). Use is made of a zeolite 5A membrane to completely separate normal alkanes from iso-alkanes (absolute separation). The catalyst utilized (AT-20), which is a chlorinated alumina catalyst containing the noble metal platinum, is a recent development of TotalFinaElf and AkzoNobel. Platinum helps hydrogenation and dehydrogenation reactions and enhances the catalyst stability while the acidic chlorinated alumina allows skeletal isomerisation. Compared to a classical catalyst, the bi-functional AT-20 shows a very high activity at low operating temperatures; this favours the formation of high octane number products. (Cf. Appendix B: Thermodynamic Equilibrium).
3.2. Process definition

The hydro-isomerisation of n-alkanes is thermodynamically limited. Consequently the design of the integrated process will be carried out in line with these constraints. This implies essentially operating at low temperatures (120°C), as the product formation is favoured at these temperatures.

3.2.1. Process options and concept chosen for the catalyst

As explained in the previous section, the process consists of a membrane reactor that will operate continuously to treat a feed of 1000 ton/day. The process will be carried out in the liquid phase to accommodate for the amount of feedstock that needs to be processed. Operating in the gas phase would require larger reaction volumes, larger installations, increased compression and overall costs.

Existing industrial processes for isomerisation of C<sub>5</sub>/C<sub>6</sub> could be classified based upon the type of catalyst employed. The following table shows the available processes alongside their relevant parameters.
Table 3.1. Comparison of different catalyst for isomerisation of C5/C6

<table>
<thead>
<tr>
<th>Using a noble metal on:</th>
<th>Chlorinated alumina</th>
<th>Amorphous silica-alumina</th>
<th>Zeolite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid Strength</td>
<td>High</td>
<td>Low</td>
<td>Medium</td>
</tr>
<tr>
<td>Temperature of Operation</td>
<td>Low (100-160°C)</td>
<td>High (424-480°C)</td>
<td>Medium (240-280°C)</td>
</tr>
<tr>
<td>Feed Pre-treatment</td>
<td>Necessary</td>
<td>Not necessary</td>
<td>Not necessary</td>
</tr>
<tr>
<td>Effluent Purification</td>
<td>Necessary</td>
<td>Not necessary</td>
<td>Not necessary</td>
</tr>
<tr>
<td>Chemical Addition</td>
<td>Necessary (Chlorinating agent)</td>
<td>Not necessary</td>
<td>Not necessary</td>
</tr>
</tbody>
</table>

An important decision in this design is to work at a low temperature 120°C as opposed to the TIP process which is operated at 250°C. From a thermodynamic point of view, this is favourable for the formation of iso-alkanes that have higher RON numbers. Table 3.2 highlights the fact that these compounds and in particular dibranched alkanes possess high RON values. The product distribution of C5, C6 and C7 alkanes are showed in thermodynamic properties (section 3.2.6). At 120°C, the product distribution of C6 and C7 is in favour of dibranched molecules and isopentane is the predominant specie of C5.

Table 3.2. RON for some paraffins

<table>
<thead>
<tr>
<th>Component</th>
<th>RON (pure component)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-butane</td>
<td>92</td>
</tr>
<tr>
<td>Isobutane</td>
<td>99</td>
</tr>
<tr>
<td>n-pentane</td>
<td>62</td>
</tr>
<tr>
<td>Isopentane</td>
<td>93</td>
</tr>
<tr>
<td>n-hexane</td>
<td>29</td>
</tr>
<tr>
<td>2-methylpentane</td>
<td>78</td>
</tr>
<tr>
<td>3-methylpentane</td>
<td>76</td>
</tr>
<tr>
<td>2,2-dimethylpentane</td>
<td>92</td>
</tr>
<tr>
<td>2,3-dimethylpentane</td>
<td>104</td>
</tr>
<tr>
<td>n-heptane</td>
<td>0</td>
</tr>
<tr>
<td>2-methylhexane</td>
<td>42</td>
</tr>
<tr>
<td>2,2-dimethylhexane</td>
<td>93</td>
</tr>
</tbody>
</table>

Hence, the catalyst chosen is a platinum chlorinated alumina because this super acidic catalyst can operate at the desired temperature. AT-20, developed by AkzoNobel and TotalFinaElf, is a very active catalyst designed for isomerisation of C5 and C6 light naphtha and C4 at temperatures as low as 120°C. Zeolites exhibit low activities at this range of operating conditions.

In general, chlorinated alumina isomerisation catalysts are more likely to undergo deactivation reactions with contaminants like water, which makes them more vulnerable. Zeolite based isomerisation catalysts are more robust. The choice of this catalytic system is motivated by a primary understanding that this drawback can be more than compensated for by the better octane yields associated with working at lower temperature.

In the case of AT-20, the use of chloride as a catalyst activator can be lowered considerably to the point where HCl recovery facilities can be eliminated. Just a few ppm
of a chlorinating agent need to be added to the feedstock in order to maintain the catalyst activity. Moreover, the ratio of Hydrogen/Hydrocarbon is very low, 0.1 to 1.5 [8] which decreases the recycle volume and hence the size of the installation.

**Table 3.3. Characteristics of chlorinated alumina catalysts AT-20**

<table>
<thead>
<tr>
<th>Shape</th>
<th>Extrudates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorine content (wt %)</td>
<td>4.5-5.2</td>
</tr>
<tr>
<td>Platinum oxide (wt %)</td>
<td>0.25</td>
</tr>
<tr>
<td>Support</td>
<td>Porous alumina</td>
</tr>
<tr>
<td>Loading Density (kg/m³)</td>
<td>795</td>
</tr>
<tr>
<td>Particle diameter (mm)</td>
<td>1.3 – 1.5</td>
</tr>
<tr>
<td>Particle length (mm)</td>
<td>3.0 – 5.0</td>
</tr>
<tr>
<td>Catalyst life</td>
<td>4 years</td>
</tr>
</tbody>
</table>

The assumption made for this basis of design is that the catalyst is active enough to help the reaction of isomerisation to reach the thermodynamic equilibrium described by the figures in Appendix B: Thermodynamic equilibrium, at the outlet of the reactor. This is justified by results of laboratory experiments [9]. The choice of extrudates can be accounted for by the low pressure drop associated with these particles, their relatively low manufacturing cost as well as their superiority in terms of ease access to the catalyst active sites, in other words absence of diffusional limitations [7].

### 3.2.2. Choice of the membrane and concept of the catalytic reactor

The feed is assumed to be of constant composition. Compositions of groups of relevant importance for the choice of the separation are presented in Table 3.4.

**Table 3.4. Composition of different groups of molecules in the feed**

<table>
<thead>
<tr>
<th>Components</th>
<th>Composition (mol %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-pentane + n-hexane</td>
<td>46.5</td>
</tr>
<tr>
<td>n-butane + n-heptane</td>
<td>4.9</td>
</tr>
<tr>
<td>Monobranch that could be isomerised (2-methylpentane, 3-methylpentane, 2-methylhexane)</td>
<td>16.4</td>
</tr>
<tr>
<td>Aromatics</td>
<td>0.7</td>
</tr>
<tr>
<td>Water (few ppm)</td>
<td></td>
</tr>
</tbody>
</table>

As indicated in the project description, possible poisons for the catalyst (water, sulphur) are absent from the feed so that the use of chlorinated alumina is made possible.

The monobranch alkanes that could be isomerised to dibranched alkanes with higher RON represent a non-negligible part of the feed. An alternative design could be to isomerise both normal and monobranch alkanes and achieve a product with a high RON but the decision that was made in this design is to only to isomerise the normal alkanes. Although processing the monobranch alkanes would yield a product with a higher RON, the option that was selected has the advantage of improving the conversion and the yield by selectively sending the reactants to the catalyst bed and removing the products. The process intensification in the latter case is made better by avoiding any additional separations (removal of isopentane from the recycle stream).
The concept retained is a membrane placed upstream of the catalyst bed. A tubular shape was chosen as it supplies a large surface area and is easier to scale up than flat membranes [12]. A wide range of applications include usage in pervaporation. The membrane is a zeolite type 5A, with small pores of 0.45 nm of diameter. The table 3.5. shows some elements for comparison between zeolite 5A and the membrane that would be used in the alternative design to allow normal and monobranched alkanes to pass, silicalite-1.

<table>
<thead>
<tr>
<th>Membrane type</th>
<th>Zeolite 5A</th>
<th>Silicalite-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pore Size (nm)</td>
<td>0.45</td>
<td>0.55</td>
</tr>
<tr>
<td>Si/Al ratio</td>
<td>1 to 3</td>
<td>Infinite</td>
</tr>
<tr>
<td>Selectivity</td>
<td>n-alkanes / (mono-dibranched)</td>
<td>(n-alkanes+mono) / dibranched</td>
</tr>
<tr>
<td>Mechanism of diffusion</td>
<td>Configurational diffusion + molecular sieving</td>
<td>Surface diffusion + activated gaseous diffusion</td>
</tr>
<tr>
<td>Separation Mode</td>
<td>Absolute separation: differences in molecular size</td>
<td>Differences in velocity in surface diffusion</td>
</tr>
<tr>
<td>Maximum theoretical RON</td>
<td>89 - 90</td>
<td>96</td>
</tr>
<tr>
<td>Cost</td>
<td>Low: no separation needed after this unit</td>
<td>More separation units needed: increase in capital and operating costs</td>
</tr>
</tbody>
</table>

The zeolite 5A will only allow normal alkanes (nC₄, nC₅, nC₆, and nC₇) to access the catalyst. The isomerisation reactions can be shifted to a better conversion than in the case where also some iso-alkanes could go through the membrane (by selective addition of the reactants and continuous removal of the products). Table 3.6. shows the kinetic diameters for pure compounds: iso-alkanes and naphtenes cannot enter the membrane since their kinetic diameter is greater than the selected pore size via a mechanism of absolute separation.

<table>
<thead>
<tr>
<th>Component Name</th>
<th>Kinetic Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-butane, n-pentane, n-hexane</td>
<td>0.43</td>
</tr>
<tr>
<td>Isobutane, Isopentane, 2 MP,</td>
<td>0.50</td>
</tr>
<tr>
<td>2,2 DMP</td>
<td>0.62</td>
</tr>
<tr>
<td>2,3 DMB</td>
<td>0.56</td>
</tr>
<tr>
<td>CycloH, cycloMH</td>
<td>0.60</td>
</tr>
<tr>
<td>Benzene, toluene</td>
<td>0.59</td>
</tr>
</tbody>
</table>

By means of molecular sieving, n-alkanes will be separated from the other components of the feed (mono, dibranched and cycloalkanes) and permeate through the membrane to the catalyst side where they will be isomerised. A pressure differential of 2-3 atm can be applied across the membrane to facilitate the passage of the normals. The feed that cannot enter the pores of the membrane is called the retentate. The surface area of the membrane is designed in order to remove all n-alkanes from the feed so that the retentate is made solely of iso-alkanes. In our design, a separation factor of 95% regarding the normal alkanes was used to account for possible imperfections in the design or shortcomings in the performance.
On the permeate side, hydrogen serves as a sweep gas to remove products of isomerisation and prevent coke formation on the catalyst. The ratio of \( \text{H}_2: \text{Hydrocarbon} \) is chosen to be 0.1:1 \[9\]. The amount of hydrogen necessary for isomerisation is low if we assume that the catalyst "works" efficiently, the consumption of hydrogen (and the amount of make-up gas) should be extremely low.

### 3.2.3. Stoichiometry

Three classes of reactions can take place during the skeletal isomerisation:
- Hydro-isomerisation
- Hydrogenation
- Cracking

As the process operates at a low temperature, it has been assumed that no cracking will take place (Prof. Dr. J.C. Jansen, personal communication, 2001 & Appendix G: Selectivities to isomerisation of n-pentane, n-hexane and n-heptane). Hydrogenation reactions are also ignored as neither olefins nor aromatics are allowed to reach the catalyst. Hence, the possible reactions are hydro-isomerisation reactions involving normal alkanes in liquid phase:

1. \( \text{n-butane} \rightarrow \text{1 isobutane} \)
2. \( \text{n-pentane} \rightarrow \text{1 isopentane} \)
3. \( \text{n-pentane} \rightarrow \text{1 2,2-dimethylpropane} \)
4. \( \text{n-hexane} \rightarrow \text{1 2-methylpentane} \)
5. \( \text{n-hexane} \rightarrow \text{1 3-methylpentane} \)
6. \( \text{n-hexane} \rightarrow \text{1 2,2-dimethylbutane} \)
7. \( \text{n-heptane} \rightarrow \text{1 2-methylhexane} \)
8. \( \text{n-heptane} \rightarrow \text{1 dibranched C7} \)
9. \( \text{n-heptane} \rightarrow \text{1 tribranched C7} \)

See Appendix C: Semi-developed and developed formulas of hydrocarbons and Appendix D: The reactions, for the formulas of these molecules.

### 3.2.4. Reaction kinetics

No kinetic data for the hydro-isomerisation of \( \text{C}_5/\text{C}_6 \) on AT-20 could be obtained from AkzoNobel. It is assumed that the catalyst is so active at the operating conditions that chemical equilibrium is reached. This is supported by the result of a study \[9\].

### 3.2.5. Block schemes and mass balance

The block schemes of the two options that are compared in this conceptual process design, together with their mass balance are presented hereafter. (Cf. Chapter 2 for the choice of these two options)

*Figures between brackets are t/t values.*

---

**Option 1:**

[Diagram of the process flow]
Table 3.7. Block scheme streams summary for option 1

<table>
<thead>
<tr>
<th>Stream number</th>
<th>Description</th>
<th>Mass Flow (kt/a)</th>
<th>Yield Factor (t/t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Straight Run Naphta Feed</td>
<td>308.07</td>
<td>1.03</td>
</tr>
<tr>
<td>2</td>
<td>Flux of n-alkane to the permeate side</td>
<td>144.56</td>
<td>0.47</td>
</tr>
<tr>
<td>3</td>
<td>Retentate from reactor = product (iso-alkanes)</td>
<td>163.50</td>
<td>0.54</td>
</tr>
<tr>
<td>4</td>
<td>Effluent from the reactor = isomerised alkanes</td>
<td>188.13</td>
<td>0.62</td>
</tr>
<tr>
<td>5</td>
<td>Final product</td>
<td>305.83</td>
<td>1</td>
</tr>
<tr>
<td>6</td>
<td>Make-up hydrogen</td>
<td>0.08</td>
<td>0.003</td>
</tr>
<tr>
<td>7</td>
<td>Top product from the flash</td>
<td>45.80</td>
<td>0.15</td>
</tr>
<tr>
<td>8</td>
<td>Bottom product from the flash</td>
<td>142.33</td>
<td>0.47</td>
</tr>
<tr>
<td>9</td>
<td>Purge: hydrogen and C4</td>
<td>2.29</td>
<td>0.008</td>
</tr>
<tr>
<td>10</td>
<td>Recycle of H₂ and C₄ to the reactor</td>
<td>43.51</td>
<td>0.14</td>
</tr>
<tr>
<td>11</td>
<td>Blending of hydrogen recycle and make-up</td>
<td>43.57</td>
<td>0.14</td>
</tr>
</tbody>
</table>
**Option 2:**

![Diagram of Option 2](image)

**Figure 3.3. Block scheme of option 2**

<table>
<thead>
<tr>
<th>Stream number</th>
<th>Description</th>
<th>Mass Flow (kt/a)</th>
<th>Yield Factor (t/t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Straight Run Naphta Feed</td>
<td>308.07</td>
<td>1.03</td>
</tr>
<tr>
<td>2</td>
<td>Flux of n-alkane from the feed side to the permeate side</td>
<td>144.56</td>
<td>0.48</td>
</tr>
<tr>
<td>3</td>
<td>Retentate from reactor = product (iso-alkanes)</td>
<td>163.42</td>
<td>0.55</td>
</tr>
<tr>
<td>4</td>
<td>Effluent from the reactor = isomerised alkanes</td>
<td>355.81</td>
<td>1.19</td>
</tr>
<tr>
<td>5</td>
<td>Final product</td>
<td>298.62</td>
<td>1</td>
</tr>
<tr>
<td>6</td>
<td>Make-up hydrogen</td>
<td>0.08</td>
<td>0.0003</td>
</tr>
<tr>
<td>7</td>
<td>Top product from the flash</td>
<td>190.16</td>
<td>0.64</td>
</tr>
<tr>
<td>8</td>
<td>Bottom product from the flash = recycle</td>
<td>165.66</td>
<td>0.56</td>
</tr>
<tr>
<td>9</td>
<td>Retentate from 2nd membrane = product (iso-alkanes)</td>
<td>135.12</td>
<td>0.45</td>
</tr>
<tr>
<td>10</td>
<td>Purge: hydrogen and C4</td>
<td>9.51</td>
<td>0.03</td>
</tr>
<tr>
<td>11</td>
<td>Recycle of H₂ and C₄ to the reactor</td>
<td>180.65</td>
<td>0.61</td>
</tr>
<tr>
<td>12</td>
<td>Blending of hydrogen recycle and make-up</td>
<td>180.73</td>
<td>0.61</td>
</tr>
<tr>
<td>13</td>
<td>Flux of n-alkane from the recycle side to the permeate side</td>
<td>30.54</td>
<td>0.10</td>
</tr>
</tbody>
</table>

### 3.2.6. Thermodynamic properties

The distribution of normal and iso-alkanes depends on temperature. Tables 3.9. contains information on this equilibrium at 120°C for C₄, C₅, C₆ and C₇ respectively at the gas phase. This equilibrium is assumed to be still valid for the liquid feed as it solely depends on the nature of the substances involved in the reactions. Appendix B:
Thermodynamic equilibrium shows the distribution of these hydrocarbons versus temperature.

_Tables 3.9. Proportion of normal and iso-alkanes according to thermodynamic at 120°C_

<table>
<thead>
<tr>
<th>Temperature</th>
<th>n-butane</th>
<th>Isobutane</th>
<th>n-pentane</th>
<th>Isopentane</th>
<th>Neopentane</th>
<th>n-hexane</th>
<th>2 MP</th>
<th>3 MP</th>
<th>2,2 DMB</th>
<th>2,3 DMB</th>
<th>n-heptane</th>
<th>Monobranch</th>
<th>Dibranch</th>
<th>Tribranched</th>
</tr>
</thead>
<tbody>
<tr>
<td>120°C</td>
<td>28.6</td>
<td>71.4</td>
<td>11</td>
<td>65</td>
<td>24</td>
<td>5.5</td>
<td>20.8</td>
<td>6</td>
<td>56.7</td>
<td>11</td>
<td>4</td>
<td>29</td>
<td>61</td>
<td>6</td>
</tr>
</tbody>
</table>

The model used for vapor/liquid equilibrium is Soave-Redlich-Kwong (SRK). It is a petroleum tuned equation state of property model that produces good results for petroleum refinery processes.

Skeletal isomerization reactions are found to be mildly exothermic. The enthalpy of reaction is of the order –5 to –21 kJ/mol (See Appendix D: The reactions).

3.2.7. List of pure components properties

Appendix E includes the formulas, RON, boiling and melting points, liquid densities, MAC and LD50 values for all components.

3.2.8. Process stream summary and overall heat and mass balance

The assumptions made on the content of these streams and on the operation of the unit are:

- The membrane achieves a complete separation, as explained in section 3.2.2, of normal and iso-alkanes. This is possible because the feed is liquid and therefore interfacial tension prevents iso-alkanes from going through the defects of the membrane. The separation factor is 95 % for normal alkanes as explained in the same section.
3.3. Basic assumptions

3.3.1. Plant capacity

The unit will have to process a stream of 1000 tons/day of light Straight Run Naphtha (SRN) : C_5/C_6 rich, low concentration of aromatics, sulphur free, dry, and low RON ($\approx 74$), to produce a product with a high RON (>80). This will be done in a continuous process, and assuming that the process will be active for 8150 hours a year, this gives a throughput of around 340 kton/year. The operating time includes scheduled shutdowns for maintenance, unplanned downtime due to mechanical failures, and/or production losses caused by capacity limitations or lack of feed. The plant is assumed to have an economic life of 10 years.

3.3.2. Location

The unit will be located at the Shell refinery in Europoort, Rotterdam, Netherlands.

3.3.3. Battery limits

The C_5/C_6 paraffin rich feed stream originates from DHS and DHA units on the site. There is therefore no need for additional dearomatisation or desulphurisation. It is also assumed that the feed is dry (<10 ppm of water). After DHS and DHA units, the feed is stocked in a drum at a pressure of 3.5 bars and a temperature of 60°C, which is outside the battery limits.

Hydrogen can be supplied to the unit free of impurities. All utilities required can be obtained on the plant site. The product will be sent to a gasoline blending unit (outside the battery limit).

3.3.4. Definition of inlet and outlet streams

The main ingoing stream is the straight run naphtha (SRN), also called TOP3 naphtha, in the liquid state. The second inlet stream is pure hydrogen in the gaseous state. There are two outlet streams: the product (liquid phase) and a purge for C_4 and hydrogen mainly (gas phase). The compositions and conditions of these streams can be found in Appendix J: Process Stream Summary.

- Product specifications:
  When mixed with other products, the final product of this unit must meet the specification of the gasoline blending. These are shown in Table 3.10. The computed RON value is around 88-89 and can therefore fulfil these specifications.
Utilities are needed to heat up the feed before the reactor from 60 to 90°C and to cool down the product before sending it to the gasoline blending unit. Electricity will be needed to pressurize the feed and recycle hydrogen and effluent from the reactor.

The catalyst is a AT-20 type from AkzoNobel and TotalFinaElf with the characteristics described in Table 3.3. It has a low density and hence leads to a lower catalyst loaded weight than classic chlorinated alumina. It also offers a better resistance and robustness to water. This category of catalyst allows a significant increase in the amount of feed as they can reach equilibrium at higher values of space velocity.

The membrane is a zeolite 5A (3 micrometers of thickness) layer on a macroporous stainless steel support of 1.5 mm coated with TiO2. It is assumed to be defect-free.

### 3.4. Feasibility of the concept

According to Weisz [13], the space time yield of an industrial catalytic reactor (rate of reaction on the catalyst) should be centered around 1 to 10 mole/(m³.s) to be in a “window of reality”. The feasibility of a membrane reactor is based on the comparison of the space time yield (mol/m³.s) and the aerial time yield (permeation flux through the membrane in mol/m².s). When the value of the ratio STY/ATY is comprised between 10 and 400, the diameter of the reactor is between 0.4 to 0.01 m that can be regarded as technically feasible.

In these two options, STY can be computed by dividing the amount converted by the catalyst volume and STY is found to be in the realistic interval: 4.7 mol/(m³.s) (Cf. Appendix Q: Design of the reactor: Option 1 (no recycle)). Finally, tubular membranes with a diameter of 0.22 m correspond to the ratio STY/ATY = 18.5.
3.5. Margin in $

The design of the plant is based on the continuous processing of 1000.06 tons/day, 8150 hours operating hours per year and the feed price is assumed to be that of SRN, 180 US$. An estimate of the financial margin, based on the amount of feed and product, is given in Table 3.12.

<table>
<thead>
<tr>
<th>Feed</th>
<th>Mass Flow (t/day)</th>
<th>Price (US$/t)</th>
<th>Total Price (MUS$/a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphtha</td>
<td>1000.00</td>
<td>180.00</td>
<td>61.13</td>
</tr>
<tr>
<td>Isomerized Product</td>
<td>992.81</td>
<td>205.00</td>
<td>69.11</td>
</tr>
<tr>
<td>Margin</td>
<td></td>
<td></td>
<td>7.99</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Feed</th>
<th>Mass Flow (t/day)</th>
<th>Price (US$/t)</th>
<th>Total Price (MUS$/a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphtha</td>
<td>1000.00</td>
<td>180.00</td>
<td>61.13</td>
</tr>
<tr>
<td>Isomerized Product</td>
<td>969.36</td>
<td>208.00</td>
<td>68.47</td>
</tr>
<tr>
<td>Margin</td>
<td></td>
<td></td>
<td>7.34</td>
</tr>
</tbody>
</table>

Margins of 7.99 and 7.34 MUS$/annum are calculated for cases 1 and 2. The margins are very sensitive to the value of the product. The financial margins are used below to calculate the allowable investment taking the following assumptions into consideration:

- Discounted cash flow rate of return (DCFRR) of 10%
- Economic plant lifetime of 12 years, of which two years are taken as start-up.

Table 3.13a &b. demonstrate that the maximum allowable investments for the two options would be 40.57 and 37.27 MUS$ for the given feed and product prices respectively.
<table>
<thead>
<tr>
<th>Year</th>
<th>Annual margin (MUS$/a)</th>
<th>Accumulated Margin (MUS$/a)</th>
<th>DCF at DCFRR = 0.1 (MUS$/a)</th>
<th>Accumulated DCF (MUS$/a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>3</td>
<td>7.99</td>
<td>7.99</td>
<td>6.00</td>
<td>6.00</td>
</tr>
<tr>
<td>4</td>
<td>7.99</td>
<td>15.98</td>
<td>5.46</td>
<td>11.46</td>
</tr>
<tr>
<td>5</td>
<td>7.99</td>
<td>23.97</td>
<td>4.96</td>
<td>16.42</td>
</tr>
<tr>
<td>6</td>
<td>7.99</td>
<td>31.96</td>
<td>4.51</td>
<td>20.93</td>
</tr>
<tr>
<td>7</td>
<td>7.99</td>
<td>39.95</td>
<td>4.10</td>
<td>25.03</td>
</tr>
<tr>
<td>8</td>
<td>7.99</td>
<td>47.94</td>
<td>3.73</td>
<td>28.76</td>
</tr>
<tr>
<td>9</td>
<td>7.99</td>
<td>55.93</td>
<td>3.39</td>
<td>32.15</td>
</tr>
<tr>
<td>10</td>
<td>7.99</td>
<td>63.92</td>
<td>3.08</td>
<td>35.23</td>
</tr>
<tr>
<td>11</td>
<td>7.99</td>
<td>71.91</td>
<td>2.80</td>
<td>38.03</td>
</tr>
<tr>
<td>12</td>
<td>7.99</td>
<td>79.9</td>
<td>2.55</td>
<td>40.57</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td></td>
<td>Total 79.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Year</th>
<th>Annual margin (MUS$/a)</th>
<th>Accumulated Margin (MUS$/a)</th>
<th>DCF at DCFRR = 0.1 (MUS$/a)</th>
<th>Accumulated DCF (MUS$/a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>3</td>
<td>7.34</td>
<td>7.34</td>
<td>5.51</td>
<td>5.51</td>
</tr>
<tr>
<td>4</td>
<td>7.34</td>
<td>14.68</td>
<td>5.01</td>
<td>10.53</td>
</tr>
<tr>
<td>5</td>
<td>7.34</td>
<td>22.02</td>
<td>4.56</td>
<td>15.09</td>
</tr>
<tr>
<td>6</td>
<td>7.34</td>
<td>29.36</td>
<td>4.14</td>
<td>19.23</td>
</tr>
<tr>
<td>7</td>
<td>7.34</td>
<td>36.7</td>
<td>3.77</td>
<td>23.00</td>
</tr>
<tr>
<td>8</td>
<td>7.34</td>
<td>44.04</td>
<td>3.42</td>
<td>26.42</td>
</tr>
<tr>
<td>9</td>
<td>7.34</td>
<td>51.38</td>
<td>3.11</td>
<td>29.53</td>
</tr>
<tr>
<td>10</td>
<td>7.34</td>
<td>58.72</td>
<td>2.83</td>
<td>32.36</td>
</tr>
<tr>
<td>11</td>
<td>7.34</td>
<td>66.06</td>
<td>2.57</td>
<td>34.93</td>
</tr>
<tr>
<td>12</td>
<td>7.34</td>
<td>73.4</td>
<td>2.34</td>
<td>37.27</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td></td>
<td>Total 73.4</td>
</tr>
</tbody>
</table>
4. Thermodynamic Properties

For petroleum refinery processes, Aspen® advises the use of petroleum tuned equations-of-state models. These are used for high and moderate pressures. Available petroleum tuned equations-of-state models are Soave-Redlich-Kwong (SRK) and Peng-Robinson (PR). Both of them are applicable for all pressure and temperature ranges. And they are suited for non-polar or mildly polar mixtures, which is the case in this project.

Process conditions are 3.5-22 bara and 38-121°C. It is clear that both PR and SRK can be employed. In general, however, SRK gives better result for low carbon number hydrocarbons strictly speaking.

Since the hydrocarbon stream in the process contains a considerable amount of low to medium carbon-number components, SRK is taken here. For some comparison with respect to a certified data see Appendix E: Pure components properties.
5. Process structure and description

5.1. Criteria and selection

The process is designed for the total hydroisomerisation of light Straight Run Naphtha. An integrated separation/catalytic reaction unit has been incorporated in the process. The process has to operate continuously. The objective is to increase the RON of the straight run naphtha up to more than 80 (specification of the gasoline blending) through skeletal Isomerisation of C5/C6, without use of any additive (lead, MTBE). The process is designed to meet the requirements specified in Table 3.10.

The final process temperature range is 28-121°C and the final process pressure range is 4.0-22 bars.

5.2. Process Flow Scheme

The process flow schemes (PFS) of the two options chosen (Cf. Chapter 2) are supplied in Appendix H and I. They show diagrammatically the units present, the streams and their operating conditions.

5.2.1. Equipment specification sheets

Specifications of the process units in the PFS concerning pressure, temperature, dimensions, type, material, etc. are provided in Appendix V: Reactor and Vessel summary and specification sheets, Appendix W: Heat Exchangers summary and specification sheets and Appendix X: Pumps and compressor summary and specification sheets.

5.2.2. Description of the process units in the PFS

Hydroisomerisation membrane reactor (R101)

- Option 1

The membrane reactor for hydroisomerisation of C4/C5/C6 is a co-current flow reactor with two inlet and two outlet streams. Use is made of a membrane in the shape of tubes of zeolite 5A of 3 micrometers thickness coated on a stainless steel support of 1.5 mm with a TiO2 coating. The sweep gas (hydrogen) and the feed are entering at the bottom of the reactor: the first on the inside of the tubes, the last in the space between the tubes and the shell. A packed bed of catalyst AT-20 (chlorinated alumina with 0.25 wt % of platinum) is located on the inside of the tubes. (Cf. Appendix O: Scheme of both options) The membrane separates the normal alkanes from the rest of the feed thanks to the pore size that allows only the normal alkanes to go through. The separation is effective at 95% for the n-C4, n-C5 and n-C6, i.e. that 95% of these normals will go through. The surface area of membrane is not designed to separate n-C7 from the rest of the feed since n-C7 has a very low permeance. For this specie, the separation is 0%. The pressure difference across the membrane is 2 bars: the feed is at 22 bars and the hydrogen is pressurised at 20 bars.

The reactor is operated adiabatically. The feed enters at 90°C and the hydrogen at 120°C. The separation and the reaction take place at the same temperature, around 120°C, because the reactions are exothermic. At this temperature, the catalyst is still
very active and the thermodynamic equilibrium can be reached (Cf. Chapter 3, section 3.2.6. for the proportion of normal and branched alkanes at this temperature).

- **Option 2**
  The reactor is made on the same principle as option 1 except that there is a recycle of the product inside smaller tubes that are inserted in the tubes of option 1. Thereby, normal alkanes can permeate to the catalyst bed from the feed side and the recycle side with the same pressure difference, 2 bars. The smaller tubes are made of the same materials as the ones in option 1.
  There are three inlet and three outlet streams in this option.

*Flash Vessel (V101)*

The product from the catalyst bed contains hydrogen, C₄, C₅ and C₆. Hydrogen and C₄ need to be separated from this product to ensure the product is not too much volatile and its Reid Vapor Pressure is not too high (Reid Vapor Pressure of the blending should be 84 kPa). The flash does not separate completely C₄ and hydrogen from the heavier molecules, the composition of the top and the bottom of the flash for both options are shown in the tables below. The top of the flash contains an important fraction of C₅ because the operating conditions of the flash are a compromise between C₅ molecules lost in the purge and C₄ molecules contained in the final product. (Cf. Appendix U: Flash: Choice of operating conditions)

<table>
<thead>
<tr>
<th>Components</th>
<th>Top (wt %)</th>
<th>Bottom (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₄</td>
<td>12.97</td>
<td>7.54</td>
</tr>
<tr>
<td>C₅</td>
<td>87.03</td>
<td>92.46</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Components</th>
<th>Top (wt %)</th>
<th>Bottom (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₄</td>
<td>28.31</td>
<td>18.78</td>
</tr>
<tr>
<td>C₅⁺</td>
<td>71.69</td>
<td>81.22</td>
</tr>
</tbody>
</table>

5.3. Process stream summary

All the process streams of the second option are specified in Appendix J: Process Stream Summary (option 2). For each stream, the flows are expressed in kg/s and kmol/s and the temperature, pressure, phase and enthalpy are reported.

5.4. Utilities

The summary of the utilities of the second option is supplied in Appendix L: Utilities Summary (option 2).

5.5. Process Yields

A summary of the in and outgoing process flows and process yields together with a comprehensive block scheme is provided in Appendix M: Process Yields (option 2).
6. Process Control

The primary objectives of the designer, when specifying instrumentation and control schemes, are safe plant operation, achieving the desired product output, maintaining product composition/quality and operating at the lowest production cost. In order to achieve all of the above, the plant must be equipped with instruments to monitor and control the key variables during its operation.

A control strategy has been developed for this purpose. This is illustrated for both options (single-pass and recycle) in the process flow schemes (PFS). (Cf. Appendix H: Process Flow Scheme of option chosen (option 2) and Appendix I: Process Flow Scheme of option abandoned (option 1)).

6.1. Key variables

The main variables to be controlled are:

- The temperature and pressure in the membrane reactor R101. The former determines the performance of the catalyst in producing the branched alkanes. The latter drives the permeation of the species across the membrane in addition to its influence on the equilibrium of the reaction.
- The pressure and liquid level in the flash separator V101 determine the composition of all the outgoing streams as well as their conditions.

6.2. Control Loops

The control structure, which can be found in the process flow schemes, comprises the following control loops:

- Ratio control for the feed and H$_2$ flow rates: depending on the feed rate, the hydrogen flow rate is adjusted by specifying the ratio required.
- Temperature control of the membrane reactor (R101): the membrane unit is a multi-tubular reactor which operates adiabatically. The feed temperature must be raised to 90°C by means of a preheater (E101). In order to control this feed temperature, a temperature controller is placed. The steam flow rate in the preheater is manipulated in order to meet the target temperature.
- H$_2$ stream pressure control: the catalyst side pressure is set to be 20 bars, that is 2 bars lower than the feed side. This enables the normal alkanes to diffuse to the catalyst bed where the reaction takes place. Pressure control here is crucial and is achieved by including a control loop between the inlet hydrogen pressure to the reactor and the hydrogen recycle flow rate. In case of an emergency, the reactor is equipped with a pressure relief valve, which is not shown on the PFS.
- Pressure control for the flash separator (V101): the flash vessel pressure is controlled by coupling the pressure with the flow rate through a control valve placed at the top of the flash vessel (stream <7>).
- Liquid level control for the flash separator: control of the level in the flash is essential not only to ensure a good separation of the light and heavy ends but also for the safe operation of both the flash and the subsequent pumps. For this, the liquid level measurement is compared to a set point (which corresponds to the maximum and/or minimum levels) and the controller acts accordingly on the flow of stream <9> through the control valve.

- Temperature control of the product: the conditions of the final product to be sent to the gasoline blending unit have been fixed. In order to control the temperature of the product stream, the flow rate of the cooling utility (cold water) can be varied.

- Flow control of product: a flow control loop is placed downstream of the product pump to adjust the flow rate.

These control loops apply in both cases; the single-pass and recycle designs. However, in the latter, a liquid recycle loop to the membrane reactor arises. In order to control the build-up of any unwanted substance, a bleed manual valve was included.
7. Mass and Heat Balance

The mass and heat balances (APPENDIX K: Mass and Heat Balance Total Streams (option 2)) are entirely outputs from ASPEN. The enthalpies are based on a reference condition of 25°C and 1 atm.

8. Process and Equipment Design

8.1. Integration by process simulation

The process was simulated with the process flow sheet simulator Aspen Plus 10.2. Prior to this, material balances have been set up in Excel, making use of the available Solver utility to converge recycle streams in the process. These balances permitted to choose two options out of the five initial alternatives. These were subsequently simulated with Aspen.

8.2. Equipment selection and design

The equipment selection and design presented hereafter concerns both options 1 and 2. Equipment design and cost estimation have been realised for both in order to compare them. The second option was found more interesting from an economic point of view and from the RON value of the product obtained.

8.2.1. Membrane reactor

The reaction unit for hydroisomerisation of C4/C5/C6 paraffins was designed to be an adiabatic, multi-tubular membrane catalytic reactor (not to confuse with a catalytic membrane reactor, where the membrane is inherently catalytic). The flow on the feed (retentate side) and permeate side are co-current. In the second option, the recycle is also co-current with the other flows. The chlorinated alumina catalyst is located on the permeate side of the tubes, between the outside tubes and the inner tubes. A scheme of the reactor is presented in Appendix O: Design of the reactor: scheme of both options.

Appendix S: Design of the reactor (Detail of Option 2) details the separation of the different streams at the inlet and outlet of the reactor.

Reactor model

The essentials assumptions for the development of the model are as follows:
1. The reactor operates at steady state.
2. The flux of liquid through the membrane is assumed to be the limiting factor that will govern the reactor performance and its size.
3. The catalyst is very active: the thermodynamic equilibrium is reached at the outlet of reactor.
4. The conditions in the reactor and the surface area of the membrane allow 95% of the normal paraffin from the feed and from the recycle to go through.
5. Permeation occurs by a mechanism of surface diffusion as shown in the figure below [11].

**Figure 8.1. Combined activated gaseous diffusion (Ng) and surface diffusion (Ns) as a function of temperature.**

In this case, the permeance (flux per unit area of membrane) can be calculated by:

\[ \Pi = \frac{N}{\Delta p} = \rho q_{sat} D \frac{\nabla \ln(1 - \theta)}{\Delta p} \]

Where \( N \) is the flux through the membrane, \( \Delta p \) the pressure difference across the membrane, \( q_{sat} \) the adsorbed phase concentration at saturation, \( D \), the corrected transport diffusivity and \( \theta \), the percentage of occupancy of adsorbed phase.

Values for \( D \) were found for n-C4, n-C5, n-C6 and n-C7:

<table>
<thead>
<tr>
<th>Corrected transport diffusivity D</th>
<th>Values (m²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-C₄</td>
<td>1.60 x 10⁻¹¹</td>
</tr>
<tr>
<td>n-C₅</td>
<td>1.28 x 10⁻¹¹</td>
</tr>
<tr>
<td>n-C₆</td>
<td>8 x 10⁻¹²</td>
</tr>
<tr>
<td>n-C₇</td>
<td>4.50 x 10⁻¹²</td>
</tr>
</tbody>
</table>
Table 8.2: Model parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>T_{feed side (inlet)}</td>
<td>90°C</td>
</tr>
<tr>
<td>T_{permeate side (inlet)}</td>
<td>120°C</td>
</tr>
<tr>
<td>T_{recycle side (inlet)}</td>
<td>120°C</td>
</tr>
<tr>
<td>Feed flow (Naphtha)</td>
<td>10.50 kg/s</td>
</tr>
<tr>
<td>Recycle flow</td>
<td>5.646 kg/s</td>
</tr>
<tr>
<td>Hydrogen Recycle Flow</td>
<td>0.1554 m³/s</td>
</tr>
<tr>
<td>D_{shell}</td>
<td>3.92 m</td>
</tr>
<tr>
<td>D_{outside tubes}</td>
<td>0.23 m</td>
</tr>
<tr>
<td>D_{inside tubes}</td>
<td>0.07 m</td>
</tr>
<tr>
<td>Surface area outside membrane</td>
<td>267.03 m²</td>
</tr>
<tr>
<td>Surface area inner membrane</td>
<td>76.40 m²</td>
</tr>
<tr>
<td>Catalyst particle shape</td>
<td>Cylindrical</td>
</tr>
<tr>
<td>Catalyst particle diameter</td>
<td>1.4 mm</td>
</tr>
<tr>
<td>Catalyst particle length</td>
<td>3 – 5 mm</td>
</tr>
<tr>
<td>Catalyst WHSV (^{(1)})</td>
<td>2</td>
</tr>
</tbody>
</table>

(1) WHSV: Weight Hour Space Velocity (kg feed/(kg catalyst.hr))

The reactor model has been applied in Aspen by using:
- two component separators for the two membranes (they separate components based on split fractions: split fraction=0.95 for n-C\(_4\), n-C\(_5\), n-C\(_6\) and 1 for other components)
- a stoichiometric reactor. The conversion fractions calculated from the figures in Appendix B: Thermodynamic equilibrium, are the input data of this reactor.

**Reactor layout**

The reactor incorporates a multiple membrane tube system (a bundle). There are outside tubes that surround smaller tubes. Each of them consists of a metal support (macroporous stainless steel) of 1.5 mm coated with 1.5 mm of TiO\(_2\) with 3 micrometers molecular sieve layer of zeolite 5A. The outside tubes are 0.23 m in diameter and the smaller ones 0.07 m.

There are 124 tubes arranged in a shell of 3.92 m like in a shell and tubes heat exchanger. Three baffles that are laid out every 0.75 m help to increase the residence time and maintain those tubes.

The naphtha feed is inserted in the space between the shell and the outside membrane tubes at a pressure of 22 bars. It permeates (only the normal alkanes) through the membrane, with a pressure difference of 2 bars across the membrane, to the packed bed of cylindrical catalyst particles located between the inside of the bigger tubes and the outside of the smaller ones.

Ultimately, the permeate is flashed then recycled (the liquid phase) back to the reactor. It is inserted on the inside of the smaller tubes and permeates with the same pressure difference of 2 bars (because the pressure on the recycle side is the same as the pressure on the feed side).
Hydrogen is inserted on the permeate side of the tubes. It is used as a reactant of hydroisomerisation reaction that is recovered after each reaction. The pressure of hydrogen (20 bars) helps to keep hydrogen molecules on the catalyst so that the reactions of hydrogenation, first step of isomerisation, are possible. Hydrogenation and isomerisation reactions are exothermic. That is why the feed does not enter the reactor at 120°C. Its temperature is subsequently raised by the reactions.

The pressure drop along the catalyst bed was calculated with Ergun's equation for pressure drop in a packed porous bed. The calculation is supplied in Appendix Q and R: Design of the reactor. The result is a pressure drop of 0.07 bars. The simulation was run on Aspen with a pressure drop of 0.5 bars in the reactor to keep a margin because the viscosity of the hydrogen recycle is not accurately known and there can be a pressure drop at the reactor inlet and outlet.

The calculations of the area of the tubes are presented in Appendix P: Calculation of the area of membrane needed.

The calculations of the diameters of tubes are presented in Appendix L and M: Design of the reactor.

The price of the membrane is around $3000/m² [18] and the price of the catalyst was supplied by Akzo Nobel: $40/lb (confidential data).

8.2.2. Flash vessels

The product from the reactor needs to be flashed to separate hydrogen and C4 from heavier. Hydrogen and C4 are not desired in the final product as C4 can make the product too volatile.

The flash vessel has been chosen as a vertical gas-liquid separator. The method in Coulson V.6 (p.459-460) was followed for the sizing and the calculations are presented in Appendix T: Design of the flash vessel. The equipment specification sheet is presented in Appendix V: Reactor and Vessel summary and specification sheets.

8.2.3. Heat exchangers

The SRN feed needs to be heated up from 60°C to 90°C so that the temperature inside of the reactor reaches 120°C, thanks to the exothermicity of the hydroisomerisation reactions.

The product needs to be cooled down, after the mixing of the outlet of the shell side (isoparaffins from the feed) and the isoparaffins of the recycle, from 79.4°C to 40°C. The conditions of the product were chosen so that it remains liquid, to avoid too large storage tanks and for safety. These conditions are: 40°C and 4.5 bars.

No heat integration between the feed and the product is possible because there is overlapping in the temperature profiles of the two streams. Heat transfer cannot take place in the reverse direction of what the second law of thermodynamics prescribes.

The equipment specification sheets are presented in Appendix W: Heat Exchangers summary and specification sheets.

1. Heat Exchanger E101

It is a shell and tube device made of carbon steel, the most common heat exchanger, with one pass in tube side. The feed is heated up by low-pressure steam at 190°C (cf.
The calculation of the area is a classic calculation, described in Coulson and Richardson, V.6, Ch.12.

### Table 8.3.: Parameters of heat exchanger E101

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure of the feed (bars)</td>
<td>22</td>
</tr>
<tr>
<td>$Q = \text{Heat Duty (kW)}$</td>
<td>762.94</td>
</tr>
<tr>
<td>$U (\text{kJ/m}^2\text{oC})$</td>
<td>420</td>
</tr>
<tr>
<td>$\Delta T_{lm}$ ($^\circ\text{C}$)</td>
<td>81.8</td>
</tr>
<tr>
<td>Area ($\text{m}^2$)</td>
<td>22.241</td>
</tr>
<tr>
<td>Cost ($)</td>
<td>12854</td>
</tr>
</tbody>
</table>

1. **Data from Aspen simulation.**
2. **Overall heat transfer coefficient.** Coulson, V. 6, p 637.
3. $Q = U.\text{Area.} \Delta T_{lm}$ and $\Delta T_{lm}$: see Coulson, V. 6, page 655.
4. **Coulson, V. 6, p.253.** Pressure factor = 1.25.

### 1. Cooler E102

It is also a shell and tube device made of carbon steel, with one pass in tube side. The product is cooled down by cooling water at 20 °C (cf. Chap.3). The calculation of the area is a classic calculation, described in Coulson and Richardson, V. 6, Ch.12.

### Table 8.4.: Parameters of heat exchanger E102

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure of the feed (bars)</td>
<td>4.00</td>
</tr>
<tr>
<td>$Q = \text{Heat Duty (kW)}$</td>
<td>1679.76</td>
</tr>
<tr>
<td>$U (\text{kJ/m}^2\text{oC})$</td>
<td>420</td>
</tr>
<tr>
<td>$\Delta T_{lm}$ ($^\circ\text{C}$)</td>
<td>32.5</td>
</tr>
<tr>
<td>Area ($\text{m}^2$)</td>
<td>202</td>
</tr>
<tr>
<td>Cost ($)</td>
<td>56250</td>
</tr>
</tbody>
</table>

1. **Data from Aspen simulation.**
2. **Overall heat transfer coefficient.** Coulson, V. 6, p 637.
3. $Q = U.\text{Area.} \Delta T_{lm}$ and $\Delta T_{lm}$: see Coulson, V. 6, page 655.
4. **Coulson, V. 6, p.253.** Pressure factor = 1.25.

### 8.2.4. Pumps

In option 2, three pumps are necessary:
- One for the feed: to achieve the required pressure in the reactor (22 bars).
- One for the recycle to the reactor: to bring back the recycle at 22 bars, operating pressure of the reactor
- One for the product: to have a product at 4.5 bars and 40°C, conditions chosen for the storage to keep the product in liquid phase.

In option 1, the pump for the recycle is obviously not included.

The equipment specification sheets are presented in Appendix X: Pumps and compressor summary and specification sheets.
1. Pump of the feed, P101

Table 8.5.: Parameters of pump P101

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow rate (m$^3$/hr)</td>
<td>69.2</td>
</tr>
<tr>
<td>Energy (kW)</td>
<td>41.83</td>
</tr>
<tr>
<td>Pressure change (bars)</td>
<td>18.5</td>
</tr>
<tr>
<td>Pressure change (m water)</td>
<td>188.65</td>
</tr>
</tbody>
</table>

(1) Data from Aspen simulation.

For such a flow rate and pressure change, a centrifugal pump high speed or multistage centrifugal pump is required. A multistage equipment has been chosen. The characteristics of a single pump are: 2900 RPM / 100 m$^3$/hr / 50 mwk (m water). The cost of this pump is 11200 Dfl (Dutch Association of Cost Engineers, 2000). The number of pumps is 4 hence the total cost is 44800 Dfl = $18177.

1. Pump of the recycle, P102

Table 8.6.: Parameters of pump P102

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow rate (m3/hr)</td>
<td>47.84</td>
</tr>
<tr>
<td>Energy (kW)</td>
<td>4.746</td>
</tr>
<tr>
<td>Pressure change (bars)</td>
<td>2.50</td>
</tr>
<tr>
<td>Pressure change (m water)</td>
<td>25.49</td>
</tr>
</tbody>
</table>

(1) Data from Aspen simulation.

For such a flow rate and pressure change, a centrifugal pump high speed is required. The characteristics of the pump chosen are: 2900 RPM / 50 m$^3$/hr / 32 mwk (m water). The cost of this pump is 8700 Dfl (Dutch Association of Cost Engineers, 2000), equivalent to $3530.

1. Pump of the product, P103

Table 8.7.: Parameters of pump P103 (option 2)

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow rate (m3/hr)</td>
<td>64.43</td>
</tr>
<tr>
<td>Energy (kW)</td>
<td>1.254</td>
</tr>
<tr>
<td>Pressure change (bars)</td>
<td>0.50</td>
</tr>
<tr>
<td>Pressure change (m water)</td>
<td>5.00</td>
</tr>
</tbody>
</table>

(1) Data from Aspen simulation.

For such a flow rate and pressure change, a centrifugal pump high speed is required. The characteristics of the pump chosen are: 2900 RPM / 100 m$^3$/hr / 20 mwk (m water). The cost of this pump is 8800 Dfl (Dutch Association of Cost Engineers, 2000), equivalent to $3570.

For the first option, the flow rate is different (86.85 m$^3$/hr) but the same pump can be used and hence, the cost is the same.
8.2.5. Compressors

The compressor is used to bring back the hydrogen recycle from 19.5 bars to 20 bars so that the hydrogen always enters the reactor at 20 bars. It is a reciprocating compressor based on the criterion in Coulson, V.6. (p. 475). The cost of this compressor has been estimated with the formula page 258 of Coulson and Richardson, Volume 6:

The equipment specification sheet is presented in Appendix X: Pumps and compressor summary and specification sheets.
9. Wastes

Direct process wastes are summarised in tables 9.1 for option 1 and 9.2 for the second option.

**Table 9.1: Waste streams in option 1**

<table>
<thead>
<tr>
<th>Waste stream</th>
<th>Amount (ton/a)</th>
<th>Remarks</th>
<th>Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>C4 purge</td>
<td>2292.34</td>
<td>C4, C5, hydrogen</td>
<td>To fuel gas</td>
</tr>
<tr>
<td>Spent Pt/H-Cl-Alumina</td>
<td>2.449</td>
<td>± 4 years</td>
<td>To supplier/regenerating company (1)</td>
</tr>
<tr>
<td>Spent zeolite A</td>
<td>2.67 m²/a</td>
<td>± 10 years (2)</td>
<td>To supplier/regenerating company</td>
</tr>
</tbody>
</table>

**Table 9.2: Waste streams in option 2**

<table>
<thead>
<tr>
<th>Waste stream</th>
<th>Amount (ton/a)</th>
<th>Remarks</th>
<th>Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>C4 purge</td>
<td>9508.26</td>
<td>C4, C5, hydrogen</td>
<td>To fuel gas</td>
</tr>
<tr>
<td>Spent Pt/H-Cl-Alumina</td>
<td>2.765</td>
<td>± 4 years</td>
<td>To supplier/regenerating company (1)</td>
</tr>
<tr>
<td>Spent zeolite A</td>
<td>2.67 m²/a</td>
<td>± 10 years (2)</td>
<td>To supplier/regenerating company</td>
</tr>
<tr>
<td></td>
<td>7.64 m²/a</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(1) The supplier or a regenerating company regenerates the spent catalyst after 4 years.
(2) The lifetime of the membrane is assumed to be 10 years if it is regenerated as often as needed by heating it up with a hot stream.
10. Process Safety

10.1 Hazop

A hazard and operability (Hazop) study has been conducted for the double membrane reactor (option 2) but it is also valid for option 1 since option 2 is globally the addition of a recycle to option 1. The reactor is considered to be a critical piece of equipment for reaching the product specifications. The Hazop is presented in Appendix AB.

10.2 Fire and Explosion Index

A Fire and Explosion Index (F&EI) calculation has been conducted for the reaction section of the process. The reaction section contains the Membrane reactor, together with accompanying units like pumps, a compressor and a flash. The detailed calculation sheet is supplied in Appendix AB. Here follow some explanations about the factors used to calculate a value for the F&EI.

Material Factor:

Our material, a TOP3 naphtha, is not listed in tables giving materials factors. Its material factor (MF) has to be determined using the Material factor determination guide, page 13 of the Dow's Fire and Explosion Hazard Classification Guide. In this method, two coefficients, \( N_F \) and \( N_R \), express respectively the flammability and reactivity of the material.

For TOP3 naphtha, these values are:

\[
N_F = 3 \quad \text{(flash point < 22.8°C & boiling point < 37.8°C)}
\]

\[
N_R = 0.
\]

The relevance of these values has been checked with Material data sheets from companies on Internet (http://www.hess.com/about/msds/Gaso_Plus_8557Clr.pdf). Hence, the material factor is 16. It represents the hazard at ambient temperature so it needs to be adjusted at 120°C, the operating temperature of the reactor and the flash. Using table 2, page 14, the correction is found to be 4 so the material factor is 20.

The material factor of hydrogen is 21, higher than the material factor of the feed. Since hydrogen is present in a significant amount, the overall material factor is assumed to be 21.

General Process Hazards:

A. Exothermic Chemical Reactions: Hydroisomerisation is an exothermic reaction for which a penalty of 0.3 has to be taken into account.

C Material Handling and Transfer: A penalty of 0.85 is applied for NF = 3 or 4 flammable liquids.

D Enclosed or indoor process units: we assume the hydroisomerisation unit will be an open and freely vented construction that permits rapid dissipation of any vapours released, reducing the explosion potential of the unit.

E Access: we assume that the process area has adequate access.
F. **Drainage and spill control**: at this stage of the design, we put no penalty for drainage and spill control. It means that the construction of the unit requires excellent drainage.

**Special Process Hazards:**

B. **Toxic material**: this is the health factor defined by NFPA (National Fire Protection Association) multiplied by 0.20. In our case, $N_H = 1$ because the material could cause irritation on short exposure but only minor residual injury, hence, the factor is equal to 0.20.

C. **Operation in or near the flammable range**: the reactor and process units operate near the flammable range resulting in a penalty of 0.80.

E. **Relief pressure**: To take in account the vessel design pressure of the reactor, the penalty is given by:

$$\text{Penalty} = \text{operating \ pressure \ penalty} \times (\text{operating \ pressure \ penalty} / \text{set \ pressure \ penalty})$$

Therefore, a penalty of 0.47 has been applied.

G. **Quantity of flammable material**: this penalty is based upon the amount of fuel for a fire that can be released from the process unit within 10 minutes. This is estimated by the quantity of material in the largest connected unit: reactor and flash, 8714.745 kg, multiplied by the heat of combustion which is 42 to 44 kJ/g, equivalent to 10000 to 10500 kcal/kg. To establish the value to be applied, the result of multiplication must be divided by 10^9.

C. **Corrosion and erosion**: As the rate of corrosion is not known but the presence of a chlorinated agent (in small quantities) is known in the make up of hydrogen and the location of the plant is in Europoort, near the sea, we chose a penalty of 0.10.

I. **Leakage-Joints and packing**: Hydrogen is a gas that is known to leak easily. A penalty of 0.1 has been applied.

D. **Rotating equipment**: Since compressors used in each option are operating at low hp (<5hp), no penalty is applied.

A final value of 125 classifies the degree of hazard for the reaction as **intermediate**.

**Area of exposure:**

According to the calculated F&EI, the exposure radius is 32 m (105 ft), corresponding to an area of exposure of 3217 $m^2$. It is the area required to retain 8 cm depth of any given volume of flammable liquid and the over-pressure radius of vapour-air mixture. The damage factor was determined as 77.5 %. This means that the conditions of the reaction section represent a 77.5 % damage probability to 3217 $m^2$ of surrounding area.

**10.3 Conclusions and recommendations**

1. Install adequate and secure extinguishing media for fire fighting: extinguishers suitable for Class B fires, dry chemical, carbon dioxide, foam for small fires and water spray, fog or fire fighting foam for large fires.
2. Install an adequate drainage system for spills and fire fighting water.
3. All electrical equipment must be earthed.
4. Equipments must comply with national codes and standards.
5. Make provision of back-up utilities and services.
6. Make provision for access of emergency vehicles and the evacuation of personnel.
7. All hot surfaces must be isolated (heat exchangers, reactor).
8. Avoid any possible source of static electricity: non-conducting shoes, material. All piping must be properly earthed and electrical continuity maintained around flanges. Entry of obvious sources of ignition must be strictly controlled: matches, lighters and battery operated equipment, portable electrical equipment, welding, spark-producing tools and petrol-driven vehicles.
9. Over-pressure is one of the most serious hazards in chemical plant operation: adequate safety valve is needed for hydrogen and a bleed valve for hydrocarbons.
10. Safe work practices and/or appropriate personal protective equipment may be needed to protect against hazards during inspection, maintenance, and turnaround activities.
11. Economy

The capital costs are calculated following the method of Coulson V.6, Ch.6. The method estimates the other costs in terms of the Purchased Equipment Costs (PEC).

The PECs here are $971,249 and $1,190,724 for options 1 and 2 respectively. (Cf. Appendix Y: Capital Investments); and the corresponding total investment costs estimated are k$ 5,386.8 & 6,643.4.

Funding is considered from an outside source and, hence, capital charges are included in the production costs (cf. Appendix Z & AA: Economic Calculations (option 1&2)). The catalyst’s cost is based on 4 years life [8]. As the process is reasonably intensified 3 operators are assumed to work in each of the three shifts. The utilities are based on the results of the heat & mass balances (cf. Appendix K: Mass and Heat Balance Total Streams (option 2)).

The interest rates are taken to be 10% as suggested by the manual. And in the cash flow calculations (cf. Appendices Z & AA: Economic Calculations (option 1&2)), the prices of the raw materials, products, utilities etc are assumed to be same as those at present time throughout the life of the project (no inflation).

The economics of the two options is summarized in table 11.1 (cf. Appendices Z & AA: Economic Calculations (option 1&2)).

*Table 11.1: Net cash flow and Economic Criteria*

<table>
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<tr>
<th>Item</th>
<th>Unit</th>
<th>Option 1</th>
<th>Option 2</th>
</tr>
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<tr>
<td>Net Cash Flow, Before Tax</td>
<td>k$</td>
<td>2,433</td>
<td>2,828</td>
</tr>
<tr>
<td>Net Cash Flow, After Depreciation</td>
<td>k$</td>
<td>1,984</td>
<td>2,275</td>
</tr>
<tr>
<td>Net Cash Flow, After Tax</td>
<td>k$</td>
<td>1091</td>
<td>1251</td>
</tr>
<tr>
<td>Pay-Out Time, Before Tax</td>
<td>Years</td>
<td>2.2</td>
<td>2.3</td>
</tr>
<tr>
<td>Rate of Return, Before Tax</td>
<td>%</td>
<td>45.2%</td>
<td>42.6%</td>
</tr>
<tr>
<td>DCF Rate of Return, Before Tax</td>
<td>%</td>
<td>36.5%</td>
<td>34.5%</td>
</tr>
<tr>
<td>Net Present Value, Before Tax</td>
<td>k$</td>
<td>8,535</td>
<td>9,564</td>
</tr>
<tr>
<td>Net Future Value, Before Tax</td>
<td>k$</td>
<td>19,213</td>
<td>21,973</td>
</tr>
</tbody>
</table>
The economics of the two options alongside with that of a TIP process that has been realized by M.L. Maloncy [16] are given in table 12.1 for comparison. Clearly, both options seem to be less attractive than the TIP process.

However, the prices of the raw material (SRN) used for the calculations differ greatly between the options ($180/ton) and the TIP process ($150.4/ton). The effect of the raw material cost is tremendous as it constitutes around 92% of the total production costs in the options (cf. APPENDIX Z, APPENDIX AA: Economic calculations).

As seen from table 12.1, the two options have somewhat similar economics. In light of a better Net present Value, and a higher-valued product (RON=90), option 2 is recommended here. It should be stressed, however, that option 1 is better than option 2 when we see, for instance, the DCF Rate of return, and it is advisable to look into both options in more depth keeping in mind the possibility of further optimising the unit operations and/or reducing the other operating costs.

The membrane-reactor technology as used for isomerisation is new, and a lot is still desired from the scientific and engineering discoveries at hand regarding their implementation in design. The economic indicators provide a good momentum for a further investigation into this technology.
List of Symbols

D  Diffusivity (m$^2$/s)
G  Mass flow rate (kg/s)
L  Length of reactor (m)
MF Material Factor (in Dow’s Fire and Explosion Index)
Re Reynolds Number
SRN Straight Run Naphtha (feed of this project)

ΔP Pressure drop
μ Dynamic viscosity (Pa.s)
ε Porosity
Literature


11. J.M. Van de Graaf, Permeation and separation properties of supported silicalite-1 membranes: a modelling approach, PhD thesis, Figure 9(a), p 41(1999).


In this report, the «Coulson» is quoted many times. The reference of this book is: **R.K. Sinnott**, Coulson and Richardson, Volume 6, Third edition, 2000.
List of Appendices

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