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Systems and Economic Analysis of the Seasonal Storage of Electricity with Liquid Organic Hydrides

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presented by
GREGOR WOLFGANG HUGO SCHERER
Dipl. Phys. ETH
born 22.8.67
citizen of Meggen LU

accepted on the recommendation of
Prof. Dr. A. Wokaun, examiner
Prof. Dr. L. Reh, co-examiner
Dr. E.J. Newson, co-examiner

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Summary

For those countries such as Canada, Norway and Switzerland with a significant production of hydroelectric power, the seasonal storage of electricity would satisfy the summer-winter supply and demand imbalance. One future alternative to hydraulic pump storage is hydrogen as an environmentally acceptable secondary energy source stored in the form of liquid organic hydrides, e.g. methylcyclohexane (MCH). This work considers the techno-economic potential of the seasonal storage of electricity with chemically bound hydrogen in liquid organic hydrocarbons in the Methylcyclohexane-Toluene-Hydrogen System (MTH). An important goal is an estimation of the future economics of the stationary MTH-System, therefore the cost and efficiency data of the plants are based on mature technology. A mobile application of the MTH-System is excluded based on inherent energetic inefficiencies and the weight of the system. Another solution for mobile applications of alternative fuels is based on methanol steam reforming with subsequent use of the hydrogen in a polymer electrolyte fuel cell (PEFC).

The seasonal MTH-System consists of five steps: using cheap summer electricity for water electrolysis to produce hydrogen and oxygen, hydrogenation of toluene to methylcyclohexane, storing the liquid organic hydrogen carrier in tanks (methylcyclohexane from summer to winter and toluene from winter to summer), dehydrogenation of methylcyclohexane, reelectrification of the hydrogen in a power plant for generating winter electricity. An initial cost estimation with sensitivity analyses showed the parameters which strongly influenced the costs of seasonally stored electricity using the MTH-System. It is shown that the efficiency of the electric power plant and its heat integration into the dehydrogenation plant are the most important system parameters in the complete MTH-System. Other important parameters are the costs and availability of the input electricity and the electrolyser costs. The heat integration and efficiency of the reelectrification by the power plant was estimated subsequently with energy and exergy analyses.

A more accurate analysis by simulation and thermodynamic calculations allowed a considerable improvement in the cost estimation of the MTH-System. Based on numerical modelling of the individual plants, simulations of several design alternatives of the total system were performed for 1000 GWh of stored summer electricity and 80 MW output. Since the reelectrification step of the winter process proved critical for the overall system efficiency, the three major design alternatives concerning the power plant used in the winter process of the MTH-System: MTH-SOFC (solid oxide fuel cells), MTH-MCFC (molten carbonate fuel cells) and MTH-Turbines (gas and steam turbines) were studied in detail. The overall efficiencies η_{tot} and the economic results of these simulations are $\eta_{tot} = 0.40$ and 0.26 $\$/kWh$ for the MTH-SOFC system alternative, $\eta_{tot} = 0.33$ and 0.30 $\$/kWh$ for the MTH-MCFC and $\eta_{tot} = 0.25$ and 0.36 $\$/kWh$ for the MTH-System with gas and steam turbines.

For comparison, the costs of winter electricity produced with a hydroelectric plant was estimated at 0.21 $\$/kWh$ for a Swiss location. Compared with the cost of electricity production using fossil fuels (0.05-0.1 $\$/kWh$), the electricity produced by the MTH-System is expensive. With respect to CO_2-emissions, the MTH-System (51 gCO_2/kWh) is superior to the best natural gas combined cycle plant (370 gCO_2/kWh). Therefore an economic comparison including a speculative energy tax was made to account for a possible scarcity of energy or the environmental impact due to the use of fossil energy resources. It concludes that the MTH-System is only competitive with a energy tax of more than 600 $\$/tonCO_2$ of an equivalent CO_2-tax. This is much more than the energy taxes (13-175 $\$/tonCO_2$) proposed by various governments.

Due to the disparities in economics and energy taxes, a best case study of the MTH-System was made to reduce its economic disadvantages. This best case study results in a maximal efficiency of the MTH-System of 0.48 with corresponding winter electricity costs of 0.17 $\$/kWh$. A higher efficiency for the solid oxide fuel cells was assumed $\eta = 0.65$ (0.61), and for the electrolyser 0.75 (0.72). The respective costs were reduced i.e. SOFC: 1100 $\$/kW$ (1500 $\$/kW$), electrolyser: 250 $\$/kW$ (672 $\$/kW$).

The methanol - steam reforming - fuel cell alternative for mobile applications was estimated to have an overall efficiency of 28%, which in a full fuel cycle analysis, is comparable to Otto engines. However, the cost of the system compared to combustion engines is excessive, depending significantly on membrane separation technology which has a potential for reduction.

The experimental part of the thesis investigated a key technology for hydrogen systems, i.e. the improvement in the scale-up of hydrogen purification membranes using $Pd - Ag_{23\%}$ tubes and composite membranes to reduce costs. With a new membrane module consisting of 34 $Pd - Ag$ tubes it was possible to exceed the goal of 1 kW (0.00414 $molH_2/s$ LHV) in hydrogen permeation experiments. Diminished hydrogen permeation rates were observed in presence of carbon monoxide in a typical reformate gas mixture. The module has a length of 300 mm and a diameter of 70 mm. It was operated up to 10 bar pressure in the temperature range 320-430$^\circ C$. The major problems of the economically interesting composite membrane (7 μm Pd on a ceramic tube support) are leaks in the membrane and its sealing. The delicate sealing was unsuitable mechanically for potential applications, but hydrogen permeation was superior to the tube module and palladium usage was reduced by a factor 25.

Zusammenfassung

Für Länder mit hohem Anteil von Wasserkraft in der Elektrizitätsversorgung wie Kanada, Norwegen und die Schweiz gleicht saisonale Elektrizitätsspeicherung die saisonalen Schwankungen in Nachfrage und Angebot aus. Eine zukünftige Alternative zur Pumpspeicherung ist Wasserstoff, gespeichert in Form von flüssigen Kohlenwasserstoffen wie z.B. Methylzyklohexan (MCH), ein ökologisch verträglicher Sekundär-Energieträger. Diese Arbeit untersucht das technisch-wirtschaftliche Potential der saisonalen Elektrizitätsspeicherung mit dem Methylzyklohexan-Toluol-Wasserstoff System (MTH). Ein wichtiges Ziel ist eine Abschätzung der zukünftigen Kosten des stationären MTH-Systems. Darum basieren die Annahmen über Kosten und Wirkungsgrade der Anlagen auf voll entwickelter Technologie. Eine mobile Anwendung des MTH-Systems wird ausgeschlossen aufgrund inhärenter energetischer Verluste und aus Gewichtsgründen. Eine andere Lösung für mobile Anwendung von alternativen Energieträgern basiert auf einem Methanol-Dampf-Reformer mit nachfolgender Verbrennung des Wasserstoffs in einer Polymer-Elektrolyt-Brennstoffzelle (PEFC).

Das saisonale MTH-System besteht aus fünf Verfahrensschritten: Umwandlung von billiger Sommerelektrizität in Wasserstoff und Sauerstoff mit Elektrolyse, Hydrierung von Toluol zu Methylzyklohexan, Speicherung der Kohlenwasserstoffe in Tanks (Methylzyklohexan vom Sommer in den Winter und Toluol vom Winter in den Sommer), Dehydrierung des Methylzyklohexans, Wiederverstromung des Wasserstoffs in einer Kraftwerksanlage zur Erzeugung von Winterelektrizität. Eine anfängliche Kostenabschätzung mit Sensitivitätsanalysen identifizierte die Parameter des MTH-Systems, welche die Kosten der gespeicherten Elektrizität am stärksten beeinflussen. Es zeigte sich, dass der Wirkungsgrad der Kraftwerksanlage und ihre thermische Kopplung mit der Dehydrieranlage die wichtigsten Parameter sind. Weitere wichtige Parameter sind die Kosten und die Verfügbarkeit der Eingangselektrizität und die Elektrolysekosten. Die thermische Kopplung und der Wirkungsgrad der Kraftwerksanlage wurden nachfolgend mit Energie- und Exergie-Analysen abgeschätzt.

Eine exaktere Analyse mit Simulation und thermodynamischen Berechnungen ermöglichte eine signifikante Verbesserung in der Kostenabschätzung des MTH-Systems. Basierend auf numerischen Modellen der Einzelanlagen wurden Simulationen von verschiedenen Anlagen-Alternativen mit 1000 GWh gespeicherter Sommerelektrizität und 80 MW Ausgangsleistung durchgeführt. Weil der Wirkungsgrad der Wiederverstromung (Kraftwerksanlage) als kritisch für den gesamten Wirkungsgrad des Systems identifiziert wurde, beziehen sich die drei wichtigsten Anlagen-Alternativen auf die Wiederverstromung im Winterprozess des MTH-Systems: MTH-SOFC (Solid Oxide Fuel Cell), MTH-MCFC (Molten Carbonate Fuel Cell) und MTH-Turbinen (Gas- und Dampfturbinen). Die Gesamtwirkunsgrade η_{tot} und die

ökonomischen Resulte der Simulationen sind: $\eta_{tot} = 0.40$ und 0.26 $\$/kWh$ für die MTH-SOFC System Alternative, $\eta_{tot} = 0.33$ und 0.30 $\$/kWh$ für MTH-MCFC und $\eta_{tot} = 0.25$ und 0.36 $\$/kWh$ für das MTH-System mit Gas- und Dampfturbinen.

Als Vergleich wurden die Kosten der Produktion von Winterelektrizität mit Wasserspeicherkraftwerken für Schweizer Verhältnisse geschätzt auf 0.21 $\$/kWh$. Die Kosten der Elektrizitätproduktion mit dem MTH-System sind sehr hoch, verglichen mit denen konventioneller, fossiler Kraftwerke (0.05-0.1 $\$/kWh$). In Bezug auf die CO_2-Emissionen zeigt das MTH-System (51 gCO_2/kWh) Vorteile gegenüber weitest entwickelten Naturgas Kombianlagen (370 gCO_2/kWh). Deshalb wurde ein ökonomischer Vergleich mit einer spekulativen Energiesteuer gemacht, um eine eventuelle Verknappung der Energieresourcen oder Umweltschäden infolge Nutzung von fossilen Energieträgern zu berücksichtigen. Daraus folgte, dass das MTH-System nur mit einer Energiesteuer von mehr als 600 $\$/tonCO_2$ der entsprechenden CO_2-Steuer ökonomisch konkurrenzfähig ist. Dies ist ein Mehrfaches der Steuervorschläge (13-175 $\$/tonCO_2$) verschiedener Regierungen.

Aufgrund dieser Missverhältnisse von Kosten und Energiesteuern wurde der beste mögliche Fall für das MTH-System studiert. Aus dieser Best Case Analyse resultierte ein maximaler Gesamtwirkungsgrad von 0.48 mit Kosten von 0.17 $\$/kWh$ für die Winterelektrizität. Dabei wurden für die SOFC höhere Wirkungsgrade angenommen $\eta = 0.65$ (0.61), und für die Elektrolyse 0.75 (0.72). Die entsprechenden Kosten sind reduziert auf SOFC: 1100 $\$/kW$ (1500 $\$/kW$), Elektrolyse: 250 $\$/kW$ (672 $\$/kW$).

Der Wirkungsgrad der Alternative Methanol-Dampfreformer-Brennstoffzellen für mobile Anwendungen wurde auf 28% geschätzt, vergleichbar mit Otto-Motoren. Die Kosten dieses Systemes sind zu hoch, hängen aber im wesentlichen von der Membranseparation ab, deren Kosten noch reduziert werden können.

Im experimentellen Teil der Arbeit wird eine Schlüsseltechnologie für Wasserstoffsysteme untersucht, nämlich die Anwendung von metallischen Wasserstoff-Trennmembranen basierend auf $Pd - Ag_{23\%}$ Röhren und von Kompositmembranen. Mit einem Membranmodul, bestehend aus 34 $Pd-Ag$ Röhren, konnte das Ziel von 1 kW (0.00414 $molH_2/s$ LHV) Wasserstoffdurchfluss in Permeationsexperimenten überschritten werden. Dabei wurde der vermindernde Einfluss von Kohlenmonoxid auf die Permeationsraten von Wasserstoff wurde mit einer typischen Reformergasmischung untersucht. Das Modul hat eine Länge von 300 mm und einen Durchmesser von 70 mm. Es kann mit Drücken bis zu 10 bar und im Temperaturbereich von 320-430$°C$ eingesetzt werden. Die Hauptprobleme einer Anwendung der ökonomisch interessanten Kompositmembranen (7 μm Pd auf einer porösen Keramik) liegen bei Lecks in der Membran und ihrer Dichtung. Die Dichtung war mechanisch ungeeignet für potentielle Anwendungen, hingegen war der Wasserstoffdurchsatz grösser als in den Membranröhren und die Palladiummenge um den Faktor 25 verringert.

Contents

Chapter 1

Introduction

Die Strasse nämlich, die Hauptstrasse des Dorfes, führte nicht zum Schlossberg, sie führte nur nahe heran, dann aber, wie absichtlich, bog sie ab, und wenn sie sich auch vom Schloss nicht entfernte, so kam sie ihm doch auch nicht näher. Immer erwartete K., dass nun endlich die Strasse zum Schloss einlenken müsse und nur, weil er es erwartete, ging er weiter.
FRANZ KAFKA, DAS SCHLOSS

1.1 Hydrogen as an Energy Carrier

More than a hundred years ago, it was remarked that hydrogen is the optimal energy carrier [1]. This reference contains the statement that the heating value of a fuel increases with its hydrogen content, e.g. methane has a higher heating value per weight than carbon. It was concluded that pure hydrogen which has the highest heating value is the ideal fuel. Scientists with a long-term perspective have to search for applications of this "fuel of the future".

With the steadily growing use of fossil fuels, another disadvantage of carbon emission became apparent. The increasing content of carbon dioxide CO_2 in the atmosphere leads to climate change. This is an additional reason for the importance of hydrogen produced from renewable energy. However, even today hydrogen as an energy carrier is economically profitable only in niche markets. Some pessimistic views [2, 3] conclude that hydrogen energy applications will never be economically competitive with conventional energy production.

Nevertheless many researchers believe that hydrogen will save the world from the ecological consequences of fossil fuel combustion [4, 5, 6, 7].

1.2 Preliminary Work

The MTH-project (Methylcyclohexane Toluene Hydrogen) has a long history in renewable energy research in Switzerland. The initial study of M. Taube [8] dates back to the year 1983. It considers the use of methylcyclohexane (MCH) as a hydrogen/energy carrier. Even though the focus of this study was the mobile application of this technology, the seasonal storage of energy from summer to winter was also in the center of interest. After the initial study many research projects have been performed. The range goes from kinetic considerations [9, 10] to pilot vehicles [11, 12]. In a ten year cooperation between Paul Scherrer Institute, ETH Zurich and Swiss industry, experience has been obtained with hydrogen engines and the catalytic dehydrogenation of MCH.

Hydrogen as energy carrier can be used for transportation of energy over a distance or for storage of energy over time. Several forms of hydrogen energy carrier are of interest in research:

- Gaseous hydrogen
- Liquid hydrogen
- Ammonia
- Liquid organic hydrides e.g. cyclohexane [13] and methylcyclohexane
- Metal hydrides

Studies with hydrogen stored in these forms were made in the context of the Euro-Québec Hydro-Hydrogen Pilot Project (EQHHPP) [14, 15, 16] which investigated electricity conversion to hydrogen, its storage and its transportation from Canada to Europe. The system output in these studies is the hydrogen. Hydrogen energy storage can be classified according to the applications:

- Short term storage (daily - weekly)
- Long term storage (seasonal)

In Switzerland hydraulic pump storage is mainly used for daily storage of electricity . An interesting form of very short term storage is a H_2/O_2-burner [17] for peak load in steam turbines with a starting time lag of only one second. The storage of hydrogen in gaseous and liquid form has been studied for intercontinental systems [16], stand-alone systems with photovoltaics [18] and pressure containers for local networks [19]. The overall efficiency of such storage systems has been established at approximately 30% [20]. Disadvantages of liquid hydrogen systems are a high energy consumption of the refrigeration step and the boil off losses during transport and storage [21]. The storage of gaseous hydrogen needs additional compression where the chemical pathways ammonia and liquid organic hydrides are associated with losses in the chemical processes. The storage and transportation of hydrogen energy in form of metal hydrides requires expensive solids processing.

1.3 Problem Definition

The MTH-System requires three chemical components: Methylcyclohexane (MCH), Toluene and Hydrogen. The hydrogen produced in summer by electrolysis is combined with toluene C_7H_8 (TOL) in an exothermic hydrogenation reaction

$$C_7H_8 + 3H_2 \Rightarrow C_7H_{14} \qquad \triangle H_{250°C} = -214.1kJ/mol$$

and confined to storage as methylcyclohexane C_7H_{14}. In winter, the latter is dehydrogenated in an endothermic reaction using heat from the power plant, Figure 1.1.

$$C_7H_{14} \Rightarrow C_7H_8 + 3H_2 \qquad \triangle H_{450°C} = 216.3kJ/mol$$

The hydrogen produced is reconverted to electricity in the power plant.

For the specific system studied here, cheap excess electricity is stored over a time period of 3200 hours in the summer months (loading time) in the form of hydrogen in methylcyclohexane. During the winter months the chemically stored energy is reconverted to electricity for 4800 hours (unloading time). For cost estimation, the available power for storage is 320 MW which corresponds to the hydroelectric expansion project Grimsel-West proposed by the Bernische Kraftwerke (1000

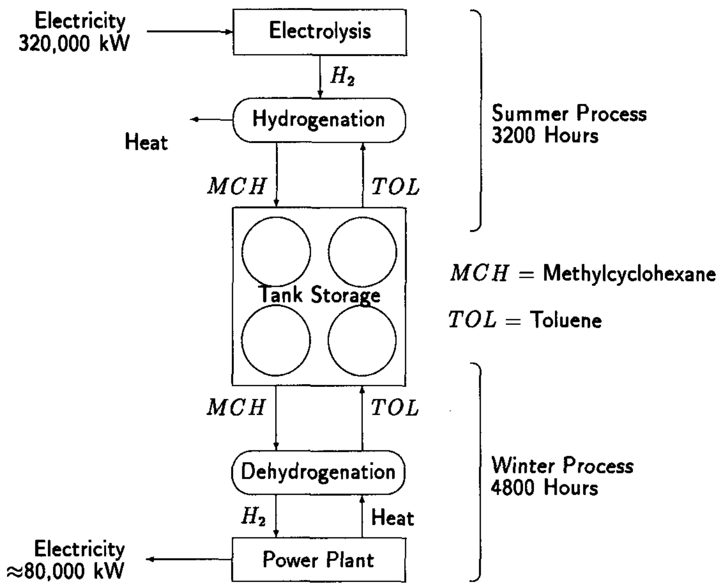


Figure 1.1: Flowsheet of the MTH-System for Stationary Seasonal Applications

GWh/year summer energy to storage ≈ 1.6% of the total electricity production of Switzerland).

The aim of this thesis is a systems and economic analysis of the seasonal storage of electricity with liquid organic hydrides. The boundaries of the system are well defined (electricity to electricity) for an unambiguous serious economic estimation of this storage method. The advantage of hydrogen chemically bound in liquid organic hydrides is that it balances the seasonal mismatch between supply and demand of electricity for those countries with significant hydropower facilities such as Canada, Norway and Switzerland. Hydraulic pump storage is meeting increasing resistance for ecological reasons, so that electricity stored in the form of hydrogen could be a future alternative as an environmentally acceptable secondary energy source.

1.4 Systems Engineering

Systems engineering was introduced mainly for military and space technology, but also for industrial problems, particularly in the oil, chemical and power generation industries. Systems engineering provides a framework to solve multidisciplinary problems with an overall approach. According to A.D. Hall's metasystems methodology [22] a project life consists of the following phases:

1. Program planning
2. Project planning and preliminary design
3. Systems development (detailed engineering)
4. Construction
5. Phase in
6. Operation
7. Retirement (Phase out)

1 and 2 are the phases that involve systems analysis. These planning phases are divided into logical steps:

- Problem definition
- Value system design (develop objectives and criteria)
- Systems synthesis (collect and invent alternatives)
- Systems analysis

This thesis considers the problem of the seasonal storage of electricity with hydrogen bound on liquid organic hydrides i.e. toluene - methylcyclohexane. The given system hydrogen - toluene - methylcyclohexane constrains the systems synthesis process. The choice of the first three plants (electrolysis, hydrogenation and dehydrogenation) is obvious, as given by the system, whereas the power plant needs some further consideration. The definition of the criterion strongly depends on the definition of the wider system (environment of the considered system). Technical systems e.g. a production plant often uses an economic criterion. Completely different criteria are used in social systems engineering. The economic environment in which the MTH-System has to compete is the market of constant winter electricity in Switzerland with and without a speculative CO_2-tax. Therefore the objective function is the cost of the output electricity.

1.4.1 Systems Analysis

Systems analysis is divided further into the following steps:

- Basic design
- Sensitivity analysis to deduce consequences of alternatives and identify the critical points of a project (chapter 3)
- Modelling of the system (chapter 5 and 7)
- Optimisation of each alternative (chapter 7)
- Decision making (chapter 7 and 9)

The approach of optimising the alternatives used for this analysis is similar to the hierarchical approaches in the chemical process synthesis, discussed in the following section 1.4.2.

1.4.2 The Hierarchical Approach of Chemical Process Synthesis

In order to reduce the large combinatorial number of process alternatives at the modelling step of a chemical plant it is important to have a hierarchical approach. It conforms to heuristic rules extracted from the sensitivity of chemical plants to its particular processes. The MTH-System is not a pure chemical plant; it includes also power generation plants. Therefore the conclusions of the sensitivity analyses in chapter 3 determine the modelling approach in chapter 5 and 7.

The onion model of systems analysis and synthesis shown in Figure 1.2 [23] is applied to all critical elements of the system e.g. electrolysis and hydrogenation; in the case of dehydrogenation and fuel cells, a combined heat and power approach was taken. Other approaches of systems synthesis have similar structures [24].

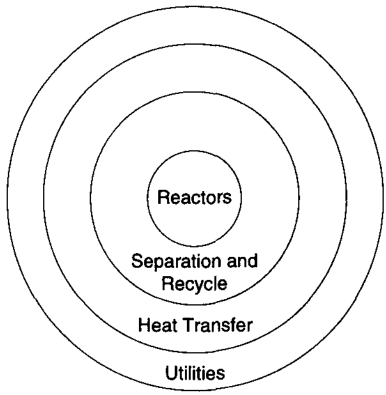


Figure 1.2: Onion Model of Systems Synthesis

1.5 Structure of the Models

The numerical implementation of the models described in chapter 5 was done in the C^{++} programming language. The most important advantage of C^{++} in simulating processes is its object based data abstraction. This technique results in shorter and more easily understandable mapping of numerical models for their implementation. Objects include functions as well as data. Each object belongs to a class, which is a user-defined type. The definition of classes shown in Figure 1.3 means numerical modelling of the plants. A derived class inherits the data and functions of the parent class and contains changed functions and added new data and functions. The models (classes) consist of several data e.g. temperatures, pressures and streams, the initialisation routines, the simulation of the plant including heat and mass balance as well as its output routines. Included in each model are some economic functions (methods) which calculate investment costs, operating costs and the land requirement by the plant.

1.6 Properties and Units

All the physical and thermodynamic properties used in this thesis and in the calculation models are taken from the data bank of the *American Institute of Chemical Engineers* [25], except the steam properties of water used in the steam turbine

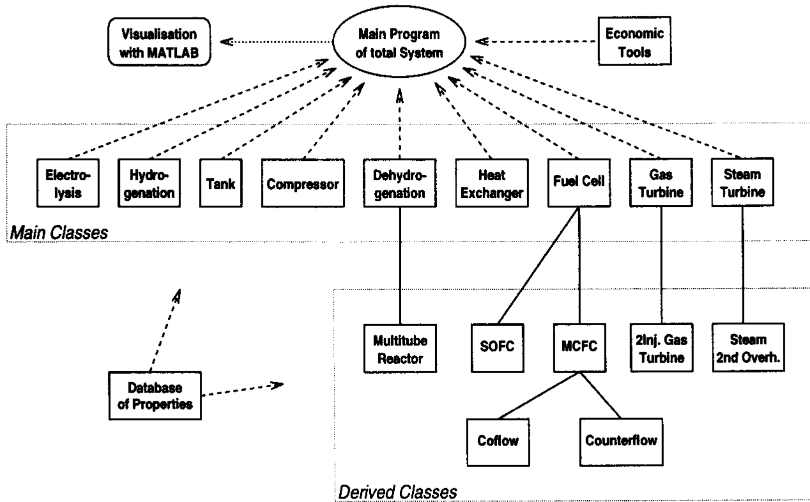


Figure 1.3: Class Hierarchy of the Models

simulation. The properties of steam are calculated with the FORTRAN-routines published by the *American Society of Mechanical Engineers* [26]. To set the calculations on a proper basis and avoid difficulties in conversion, only SI-units are used. Exceptions are the energy content of electricity expressed in kWh and costs in US-$ (1995).

Chapter 2

Alternative Fuels for Mobile and Stationary Application

2.1 Environmental Purposes

There are four major environmental problems, originating from the use of fossil fuels:

- carbon monoxide CO
- nitric oxides emissions NO_x
- unburnt hydrocarbons HC
- carbon dioxide CO_2

The combination of carbon monoxide CO, nitric oxides NO_x and unburnt hydrocarbons HC is responsible for severe air quality problems in urban areas. This problem refers in a locally different manner to the automotive use of fuels as well as to coal power plants. The last mentioned emission (carbon dioxide CO_2) is a 'greenhouse' gas. The widespread burning of fossil fuels in the last two hundred years has changed the content of CO_2 in the atmosphere significantly. This CO_2 content plays amongst other influences an important role in determining the temperature of the atmosphere. Therefore all gases which are regarded to cause a warming up of the atmosphere are called 'greenhouse' gases. The most important of them is carbon dioxide CO_2, but others such as methane CH_4 and nitrous oxide N_2O are

		$[MJ/kmol]$	$[MJ/kg]$	$[GJ/m^3]$	Remarks
Sustainable Fuels					
Hydrogen	H_2	241.82	119.95	4.32	at 400.00 bar
Liq. Hydrogen	H_2	241.82	119.95	8.47	
MTH-System		173.56	1.77	1.35	
Methanol	CH_3OH	676.49	21.11	16.62	
Ethanol	C_2H_5OH	1278.07	27.74	21.84	
Hydrocarbons (non-sustainable)					
Methane	CH_4	802.64	50.03	14.33	at 400.00 bar
Liq. Methane	CH_4	802.64	50.03	21.14	
Natural Gas	$C_{1-4}H_{4-10}$		46.95	14.57	at 400.00 bar
Liq. Natural Gas	$C_{1-4}H_{4-10}$		46.95	21.85	
Gasoline	$C_{4-9}H_{6-18}$		42.40	30.95	
Diesel	$C_{6-11}H_{6-22}$		41.80	35.95	

Table 2.1: Energy Content of Selected Fuels (Lower Heating Values)

claimed to contribute also to climate change. The global CO_2 production by the use of fossil fuels comes mainly from power production and heating. The automotive use of liquid fossil fuels also contributes remarkably to the CO_2-emissions. To reduce the pollution problems at all levels, alternative additional fuels are considered for cleaner and more efficient energy conversion technology.

2.2 Application of Alternative Fuels

The energy densities of alternative fuels are compared with gaseous and liquid fossil fuels in Table 2.1. Alcohol (methanol or ethanol) which could be produced in carbon neutral cycles [27] are competitive with fossil fuels on an energy content basis. Pure hydrogen fuels which could be produced from hydroelectricity, solar and nuclear primary energy sources in carbon-free systems are less on an energy content basis.

Additionally, the storage of hydrogen in liquid or gaseous form for mobile application implies new infrastructure in the distribution of the fuel. It is difficult to estimate the cost effect of such a distribution system. The same problem appears with the alternative of hydrogen storage in metal alloy. It is expected that customers do not accept these distribution systems (refuelling stations), because the refuelling of cars with liquid hydrogen or gaseous hydrogen at a pressure of 400 *bar* is not as easy and safe as gasoline refuelling. An essentially better solution is the use of methanol as liquid fuel, which could be distributed with a conventional net of filling stations at extra costs. From a customer viewpoint, the refuelling of a car with methanol or ethanol makes no difference compared to the refuelling with gasoline. Therefore it is easier to store hydrogen in methanol on board than using hydrogen in gaseous or liquid form.

2.3 Range-Extender for Electric Vehicles

The analysis of the storage of hydrogen or hydrogen based renewable fuels on vehicles leads to two decisive questions: How much energy can be stored per weight and per volume? The tank of the vehicle should be as small and as light as possible. The range of a vehicle depends linearly on the energy content of the fuel. As it is shown in Table 2.1 hydrogen stored with the MTH-System does not represent an optimal solution for mobile applications. Gaseous and liquid hydrogen, methanol and ethanol are better suited as renewable fuels for transportation from a storage point of view.

In contrast to the conventional automotive power supply (Otto- or Diesel-engine) in dynamic operation, a range-extender provides a constant power supply for an electric vehicle. It reloads the battery with electricity. The battery itself covers the peak demand of power. A constant power supply facilitates the operation and control because the delay times in chemical reactor operation are too long for rapid dynamic response.

A range-extender essentially consists of two components: the supply of hydrogen and its conversion to electricity. The hydrogen could be produced on board with steam reforming of methanol. The best way to produce electricity from hydrogen is through fuel cells (no noise, zero emission, high efficiency). Alternatives are internal combustion engines and small gas turbines. Table 2.2 shows the technical parameters of applicable fuel cells.

As pointed out above, the crucial parameters of a range-extender for cars are the weight and the start-up time of the system. The weight of the fuel cell is inversely proportional to its power density and the start-up time is linearly proportional to the

Fuel Cell Type	Fuel	Oxidant	Efficiency	Temp. [°C]	Power [mW/cm^2]
AFC Alkaline Fuel Cell	H_2	O_2	0.6	70-100	300-500
PEFC Polymer Electrolyte Fuel Cell	H_2,CH_4	O_2,Air	0.5-0.6	70-110	400
PAFC Phosphoric Acid Fuel Cell	H_2,CH_4	O_2,Air	0.4-0.45	160-210	200-300
MCFC Molten Carbonate Fuel Cell	CH_4	O_2,Air	0.5-0.55	650	80-250
SOFC Solid Oxide Fuel Cell	H_2,CH_4	O_2,Air	0.55-0.6	900-1000	80-240

Table 2.2: Properties of Fuel Cells

product of weight and operating temperature. With the constraint that a range-extender should work with air, the polymer electrolyte fuel cell seems to be the optimal choice for mobile application.

2.3.1 System Description

The flowsheet of a range-extender based on methanol steam reforming combined with a polymer electrolyte fuel cell is shown in Figure 2.1. A mixture of methanol and water is fed with a pressure of 11 *bar* to the steam reformer which produces hydrogen, carbon dioxide and carbon monoxide CO [28, 29]. Due to the endothermic reaction, one part (38%) of the produced hydrogen must be burnt catalytically to supply the heat of reaction. This catalytic burner is integrated into the steam reformer to enable an efficient heat transfer. The other part of hydrogen (62%) diffuses through the *Pd-Ag* membrane with a CO content less than 10 *ppm*, installed as a hydrogen pressure vessel leading to the anode of the fuel cell. The anodes of polymer electrolyte fuel cells are very sensitive to the CO content of the feed gas. They allow a maximum concentration of CO between 10 and 100 *ppm* [30, 31]. The hydrogen and the air fed to the fuel cell must both be saturated with water. The operating pressure of the fuel cell is 2.5 *bar*. Therefore a compressor (turbocharger) is necessary, which is driven by an exhaust turbine and an electric motor with a power of 2.5 kW.

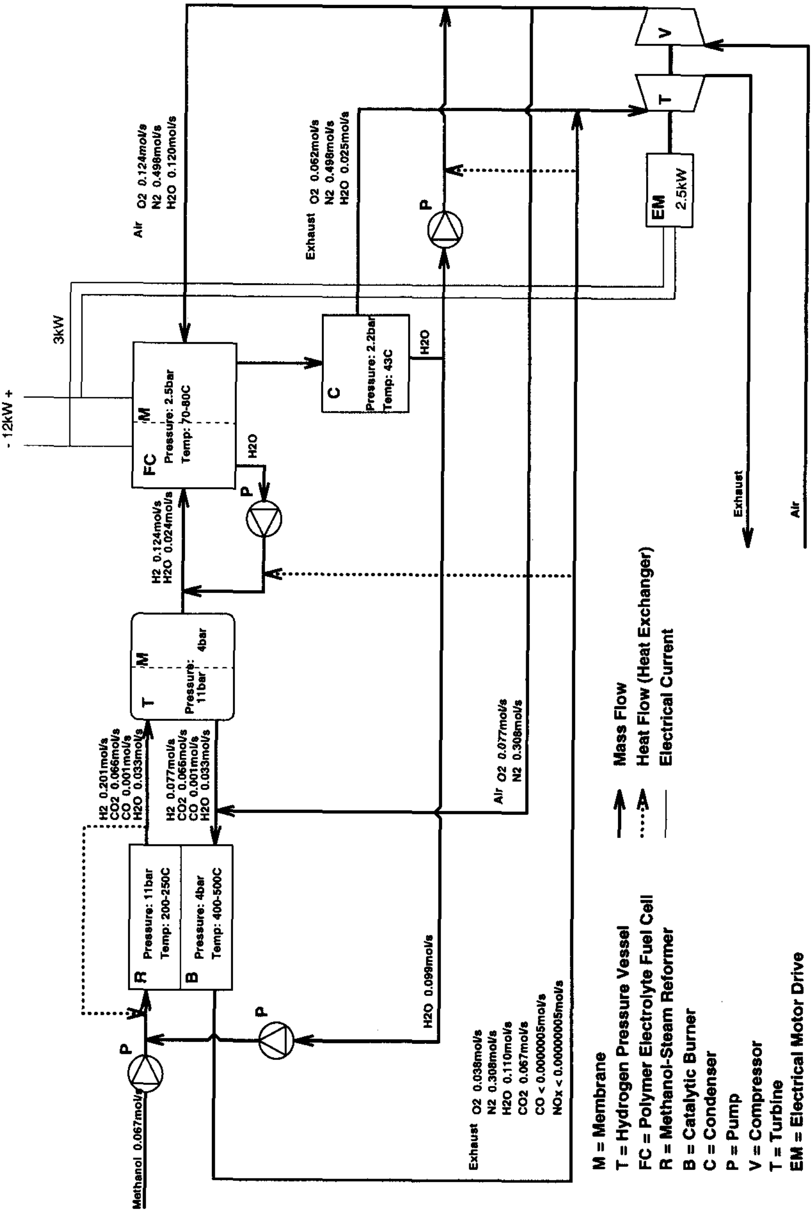


Figure 2.1: Flowsheet of a Fuel Cell Range-Extender for Methanol

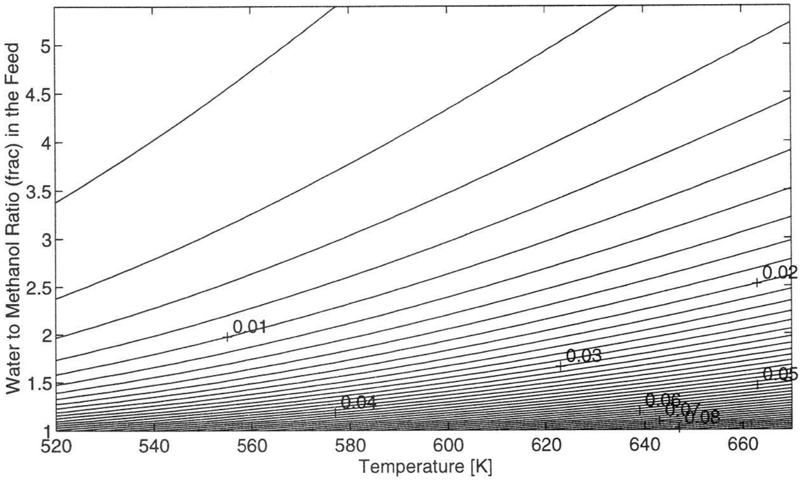


Figure 2.2: Effect of Water to Methanol Ratio on Carbon Monoxide Content at Equilibrium

The assumed efficiencies of these devices are 0.9 for the motor and 0.62 (isentropic efficiency) for the turbine and compressor. As a consequence of the cell reaction, water vapor forms at the cathode of the fuel cell. The condensed water is fed back to the steam reformer.

Steam Reforming of Methanol

The reaction mechanism of methanol steam reforming consists of the following three reactions: the steam reforming

$$CH_3OH + H_2O \rightarrow CO_2 + 3H_2 \tag{2.1}$$

the parallel reaction which produces the byproduct carbon monoxide

$$CH_3OH \rightarrow CO + 2H_2 \tag{2.2}$$

and the water gas shift reaction:

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{2.3}$$

Equilibrium calculation shows that a higher water fraction in the input stream suppresses the formation of carbon monoxide. The system of nonlinear equations (equilibrium equation of the reaction 2.1-2.3, initial condition $frac$ and normalisation) is solved with the Newton-Raphson method. In Figure 2.2 the molar fraction of carbon monoxide in the reformate gas at equilibrium is presented as a function of temperature and feed mixture (pressure 11 bar). $frac$ means the molar fraction of water to methanol in the feed:

$$frac = \frac{x_{H_2O}^{in}}{x_{CH_3OH}^{in}} \tag{2.4}$$

A catalytic burner provides the steam reformer with heat. The operating temperature of the catalytic burner is 400-500°C, to avoid NO_x emission. The hydrogen stored in the pressure vessel can be used to supply the reformer with initial heat for start-up.

Hydrogen Pressure Vessel and Membrane Separation

To prevent the fuel cell from coming into contact with the reformer byproduct carbon monoxide CO it is necessary to purify the hydrogen by means of membrane separation (*Pd-Ag* membrane). The byproduct carbon monoxide CO is converted totally to carbon dioxide CO_2 in the catalytic burner. The remaining methanol is also burnt catalytically. The high cost of the membrane results essentially from the high material cost of palladium. A fraction of this cost could be recovered by recycling. The membrane has an area of approximately 1.7 m^2 and a thickness of 50 μm to yield a hydrogen flow of 0.124 mol/s equivalent to 30 kW hydrogen energy based on lower heating value.

Polymer Electrolyte Fuel Cell

The key components of a polymer electrolyte fuel cell (PEFC) are the anode, to which the hydrogen is supplied, the electrolyte membrane, through which the H^+-ions can pass, and the cathode at the oxidant side. The chemical reaction of hydrogen oxidation is split into two processes: $H_2 \rightarrow 2H^+$ at the anode and $2H^+ + 1/2O_2 \rightarrow H_2O$ at the cathode. The electrical current is carried by the external flow of electrons compensated by the flow of H^+-ions through the electrolyte membrane. The humidification of the membrane is very important. Otherwise the electrolyte would dry out and increase the electrical resistance of the membrane.

2.3.2 Results

Overall Efficiency

The efficiency of the steam reformer is assumed to be 0.7, the one of the fuel cell 0.5. Due to the electricity requirement of auxiliaries in the overall system e.g. air compressor, the efficiency is diminished by a factor of 0.8. Therefore the overall efficiency becomes 0.28 ($=0.7 \cdot 0.5 \cdot 0.8$). No losses are assumed to occur during the refuelling of the car and when the car is not in use (in contrast to the systems fuelled by liquid hydrogen).

Control

The start-up of the range-extender takes between 7 and 10 minutes. During this start-up period the hydrogen from the pressure vessel heats up the catalytic burner integrated into the reformer and the fuel cell. The shutdown of the range-extender also takes some minutes. After stopping the car, the range-extender still recharges the battery and fills up the pressure vessel with hydrogen.

Emissions

An electrical car with a range-extender power supply has to compete with conventional cars in a market with environmental legislation. A paragon for future legislation is the proposal of the State of California, which intends to introduce different types of cars with emission constraints [32]. The estimated emissions in Table 2.3 are more than zero (zero emission vehicle) but much lower than the definition of the ultra low emission vehicle (ULEV). Carbon dioxide is not restricted in the California State proposal for future environmental legislation [32].

The grey emission of carbon dioxide due to conventional petrochemical methanol production from natural gas increases the carbon dioxide emission by a factor 1.75. No carbon dioxide emissions are expected with the use of methanol from renewable sources (biomethanol). Noise is expected only from pumps, the compressor and the turbine. The steam reformer and the fuel cell operate with minimal noise levels.

Component		Emission [g/km]	ULEV [g/km]
Nitric Oxides	NO_x	≤ 0.0016	0.12
Carbon Monoxide	CO	≤ 0.010	1.06
Hydrocarbons	C_xH_y	-	0.025
Carbon Dioxide	CO_2	201	

Table 2.3: Expected Specific Emission of a Vehicle with Range-Extender

Volume and Weight

As pointed out in section 2.3, volume and weight of fuel and devices are decisive for mobile application. Due to the lower energy content of methanol, the tank is twice as large and heavy as a conventional gasoline tank. Table 2.4 shows that the volume of the range-extender investigated is 100 dm^3 and its weight lower than 100 kg.

Device	Weight [kg]	Volume [dm^3]	Remarks
Steam Reformer	20	20	2.5 kg CuO/ZnO catalyst [28]
Fuel Cell	20	20	
Compressor, Pumps and Heat Exchangers	20	20	
Methanol Tank		60	range 500 km
Pressure Vessel, Membrane	10-15	40	H_2 separation and storage

Table 2.4: Estimated Weight and Volume of Range-Extender investigated

Costs

The cost estimation of the range-extender components presented in Table 2.5 is based on mass-production for mature technology. The main part of the membrane costs derives from the material (75% palladium, 25% silver). Assuming a recycle of this expensive material the range-extender has a relatively high recovery value.

During the years 1995/96, the average price of methanol on the market was 186 $\$/t$ [34], which is equivalent to 0.151 $\$/l$, whereas the production costs of methanol were only about 0.079 $\$/l$ (0.30 $\$/gallon$) and the distribution costs 0.066 $\$/l$ (0.25

Device	specific Costs [$/kW]	total Costs [$]	Remarks
Steam Reformer	80	1200	with catalytic burner
Fuel Cell	100	1500	[33]
Compressor/Turbine		130	
Methanol Tank		-	is a part of the car body
Pressure Vessel with Membrane		5000	
Total		7830	

Table 2.5: Estimated Cost of a Range-Extender investigated

$\$/gallon$) [32]. From a methanol consumption of 12.0 $l/100km$ (0.097 kg/km) we can obtain fuel costs without taxes of 0.018 $\$/km$. With the calculated overall efficiency of 0.28 the range extender system supplies the electric part of the vehicle with 14.4 kWh/km. This value compares to the 12 kWh/km for a steam reformer-fuel cell system of an other study [30]. However, its methanol consumption of 5.7 $l/100km$ is based on a very optimistic overall efficiency of 0.48.

It is assumed that the additional maintenance costs are slightly higher than for normal car.

A simplification of the range-extender system would result in the development of a direct methanol fuel cell (DMFC). Then steam reformer and catalytic burner would not be necessary and savings in cost, volume and weight should result.

2.4 Stationary Application

Stationary application of energy storage in the form of hydrogen focuses on subsequent use in heating and power production to bridge daily, weekly or seasonal gaps in the electricity supply. Daily or weekly storage of electricity in Switzerland is mainly solved with pump storage.

For such short storage periods the petrochemical processes used in the MTH-System are too expensive. Gaseous and liquid hydrogen are better suited for short term storage. The advantage of the MTH-System lies in the easy storage of the liquid organic hydrogen carrier in tanks. Therefore, the MTH-System is better suited for hydrogen storage on a seasonal basis [35].

In every case a high efficiency in the reelectrification of the hydrogen energy is very important (sensitivity analyses in chapter 3). Therefore fuel cells also seem to be a attractive solution for hydrogen energy storage in stationary applications. Also very important in the context of fuel cells are hydrogen purification systems, such as *Pd-Ag* membranes. The experimental results concerning performance and operability are discussed in chapter 8.

2.5 Conclusion

The overall efficiency of a range-extender in an electrical car estimated to 28% is comparable to those of Otto-engines. The main loss occurs in the fuel cell itself (efficiency 50%). Still, the cost of such a system is too high compared to combustion engines. However, significant potential exists for cost savings using thinner *Pd-Ag* membranes (chapter 8). Another disadvantage occurs when the range-extender is operated at temperatures below $0°C$ due to the risk of freezing dissolved water in the system.

An electric car with a range-extender power supply can compete with conventional car based on gasoline combustion only when some additional environmental legislation (California [32]) is introduced.

Leer - Vide - Empty

Chapter 3

Sensitivity Analyses of the MTH-System

3.1 Introduction

Sensitivity analysis is a technique for optimising a system with respect to the desired output characterised by a well-defined objective function. Based on the results, decisions in the selection and design of chemical plants and processes can be made. In the present study of the MTH-System for Swiss seasonal conditions, the objective function is the production cost of winter electricity. Such sensitivity analyses are undertaken for all important input parameters of the MTH-System, as shown in Figure 1.1. The sensitivity of the kWh-costs to several input parameters is considered in section 3.3.

The following equation describes the influence of the input parameters I on the kWh-costs $\mathcal{K}_{kWh}$:

$$d\mathcal{K}_{kWh} = \nabla\mathcal{K}_{kWh} \cdot \mathbf{dI} = \sum_i \frac{\partial\mathcal{K}_{kWh}}{\partial I_i}\, dI_i \tag{3.1}$$

The particular contributions to the sum above provide insight on the influence of the input parameters to the objective function. In the next section 3.2, the cost of winter electricity, produced by the MTH-System, will be roughly estimated to define a reference point.

3.2 The Reference Point

In order to calculate the sensitivity of the objective function to the input parameters it is necessary to calculate the reference point with the expected values of the input parameters. This calculation with assumed values is a rough estimation of the objective function. To estimate the future potential of the MTH-system, costs and efficiencies of developed technologies are assumed.

3.2.1 Estimation of Efficiency

The efficiencies assumed for individual plants are decisive for the economics of the total system. The efficiency $\eta_{el} = 0.75$ of the electrolysis is calculated with respect to the lower heating value $\triangle H_{H_2O} = 241.8\ kJ/mol$ of hydrogen, i.e. an efficiency of 0.75 implies an energy consumption of 4 kWh per cubic metre H_2 at normal conditions (273.15 K, 1.013 bar). The exothermic hydrogenation reaction converts hydrogen stoichiometrically into methylcyclohexane. Energy losses are only caused by the electricity consumption and heat losses of the plant. Therefore a stoichiometric efficiency $\eta_{hyd} = 0.99$ is assumed for the hydrogenation plant. The efficiency of the dehydrogenation reaction depends significantly on the available heat from the reelectrification step (fuel cells or turbines). The high efficiency $\eta_{dhy} = 0.85$ of the dehydrogenation can only be attained by heat recovery from the power plant. The power plant is assumed to have an efficiency of $\eta_{pp} = 0.60$. Therefore the total electric power efficiency of the system becomes $\eta_{tot} = \prod \eta_i = 0.38$.

3.2.2 Specific Investment Costs

Electrolysis	400.00 $\$/kW_{in}$	[36]
Hydrogenation	141.00 $\$/kW$	[37]
Dehydrogenation	282.00 $\$/kW$	
Power Plant (SOFC)	1500.00 $\$/kW_{out}$	[38]
Tank Storage	250.00 $\$/m^3$	[39]
Toluene	0.26 $\$/kg$	[34]

Table 3.1: Specific Investment Costs for a 80 MW MTH-System

Table 3.1 shows the specific investment costs per kilowatt for the individual plants. The costs for mature technology are assumed. The values for electrolysis (400 $\$/kW$ [36]) and for the solid oxide fuel cells SOFC (1500 $\$/kW$ [38]) as a power plant are low compared to the current costs, since commercial technology is not yet available at the low costs assumed in Table 3.1 . The assumed values are more pessimistic than those in the U.S. DOE Hydrogen Program Plan [40]: 250 $\$/kW$ for electrolysis and 300 $\$/kW$ for the fuel cells.

3.2.3 Other Input Parameters

Based on information from electricity producers, the tariff for excess summer electricity in Switzerland amounts to 0.029 $\$/kWh$. For 3200 hours during the summer months (loading time), this cheap electricity is stored in the form of hydrogen in methylcyclohexane. During the winter months for 4800 hours (unloading time), the chemically stored energy is reconverted to electricity. For cost estimation, the available power for storage is 320,000 kW which corresponds to the hydroelectric expansion project Grimsel-West proposed by the Bernische Kraftwerke (1000 $GWh/year$ summer energy to storage).

To calculate annual costs a capital rate of 10% is assumed, 4% interest and 6% depreciation for a chemical plant life of 17 years [41]. A rate of 5% on capital costs is estimated as annual costs for maintenance and operating. Depreciation and operating cost rates for the toluene inventory and storage are both 2%, significantly less than for the chemical plants (electrolysis, hydrogenation, dehydrogenation and fuel cells).

	Investment Costs	Annual Costs	Specific Costs
Input Electricity		29.7 $M\$/year$	0.0766 $\$/kWh$
Electrolysis	128.0 $M\$$	19.2 $M\$/year$	0.0495 $\$/kWh$
Hydrogenation	33.5 $M\$$	5.0 $M\$/year$	0.0130 $\$/kWh$
Dehydrogenation	44.7 $M\$$	6.7 $M\$/year$	0.0173 $\$/kWh$
Power Plant	121.2 $M\$$	18.2 $M\$/year$	0.0469 $\$/kWh$
Tank Storage	120.5 $M\$$	9.6 $M\$/year$	0.0249 $\$/kWh$
Toluene	90.4 $M\$$	7.2 $M\$/year$	0.0187 $\$/kWh$
Total	538.3 $M\$$	95.7 $M\$/year$	0.247 $\$/kWh$

Table 3.2: Specific Cost Contributions ($M = 10^6$) per kWh Power Output

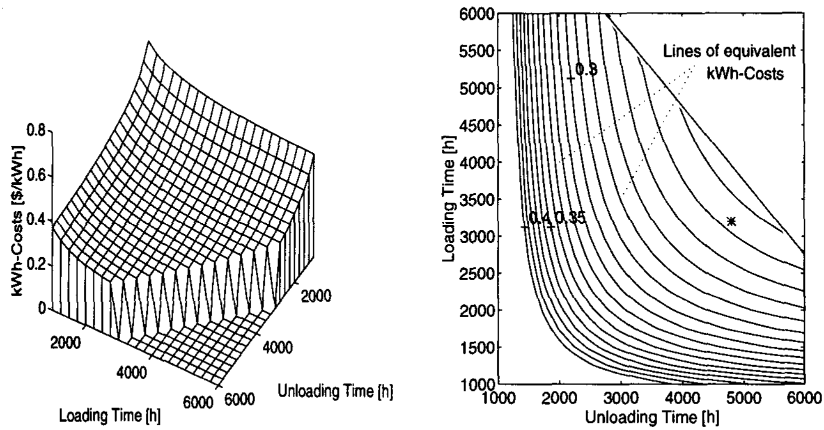


Figure 3.1: Electricity Output Costs per kWh as Function of Loading and Unloading Time

3.2.4 Results

The calculated investment costs and annual costs of the individual plants are shown in Table 3.2. One of the most important cost parameters is the electricity input. Its costs amount to one-third of the total annual costs. The electrolysis and the power plant have a similar effect. Because the power plant contributes only about 20% to the annual costs, an error in the assumed investment costs for fully developed fuel cells is not significant. The smallest cost derives from the hydrogenation plant. Dehydrogenation costs are coupled with toluene makeup, since excessive byproduct formation in dehydrogenation [35, 42] results in an increase of toluene makeup.

The system delivers 81,000 kW power output. In consequence the production costs of the stored electricity amounts to 0.247 \$ per kWh output electricity.

3.3 Sensitivity Calculation

The exact values in the gradient vector $\nabla \mathcal{K}_{kWh}$ defined in equation 3.1 are:

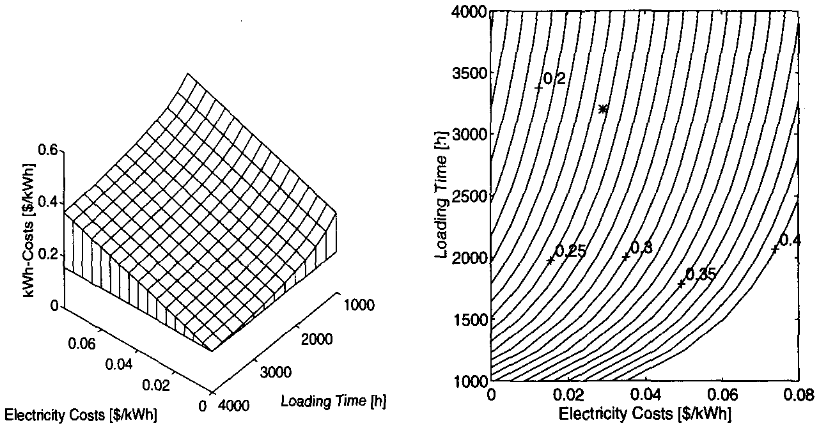


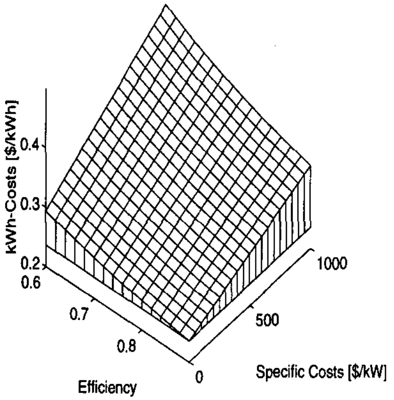
Figure 3.2: Electricity Output Costs per kWh as Function of Loading Time and Costs of Electricity

input electricity	2.64 $\frac{\$}{\$}$
loading time	-0.0195 $\frac{\$}{1000 hours}$
unloading time	-0.0134 $\frac{\$}{1000 hours}$
electrolysis efficiency	-0.168 \$
electrolysis investment cost	0.0124 $\frac{\$}{100\$/kW}$
hydrogenation efficiency	-0.127 \$
hydrogenation investment cost	0.00919 $\frac{\$}{100\$/kW}$
storage investment cost	0.00994 $\frac{\$}{100\$/kW}$
toluene investment cost	0.0718 $\frac{\$}{\$}$
dehydrogenation efficiency	-0.235 \$
dehydrogenation investment cost	0.00613 $\frac{\$}{100\$/kW}$
power plant efficiency	-0.333 \$
power plant investment cost	0.00312 $\frac{\$}{100\$/kW}$

The interpretation of these values is given in the following sections 3.3.1-3.3.6.

3.3.1 Sensitivity to Loading Time and Unloading Time

Short time loading or unloading is uneconomic. Figure 3.1 shows the sensitivity to these two parameters. The 3200 *hours* loading time and 4800 *hours* unloading time (typical numbers for a seasonal storage system, marked by $*$ in Figure 3.1)



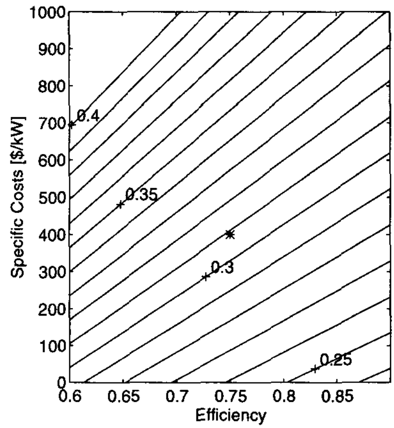


Figure 3.3: Electricity Output Costs per kWh as Function of Electrolysis Parameters

are near the minimum of kWh-costs (0.235 $\$/kWh$), meaning that seasonal storage is optimal. The MTH-System is not suited for storage of electricity on a daily or weekly basis.

3.3.2 Sensitivity to Loading Time and Electricity Costs

It is important to know for the economic calculations how many hours of cheap electricity are available during summer, and the associated cost. Following P. Weyermann from BKW [43] a kWh of electricity in summer costs between 0.021 and 0.042 \$ (0.025-0.05 SFr). Thus the minimum cost of seasonally stored electricity is 0.247 $\$/kWh$ as shown in Figure 3.2 for a loading time of 3200 *hours*.

3.3.3 Sensitivity to Efficiency and Cost of Electrolysis

The efficiency of electrolysis (based on the lower heating value $\triangle H_{H_2O} = 241.8$ kJ/mol) is not so important compared with the specific costs. A change of 0.06 in the efficiency causes a change of 0.01 $\$/kWh$ in the output electricity costs. Therefore the objective function depends weakly on the efficiency of the electrolysis. On the other hand an increase in the specific costs of 200 $\$/kW$ over the 400 $\$/kW$ assumed results in additional 0.025 $\$/kWh$ in output electricity costs.

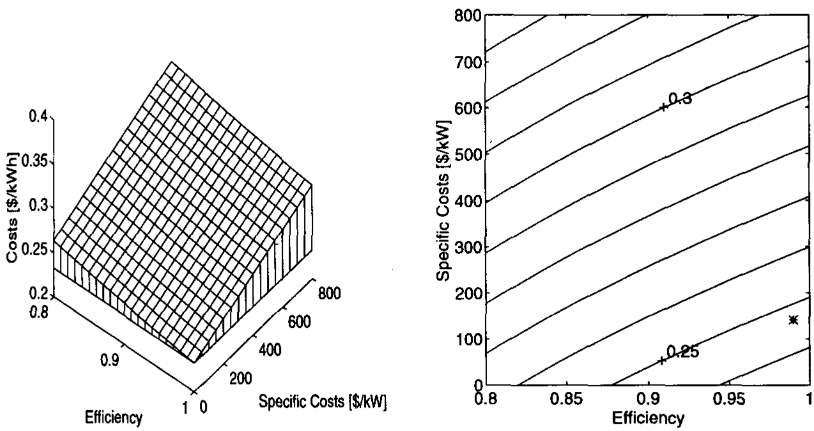


Figure 3.4: Electricity Output Costs per kWh as Function of Hydrogenation Parameters

3.3.4 Sensitivity to Efficiency and Cost of Hydrogenation

In this case efficiency is measured by selectivity, or how much H_2 in the input stream is bound to toluene? The heat generated by the exothermic reaction $TOL + 3H_2 \rightarrow MCH$ is not included in the efficiency of the hydrogenation. This loss of enthalpy will be considered in the next step, the dehydrogenation plant. The efficiency (yield) is assumed to be 99%. There is no significant reduction of output electricity costs to be gained by optimising this plant. The output electricity costs are also not too sensitive to the specific costs.

3.3.5 Sensitivity to Efficiency and Cost of Dehydrogenation

The endothermic dehydrogenation reaction, $MCH \rightarrow TOL + 3H_2$, is the reverse of the hydrogenation. The heat demand for this reaction should be satisfied by system design which depends on the heat integration of the dehydrogenation plant with the power plant (fuel cells). When the power plant supply all the endothermic heat of reaction, the efficiency is 0.99. If hydrogen produced by dehydrogenation must be partially burnt for covering the heat of reaction, then the efficiency decreases to 0.7. The wide span of possible efficiencies makes an optimisation of this plant including the heat transfer from the fuel cells interesting. The costs of output electricity are

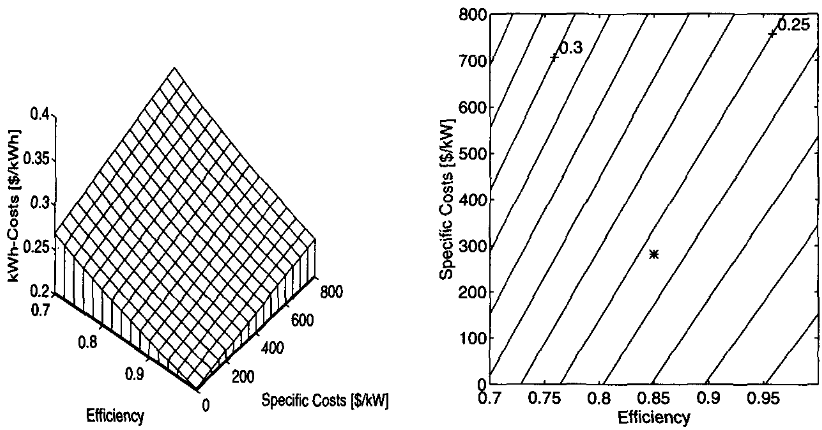


Figure 3.5: Electricity Output Costs per kWh as Function of Dehydrogenation Parameters

strongly sensitive to both parameters of the dehydrogenation plant, the specific costs and the efficiency.

3.3.6 Sensitivity to Efficiency and Cost of Power Plant

The specific costs of the power plant have only a weak influence on the costs of output electricity as shown by the steep contours in Figure 3.6. An error in the assumed investment costs for fully developed fuel cells is therefore not significant.

To decide what kind of power plant should be used it is necessary to evaluate the heat integration with the dehydrogenation plant operating at 400-500°C. The possible power plants are

- Gas and Steam Turbines
- Low Temperature Fuel Cells 70-200°C
  - Phosphoric Acid Fuel Cells (PAFC)
  - Polymer Electrolyte Fuel Cells (PEFC)
- Molten Carbonate Fuel Cells (MCFC) 650°C

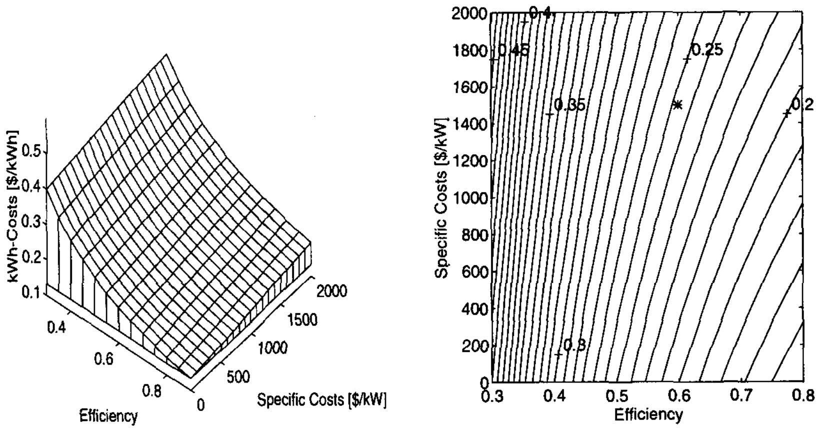


Figure 3.6: Electricity Output Costs per kWh as Function of Power Plant Parameters

- Solid Oxide Fuel Cells (SOFC) 1000°C.

In view of the temperature level at which heat is required for the dehydrogenation, the gas turbines, MCFC and SOFC are possible solutions. From the viewpoint of this sensitivity analysis it seems to be advantageous to choose fuel cells instead of gas turbines to generate the output electricity (fuel cells cost more but they have a better efficiency than gas turbines). Another advantage of high temperature fuel cells (SOFC or MCFC) is the possibility to use the waste heat in the dehydrogenation plant. On the other hand gas turbines as combined cycle plants can also reach an electrical efficiency of 60%. But the temperature level of the waste heat is too low for heat requirement of the dehydrogenation plant.

3.4 Conclusion

The sensitivity analyses of output electricity costs show that the most important parameters are

- efficiency of the power plant
- waste heat level of power plant

- costs of input electricity
- electrolyser costs
- dehydrogenation plant and heat integration.

Unimportant are hydrogenation efficiency and costs. The four main cost-sensitive parameters can be divided into two groups:

- economic parameters
  - costs and availability of input electricity
  - electrolyser costs
- technical parameters
  - efficiency of the power plant
  - dehydrogenation plant and heat integration.

Considering the particular contributions to the objective function output *kWh*-costs given in section 3.3 shows that the efficiency of the power plant has the strongest influence on output kWh-costs. Having a high efficiency at the last step of the MTH-system is the best way to reduce costs.

While the technical parameters are considered in more detail in the following chapters 4 and 7 the value of the economic parameters are estimated more accurately in chapters 6 and 5.

Chapter 4

Energy-Exergy Analysis

4.1 Introduction

It is often said that we have an 'energy problem', too much energy is lost in conversion and storage processes. In fact, energy cannot be lost from a closed system as a consequence of the first law of thermodynamics. This does not mean that we don't have a problem with energy. The 'energy problem' refers to the second law of thermodynamics and the increasing entropy in every closed system. It can be handled with the concept of exergy which expresses the maximum obtainable work. Exergy analysis, as a simplification of the second law of thermodynamics, is a method for evaluating the thermodynamic quality of energy streams. To distinguish between the concepts of energy and exergy, the definitions are compared in the following section 4.2.

4.2 Definitions

In the case of electricity, the exergy is equal to the energy. The exergy of a heat source is coupled with the energy content of the heat source by multiplication with the exergetic temperature (Carnot efficiency)

$$\tau = 1 - \frac{T_{env}}{T} = \frac{T - T_{env}}{T} \tag{4.1}$$

Chemically bound energy is a physical kind of potential energy. The total exergy of a combustion fuel at temperature T is equal to the difference of the Gibbs potential (also called free energy) $\triangle_{comb}G(T)$ of the reactants and combustion products and the correction terms, which takes the exergy of the oxygen feed stream and the combustion products into account.

$$exergy = \triangle_{comb}G(T) + \int_{T_{env}}^{T} \frac{T - T_{env}}{T} \left(C_{p_{Products}} - C_{p_{Oxygen}} \right) dT \tag{4.2}$$

where the difference between the Gibbs potentials is

$$\triangle_{comb}G(T) = \triangle_{comb}H(T) - T\triangle_{comb}S(T) \tag{4.3}$$

If the temperature of the environment and the fuel is equal to the standard ambient temperature $T_0 = 298K$ the exergy becomes simply

$$exergy = \triangle_{comb}G_0 = \triangle_{comb}H_0 - T_0\triangle_{comb}S_0 \tag{4.4}$$

The entropy of mixtures is not considered.

Similar to the definition of the energetic efficiency of an energy conversion plant

$$\frac{energy\ of\ useful\ outputs}{energy\ of\ inputs} \tag{4.5}$$

the exergetic efficiency is defined as follows:

$$\frac{exergy\ of\ useful\ outputs}{exergy\ of\ inputs} \tag{4.6}$$

For example, the inputs of the dehydrogenation are the methylcyclohexane MCH feed and the heat recovered from the power plant, whereas the toluene TOL and the hydrogen represents the useful outputs. The energy and exergy efficiencies of electricity storage systems are the same (input and output are both electricity).

4.3 Energy Analysis of the MTH-System

Figure 4.1 shows the energy flows of the different streams between the plants. It is seen that the contribution of hydrogen to the total combustion enthalpy of methylcyclohexane (MCH) is only 12%. Relatively large quantities of methylcyclohexane are necessary to store the hydrogen. Therefore only a small fraction of formed byproducts at the reaction steps hydrogenation (hyd) and dehydrogenation (dhy) can be tolerated for high energy efficiency. The hydrogenation of toluene is similar

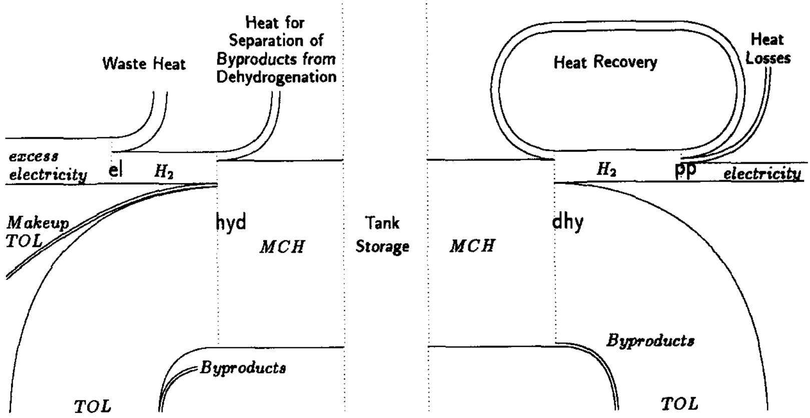


Figure 4.1: Energy Flow

el = Electrolysis, hyd = Hydrogenation, dhy = Dehydrogenation, pp = Power Plant

to the hydrogenation of benzene [44] which produces only an insignificant amount of byproducts. More critical is the dehydrogenation step with a higher fraction of byproducts. Progress has been made in laboratory reactors (e.g. 0.6% byproducts at 98% toluene yields [35]). As a consequence of this relation between the quantities of hydrogen and methylcyclohexane the MTH-System is more suited for stationary long term storage than short term storage of electricity.

In electrolysis large energy losses occur because vaporisation heat of the feed water must be supplied during the dissociation into hydrogen and oxygen gases. Calculation with the lower heating value accounts for this heat of vaporisation at the electrolysis step. Using the higher heating value would mean its loss at the reelectrification step (pp = power plant in Figure 4.1). To avoid ambiguity, the efficiencies in the following text are based on the lower heating value. Minor losses are due to the irreversible cell reaction. This heat cannot be used due to the low operating temperature of the electrolysis plant.

During the summer cycle, low level heat from the exothermic hydrogenation reaction (250°C) can only be used for the separation of byproducts, produced by dehydrogenation during the preceeding winter cycle.

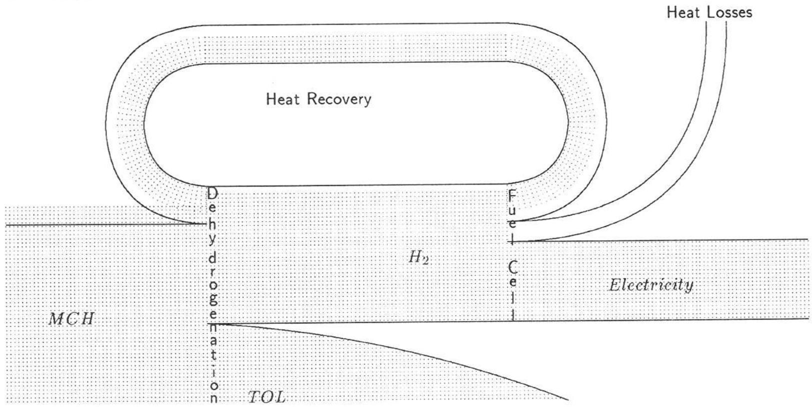


Figure 4.2: Energy and Exergy Flow

4.4 Exergy Analysis of the MTH-System

Figure 4.2 shows further clarification of the MTH-winter-process. It shows the energy and exergy flow (shaded in Figure 4.2) with heat integration between the dehydrogenation and the power plant (fuel cells). Surprisingly the exergy of the methylcyclohexane MCH is larger than its enthalpy. In fact the exergy loss in the hydrogenation step is smaller than the energy loss. This does not mean that the exergy of the products is higher than the exergy of the feed and does not violate the second law of thermodynamics.

The efficiencies of the several conversion steps of the MTH-storage method are compared in Table 4.1. Similar values for electrolysis (0.77 and 0.67) have been obtained by Rosen [45]. The efficiencies of the hydrogenation and dehydrogenation are based on the combustion enthalpy (Gibbs potential) of the MCH according to the definitions 4.5 and 4.6. The values for efficiency of the hydrogenation and dehydrogenation are close to 1 because the hydrocarbons flow relative to hydrogen in the respective plants are so large.

To calculate overall efficiency, the individual plant efficiencies cannot be multiplied together because of heat and mass recovery streams in the system. The overall efficiency of 0.39 derives simply from the quotient of electricity in and electricity out.

	Energy efficiency	Exergy efficiency
Electrolysis	0.720	0.681
Hydrogenation	0.954	0.978
Storage Tanks	≈ 1	≈ 1
Dehydrogenation	0.997	0.991
Fuel Cells	0.844	0.771
total	0.391	0.391

Table 4.1: Energetic and Exergetic Efficiencies

In practice the dehydrogenation reaction needs a heat source at a temperature level of 750 K. This corresponds to an exergetic temperature $\tau = 0.609$. The waste heat of the high temperature fuel cells (MCFC, SOFC) satisfies this requirement. The energy which does not leave the system as electrical current, occurs as heat at a high temperature level (MCFC: 650°C, SOFC: 900-1000°C) [46]. This heat can supply the necessary energy for the endothermic reaction in the dehydrogenation plant.

Gas turbines in a combined cycle power plant can achieve an efficiency of nearly 60%, but in this case no heat at sufficiently high temperature would be available for the dehydrogenation plant. The same limitation exists in the case of the low temperature fuel cells (PAFC, PEFC), therefore they can be excluded as well. The exergy of their waste heat is too small due to their low operating temperature. The efficiency of dehydrogenation would be less than 70% since a part of the hydrogen must be burnt to supply the heat of reaction. If the heat of exhaust gases of the gas turbines ($\approx$ 550°C) would be used for dehydrogenation, the efficiency would be much smaller than 60% (not a combined cycle power plant). Gas turbines only have an efficiency of 33-38% [47].

4.5 Conclusion

Most of the energy and exergy losses are due to the electrolysis and the power plant (high temperature fuel cells). Nevertheless the overall efficiency of the MTH-System is relatively high, 39% compared to 20-40% of storage system with gaseous hydrogen [19].

It is obvious that high temperature fuel cells (MCFC, SOFC) are a first choice for the reelectrification problem in the MTH-System. The influence of insufficient CO_2 on the efficiency of the molten carbonate fuel cell has to be considered in more detail (section 5.6.4). The other alternatives, low temperature fuel cells (PAFC, PEFC) and gas/steam turbines in a combined cycle power plant are not optimal choices from an exergy viewpoint. On the other hand gas/steam turbines are the only available technology today. Therefore the simulation of the MTH-System with this power plant alternative is also made and considered in sections 5.7, 5.8 and 7.2.4.

Chapter 5

Modelling of Chemical and Power Plants

5.1 Electrolytic Hydrogen Production

Electrolysis, discovered in 1800 by Carlisle and Nicholson [48], is the classic method of hydrogen production from non-fossil fuel sources. Comparable high temperature methods are also technically feasible, but in all cases, including solar-hydrogen, the most economic route is hydrogen from fossil fuels.

5.1.1 Production of Hydrogen by Other Techniques

Hydrogen from Fossil Fuels

Fossil fuels (natural gas, higher hydrocarbons and coal) are mainly used for hydrogen production in industry. Natural gas as feedstock represents the cheapest alternative (0.04 $\$/kWh$ [49]) to produce hydrogen, but the method is not carbon free. In contrast, the MTH-System produces hydrogen from renewable sources, e.g. hydropower used for electrolysis, and comes closer to the ideal carbon free system.

Hydrogen Production by Thermochemical Processes

Thermochemical processes achieve water-splitting into hydrogen and oxygen by heat input and chemicals which are recirculated completely in a closed system. An example of such a thermochemical reaction system proposed is [50]:

$$\begin{array}{lll} \text{first reaction step:} & Fe_3O_4 & \longrightarrow \quad 3FeO + {}^1/_2O_2 \\ \text{second reaction step:} & 3FeO + H_2O & \longrightarrow \quad Fe_3O_4 + H_2 \end{array}$$

A summary of the most significant thermochemical water decomposition processes is given in [51]. Most of these thermochemical processes have one or more reactions which require heat input at a high temperature (600-1500°C). The techniques of thermochemical water decomposition have been developed to produce hydrogen more from high temperature heat sources such as nuclear or solar reactors than from electricity. Generating the necessary heat from the input electricity available in the MTH-system makes the production of hydrogen too inefficient compared with the electrolyser, as in industrial use.

Thermal Water Splitting

Water vapour, heated to very high temperatures (2500-3000 K) dissociates directly into hydrogen and oxygen. It is theoretically possible to obtain hydrogen with this method by separation from the mixture of the remaining water vapor and the dissociated hydrogen and oxygen, but the method is not suitable for technical implementation and is uneconomical. It exhibits an achievable process efficiency of only between 0.1% and 6% [52].

Solar Hydrogen

With the increasing use of solar energy, the seasonal storage of electricity is becoming more important. The difference between supply and demand for electricity in summer and winter grows with increasing utilisation of solar energy. Two interesting methods for producing solar hydrogen comprise the indirect process of a photovoltaic plant combined with an electrolyser as operational in small scale and a proposed thermochemical process with solar heat input. Solar hydrogen is very expensive (present costs are 1 $\$/kWh$ [53]) and is not an alternative to hydrogen production by electrolysis (0.10-0.16 $\$/kWh$ [49]) using cheap hydropower in the summer season.

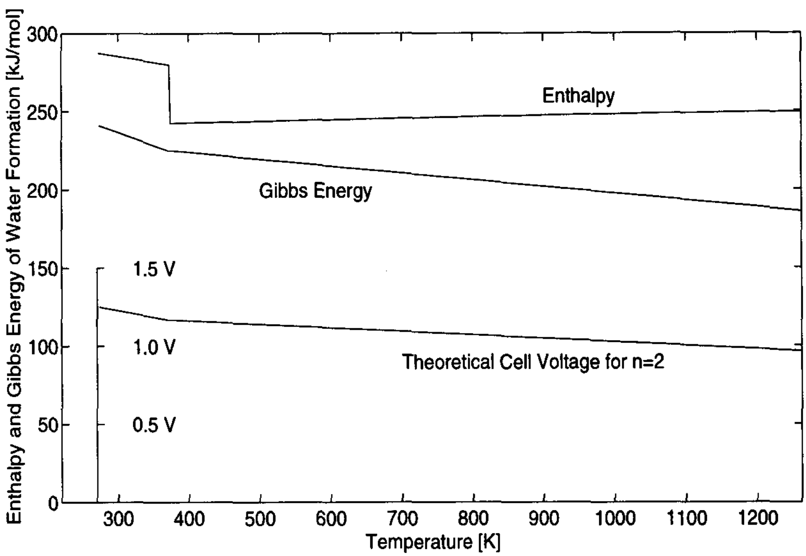


Figure 5.1: Temperature Dependence of Water Formation

5.1.2 Efficiency of Electrolysis

The efficiency of electrolysis depends directly on its cell voltage. The theoretical cell voltage U_{theo} could be calculated from the Gibbs energy difference $\triangle G$ of the water decomposition:

$$U_{theo} = \frac{-\triangle G}{nF} = -\frac{\triangle H - T\triangle S}{nF} \tag{5.1}$$

with n = number of elementary charges transferred per ion and F = Faraday constant. This theoretical cell voltage represents the minimum voltage at which the reaction can occur. In Figure 5.1 the relationships between the enthalpy $\triangle H$, Gibbs energy $\triangle G$ of reaction and theoretical cell voltage are shown as functions of temperature. In practice the theoretical cell voltage is increased by several kinds of overpotentials:

- Anodic overpotential U_{an}
- Cathodic overpotential U_{cat}
- Ohmic losses U_{IR}

Therefore the cell voltage of electrolysis is:

$$U = U_{theo} + U_{an} + U_{cat} + U_{IR} \tag{5.2}$$

To calculate the energy efficiency of electrolysis, two reference voltages are in use. One corresponds to the higher heating value (HHV) of $\triangle H = 285.8kJ/mol$ and amounts to $U_{HHV} = 1.481V$. The other efficiency is based on the lower heating value (LHV) of $\triangle H - \triangle_{vap}H = 241.8kJ/mol$ and amounts to $U_{LHV} = 1.253V$. All these enthalpy values hold at the standard ambient temperature of 298 K and atmospheric pressure. The higher heating value (HHV) includes the vaporisation heat of water (which must be included as electrolysis starts from liquid water). Therefore the efficiency of an electrolyser is higher with the higher heating value as reference. The two efficiency are defined as

$$\eta = \frac{U_{LHV}}{U} = \frac{1.253V}{U} \qquad \eta = \frac{U_{HHV}}{U} = \frac{1.481V}{U} \qquad for\ n = 2 \tag{5.3}$$

The efficiency calculated using the higher heating value is the correct one when considering electrolysis alone. However, when calculating overall efficiency of a cycle that includes eventual electricity generation from the hydrogen produced, one has to account for a loss due to the fact that the heat of the condensing water vapour from the combustion of hydrogen can be recovered only in special cases. This may be taken into account by using a lower efficiency for the electrolysis step, i.e. calculating η with respect to the lower heating value $\triangle H_{LHV}$. It is not possible to use this heat in the case of the MTH-System, since then the vaporisation heat of water, which is brought into the system on electrolysis, would be lost. Both these efficiency definitions appear in the literature. For clarity, the appropriate heating value must be specified together with the efficiency.

Another customary method to characterise the efficiency of an electrolyser was the relation between the input electricity and the produced hydrogen. This specific electricity consumption is expressed in $kWh/m_n^3H_2$ ($m_n^3H_2$ means a cubic meter hydrogen at the normal condition of 273.15 K and 1.013 bar). Like the cell voltage, the specific electricity consumption exactly defines the efficiency of the electrolyser. The vertical axis in Figure 5.2 is labeled with both the cell voltage and the specific electricity consumption.

Additionally important for the performance (specifically the cost) of an electrolyser is the current density of the cell. It is inversely proportional to the required

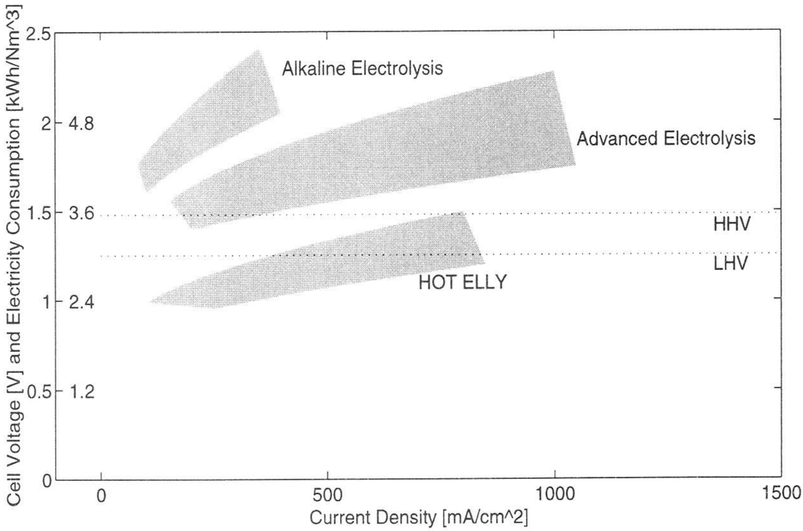


Figure 5.2: Specific Electricity Consumption of Electrolyser
HHV = 3.55 $kWh/m_n^3 H_2$ Higher Heating Value ($1.481V$) at 298 K
LHV = 3.00 $kWh/m_n^3 H_2$ Lower Heating Value ($1.253V$) at 298 K

cell area. In Figure 5.2 the efficiencies of several types of electrolyser are shown as a function of the current density. The two heating values split the plane into three regions:

Below LHV: The electrical efficiency (with respect to LHV) is higher than 100%. An external heat supply is necessary for vaporising the water (HHV $\rightarrow$ LHV) and heating the cell.

Between LHV and HHV: An external heat supply is necessary only for vaporising the water.

Above HHV: The efficiency is so low that the electrolyser produces more than enough heat and no additional heat is required for the water decomposition.

Alkaline Water Electrolysis

Water could be decomposed into hydrogen and oxygen according to the reaction $H_2O \rightarrow H_2 + \frac{1}{2}O_2$ by a direct electrical current between two electrodes. Because water is a poor conductor, it is necessary to add a conducting electrolyte to the water. Usually a potassium hydroxide solution of 30% is used as an electrolyte. Also used are aqueous sodium hydroxide and sodium chloride. The operating temperatures lie between $70 - 90°C$: as high as possible for an increased conductivity but below the boiling point of the solution. The pressure electrolysers operate at higher temperatures. The efficiency of classical alkaline water electrolysis is not very high (see Figure 5.2). For example an electricity consumption of 4.8 $kWh/m_n^3 H_2$ corresponds to an efficiency of 62.5% based on the lower heating value (LHV). Progress has also been made with advanced technology in alkaline water electrolysis, with efficiencies between 72 and 75% (LHV).

Polymer Electrolyte Membrane Electrolysis

Another type of advanced electrolysis utilises polymer electrolyte membrane. The electrolyte consists of a solid semipermeable H^+-exchanger membrane, which is also used in polymer electrolyte fuel cells (PEFC). The cost of these polymer electrolyte membranes is relatively high. A reversible use of the cell stacks as fuel cells (PEFC) in the MTH-winter process is not attractive because the operating temperatures $(70 - 90°C)$ of this cell type are too low for cogeneration.

High Operating Temperature Electrolysis (HOT ELLY)

This kind of electrolyser employs an O_2^- conducting solid oxide electrolyte, which consists of yttria (Y_2O_3) stabilised zirconia (ZrO_2). The operating temperature of such an electrolyser is very high: between 1200 and 1300 K. The Gibbs energy $\triangle G$ of reaction at this temperature is very small (see Figure 5.1). It is possible that the electricity input for the water vapor decomposition lies below the lower heating value (LHV) and $\triangle G(T = 1200K)$ is smaller than the lower heating value $\triangle H_{HHV} - \triangle_{vap} H$ according to the region below the LHV-line in Figure 5.2. Therefore the apparent electrical efficiency could be higher than 100%. With respect to the laws of thermodynamics, the missing energy must be supplied from an external heat source. One part of the heat must be available at the operating temperature of

1200-1300 K, the other part ($\triangle_{vap}H$) at the vaporisation temperature of the water, which depends on the operating pressure. The MTH-System yields waste heat only from the hydrogenation at low temperature. Therefore the HOT ELLY can be supported at maximum with the vaporisation heat of the water feed and requires exceptionally high efficiency in the heat exchanger network and insulation. In this case an efficiency of 95% may be technically feasible.

The most important advantage of this electrolyser type is the possibility of application as a fuel cell in the winter process of the MTH-project. The solid oxide fuel cell (SOFC) operates with the same electrochemical reaction and the same electrolyte as does the high operating temperature electrolysis (HOT ELLY). In principle, it is possible to use the electrochemical cell in both periods of the seasonal process, in summer for the electrolysis and in winter for reelectrification of the hydrogen energy. This fact enables a saving in total investment costs of the MTH-System. Experimental data about the reversibility of these solid oxide electrolyte cells and cell stacks were obtained recently [54].

5.1.3 Economics of Advanced Electrolysis

Recent advances in materials technology have allowed the operation at 30*bar* of advanced electrolysers with efficiencies of 75%. This pressure is useful for the subsequent catalytic hydrogenation step.

Present Cost

The energy unit used in Table 5.1 signifies the input electricity in direct current (dc) after the power conditioner, except the data marked with * which are based on an input electricity in alternating current (ac). The power conditioner itself needs electricity as well as the other chemical plants in the summer process. A loss of 3% of the alternating current input electricity is assumed (320 $MW_{ac}\cdot$ 0.97 = 310 MW_{dc}). The degression exponent for the cost calculation of a scaled up electrolyser is approximately 0.9, which means that the cost of an electrolyser is nearly linear to its capacity. In the last row, the investment costs are normalised to 1995 US$ with the currency data from Figure 6.1 and the Chemical Engineering plant cost index (Table 6.1). They are also scaled up to the capacity of the electrolyser used in the MTH-System.

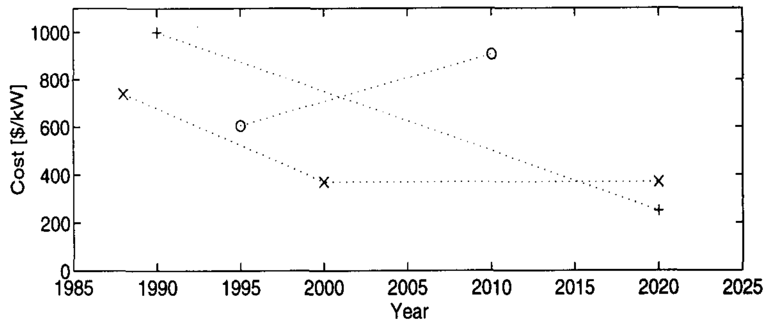
Company or Author (Technology)	Investment Cost (year) [1/kW]	Electricity Consumption [$kWh/m_n^3H_2$]	Plant Capacity [MW]	Ref.	Investment Cost MTH [$\$/kW_{dc}$]
ABB	900SFr (1989)	5.0*	1.5*	[55]	363 †
ABB	615$ (1983)	5.51*	2*	[56]	468 †
Teledyne (ALK)	117$ (1978)	4.41 (1.84V)	51.1	[57]	171 †
Teledyne	1214$ (1983)	5.65*	0.25*	[56]	747 †
Lurgi (ALK)	195$ (1978)	4.41 (1.84V)	73.0	[57]	294 † ‡
Bamag (ALK)	160$ (1978)	4.60 (1.92V)	16.7	[57]	208 †
Norsk Hydro (ALK)	182$ (1978)	4.48 (1.87V)	197	[57]	304 † ‡
Norsk Hydro	458$ (1984)	4.40*	2*	[56]	343 †
General Electric (SPE)	330$ (1980)	4.55 (1.9V)	0.2	[58]	231 †
Electrolyser (ALK)	317Can$ (1980)	4.89 (2.04V)	50-100	[59]	344 †
Electrolyser (ALK)	298Can$ (1980)	4.55 (1.9V)	50-100	[59]	324 † ‡
Electrolyser (ALK)	338Can$ (1980)	4.31 (1.8V)	50-100	[59]	367 †
Alsthom (SPE)	2500FF (1988)	5*	20*	[60]	372 †
C.Bailleux (ALK)	2400FF (1982)	4.8*		[61]	401
R.Aureille (ALK)	2300FF (1981)	4.8*		[62]	492
C.-J.Winter	1300DM (1988)	4.5*		[36]	745
K.Andreassen	1040DM (1993)	4.8*	100*	[21]	632
E.Fein	321$ (1983)	4.35*	2.4	[63]	249
Lurgi (Giovanola) (ALK)	1120SFr (1996)	4.2	2.8	[64]	560 †

*Electricity consumption includes power conditioning and electricity demand of equipment. Plant capacity with losses at the power conditioning.

†Scaled up to MTH-System capacity (320 MW) with a degression exponent of 0.9, cost adjusted to 1995.

Table 5.1: Electrolyser Investment Costs and Scale-up to MTH-System Capacity

The average of the specific investment cost of electrolyser with a high capacity (only values with ‡) is 307 $\$/kW_{dc}$. Estimates from the last 10 years are between 360 and 745 $\$/kW_{dc}$. The latest reference (1996) in Table 5.1 concludes in specific investment cost of 560 $\$/kW_{dc}$ based on a plant capacity of 2.8 MW (scaled up with a degression exponent of 0.9). For further economic consideration of the MTH-System in chapter 7, a specific investment cost of 672 $\$/kW_{dc}$ (including 20% for buildings and externalities [65]) and an efficiency of 4.2 $kWh/m_n^3H_2$ are assumed. In addition, power conditioning and auxiliary equipment diminishes the efficiency by a factor of 0.97. According to the sensitivity analyses in chapter 3 a specific investment cost of 672 $\$/kW_{dc}$ [64] instead of 400 $\$/kW_{dc}$ increases the output electricity costs by 0.034 $\$/kWh$. For the economic calculation, a lifetime of 30 $years$ and annual operating and maintenance costs of 6% of the investment costs [5] are assumed. The land



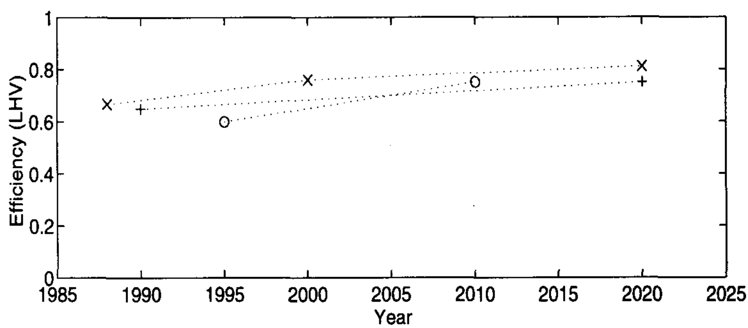


Figure 5.3: Prediction of Cost and Efficiency of Electrolysers
+ DOE Hydrogen Program Plan [40] (1992)
o K.Hassmann et al. [49] (1993)
× C.-J.Winter et al. [67] (1988)

requirement of an electrolysis plant lies between 50 m^2/MW_e [64] and 100 m^2/MW_e [66].

Future Cost Predictions

The cost predictions from different sources for the future development of electrolysers are shown in Figure 5.3. These predictions are partly contradictory in themselves when compared to the values in Table 5.1. Nevertheless a cost reduction to 250 $\$/kW$ and an efficiency improvement to 4 $kWh/m_n^3H_2$ could be expected for the year 2020 according to the DOE Hydrogen Program Plan [40].

Because high operating temperature electrolysis (HOT ELLY) is still in a development state, no present day costs for a commercial plant on an industrial scale are available. An estimate [7] suggests a cost of 443 $\$/kW_{dc}$ with an electricity consumption of 3.15 $kWh/m_n^3H_2$.

5.2 Hydrogenation

Hydrogenation of toluene to methylcyclohexane at 30 *bar* pressure is very similar to the hydrogenation of benzene to cyclohexane [44]. Therefore the cost data and technical specifications [37] for this process are used for the hydrogenation of toluene. This catalytic reaction produces very few byproducts [68]. The feed toluene from the purification plant is combined catalytically in a liquid phase reactor with hydrogen from the electrolysis and the hydrogen recycle stream exiting the hydrogenation.

Excess heat from the exothermic hydrogenation reaction

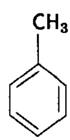
$$C_7H_8 + 3H_2 \Leftrightarrow C_7H_{14} \qquad \triangle H_0 = -204.77kJ/mol$$

is removed in a heat exchanger for the purification plant. After the finishing reactor, which converts remaining toluene from the liquid phase reactor to methylcyclohexane, the reaction products are cooled and flashed in a high pressure separator. The vapor is recycled to the hydrogen feed stream. The condensate is fed to the stabiliser which removes dissolved hydrogen and other light gases.

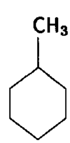
The cost of the hydrogenation plant amounts to 4.57 $M\$_{(1995)}$ based on a plant capacity of 12.5 *ton/hour* and a degression exponent of 0.6. Not included in this cost is the initial catalyst load of 0.117 $M\$_{(1995)}$ for a plant capacity of 12.5 *ton/hour*. The specific catalyst cost of the plant in operation is 2.87 $\$_{(1995)}$ per ton of product [37]. The hydrogenation plant in the summer process of the MTH-System has a capacity of 120 *ton/hour*. With an assumed life time of 19 *years* and yearly operating and maintenance costs of 3% of the investment costs, only the seasonal operation of this plant is accounted for.

5.3 Toluene Purification

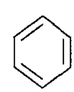
The toluene from the storage tanks contains a range of byproducts from the dehydrogenation reaction in the winter process. Without separation of byproducts, their accumulation in the closed system [42] would result in a loss of efficiency in the hydrogenation-dehydrogenation process steps. Purification of the toluene from byproducts is achieved by distillation. The byproducts are then treated by total oxidation, resulting in carbon dioxide emissions associated with output electricity. The feed stream to the purification plant contains the following components which have similar chemical properties:



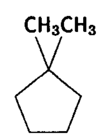
Toluene
C_7H_8



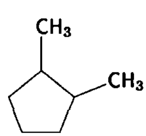
Methylcyclohexane
C_7H_{14}



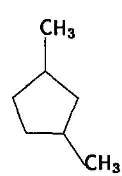
Benzene
C_6H_6



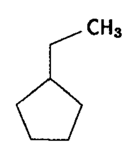
1,1-Dimethylcyclopentane
C_7H_{14}



cis-1,2-Dimethylcyclopentane
trans-1,2-Dimethylcyclopentane
C_7H_{14}



cis-1,3-Dimethylcyclopentane
trans-1,3-Dimethylcyclopentane
C_7H_{14}



Ethylcyclopentane
C_7H_{14}

Toluene is the highest boiling component and is separated by distillation. Table 5.2 shows the results of the distillation column simulation calculated with ASPEN PLUS 8.5. The physical properties of the components are taken from the ASPEN Pure Component Database and from the AIChE Data Compilation [25], the activity coefficients are calculated with the UNIFAC model. The simulation results of Table 5.2 show that the separation of ethylcyclopentane is very difficult. Only 20% is separated by distillation. Therefore ethylcyclopentane will be accumulated in the MTH-system which has to use the toluene many times in its closed winter-summer

Component	Byproducts from the Dehydrogenation	Distillation Column Boiling Point	Split Fractions Top	Bottom	Accumulated Byproducts in System
Toluene	0.9800	383.8K	0.0029	0.9971	-
Ethylcyclopentane	0.0030	376.6K	0.2003	0.7997	0.0150
Methylcyclohexane	0.0060	374.1K	0.4598	0.5402	-
cis-1,2-Dimethylcyclopentane	0.0028	372.7K	0.6011	0.3989	0.0047
trans-1,2-Dimethylcyclopentane	0.0032	365.0K	0.9712	0.0288	0.0033
trans-1,3-Dimethylcyclopentane	0.0012	364.9K	0.9718	0.0282	0.0012
cis-1,3-Dimethylcyclopentane	0.0012	363.9K	0.9778	0.0222	0.0012
1,1-Dimethylcyclopentane	0.0016	361.0K	0.9920	0.0080	0.0016
Benzene	0.0010	353.2K	0.9891	0.0109	0.0010

Table 5.2: Simulation Results of Distillation

cycle. Under equilibrium condition ethylcyclopentane is accumulated to an impurity level of 1.5%.

$$Accumulated\ Byproduct = \frac{Reaction\ Byproduct}{Split\ Fraction\ Top}$$

This is a maximum value because the isomerisation reaction of the cyclopentanes back to toluene in the hydrogenation and dehydrogenation reactors is not taken into account in this calculation. All other components except toluene and methylcyclohexane are subject to the same accumulation principle. The accumulated byproducts define the composition of the input stream to the purification plant in the equilibrium state of the system. The total stream at the top of the distillation column amounts to 1.96% of the total input stream. It includes also a fraction of the toluene and methylcyclohexane.

The total investment cost of the distillation plants including condenser and reboiler is 13.9 $M\$$ [69] (for comparison ASPEN carbon steel cost = 1.7 $M\$$). Other cost calculation parameters have been assumed equal to those of the hydrogenation step: life time 19 *years* and annually operating costs 3% of the investment costs.

5.4 Storage Tanks

5.4.1 Technical Requirements

As an additional safety measure and to prevent oxygen in the free space of the tanks from diffusing into the toluene or methylcyclohexane and oxidising the reduced catalysts, a blanket of pure nitrogen is employed.

5.4.2 Arrangement of Tanks

Large scale storage tanks for petrochemicals in Switzerland have a capacity of 20,000 m^3. With 25 of these tanks the MTH-System storage requirement of 500,000 m^3 is satisfied. Two additional empty tanks are needed: One for maintenance of the tanks, the other due to the schedule of refilling with the dehydrogenation or hydrogenation product. Therefore 27 tanks with a total volume of 540,000 m^3 are considered. The minimal land area demand of 6 m^3 storage tank at this scale is 1 m^2, giving an area of 0.09 km^2 (e.g. an area $300m \times 300m$) for the storage tanks.

5.4.3 Cost of Storage

The specific investment costs of the storage of liquid hydrocarbons at the scale of the MTH-System are 237 $\$/m^3$ (280 SFr/m^3 [39]). This value includes Swiss security requirements and the plant which manages the nitrogen blanket. The life time of such petrochemical tanks is 65 *years*. The operating and maintenance costs are estimated at 5.1 $\$/m^3 year$ (6 $SFr/m^3 year$ [39]).

5.5 Dehydrogenation Reactor

5.5.1 Reaction Kinetics

The equilibrium of the dehydrogenation reaction was experimentally determined in a previous Ph.D. thesis [9]:

$$K_{eq} = A_{eq} e^{\frac{-\triangle H_r}{R}\left(\frac{1}{T} - \frac{1}{650K}\right)} \tag{5.4}$$

with

$A_{eq} = 4.61\ 10^{18} Pa^3$

$\triangle H_r = 216.3\ 10^6 J/kmol$

The reference temperature of this equilibrium equation is $650K$. T is the temperature in K and $R = 8314.5 J/Kkmol$ the gas constant. Figure 5.4 shows the equilibrium curves of the dehydrogenation reaction for two inputs, i.e. four moles of

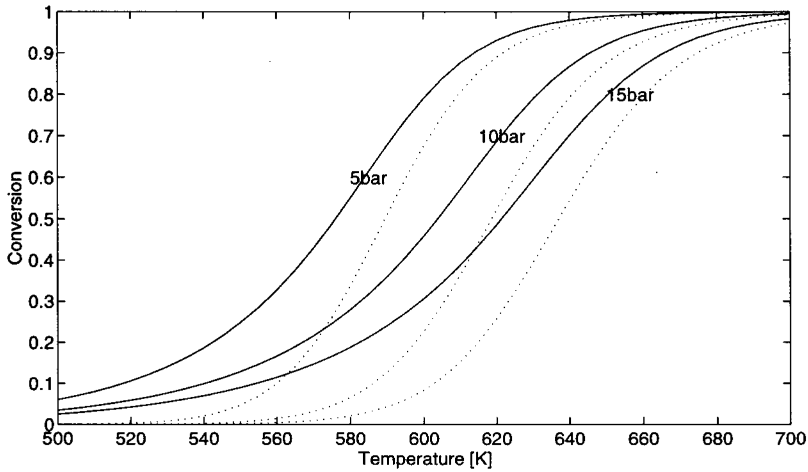


Figure 5.4: Equilibrium of the Methylcyclohexane Dehydrogenation

········ Feed Composition: Hydrogen/MCH = 4/1

——— Feed Composition: Hydrogen/MCH = 0/1

hydrogen for one mole of methylcyclohexane (MCH) and pure methylcyclohexane feed at different pressures.

$$conversion = \frac{p_{TOL}}{p_{TOL} + p_{MCH}} \tag{5.5}$$

According to a Langmuir-Hinshelwood kinetic model [12] the reaction rate is:

$$\begin{aligned} r &= \frac{k_1\, p_{MCH}}{1 + k_2\, p_{TOL}}\left[1 - \frac{p_{TOL}\, p_{H_2}^3}{K_{eq}\, p_{MCH}}\right] \\ k_1 &= A_1 e^{\frac{-E_1}{R}\left(\frac{1}{T} - \frac{1}{T_m}\right)} \\ k_2 &= A_2 e^{\frac{-E_2}{R}\left(\frac{1}{T} - \frac{1}{T_m}\right)} \end{aligned} \tag{5.6}$$

p_{MCH}, p_{TOL} and p_{H_2} are the partial pressures of the particular reaction components. The parameters A_1,E_1,A_2,E_2 and the average temperature T_m depend on the catalyst type and are determined by experiments [12]. Examples of such catalyst parameters are given in Table 5.3. The equation for the reaction rate r holds for a fresh catalyst at outer surface condition. That means that coke does not diminish catalyst activity and diffusion limitations are negligible. The coke content diminishes the reaction rate for a coked catalyst.

$$r_{coke} = \eta_{coke} r \tag{5.7}$$

In subsequent reactor simulations, it is assumed that $\eta_{coke} = 0.1$ (end of run condition). The effective reaction rate is also limited by diffusion

$$r_{eff} = \eta_{coke}\eta_{diff}r \tag{5.8}$$

The diffusion efficiency η_{diff} is given by

$$\eta_{diff} = \frac{1}{\Phi}\left(\frac{1}{\tanh(3\Phi)} - \frac{1}{3\Phi}\right) \tag{5.9}$$

For a first order reaction in a spherical catalyst pellet the Thiele modulus Φ [70] is

$$\Phi = \frac{d}{6}\sqrt{\frac{r_{coke}RT\rho_p}{p_{MCH}D_{eff}}} \tag{5.10}$$

with an effective diffusivity (parallel pore model)

$$D_{eff} = \frac{\frac{\epsilon}{\delta}}{\frac{1}{D_{AB}} + \frac{1}{D_{Knudsen}}} \tag{5.11}$$

According to the Chapman-Enskog formula [70] the bulk diffusivity of methylcyclohexane in its reaction product is

$$D_{AB} = 8.35\ 10^{-4}\frac{m^2 Pa}{sK^{1.5}}\frac{T^{1.5}}{p} \tag{5.12}$$

and the Knudsen diffusivity [70, 9]

$$D_{Knudsen} = 97.0\frac{mkg^{0.5}}{sK^{0.5}kmol^{0.5}}R_{pore}\sqrt{\frac{T}{M_{MCH}}} \tag{5.13}$$

5.5.2 Pressure Drop in the Fixed Beds

Based on experimental data, S. Ergun [71] has established a comprehensive equation, applicable to a broad range of two-phase fixed bed flow:

$$\triangle p = f_k l \frac{G_m v_0}{d_p}\frac{(1-\epsilon_{bed})}{\epsilon_{bed}^3} \tag{5.14}$$

with the so-called friction factor

$$f_k = 150(1-\epsilon_{bed})/Re + 1.75 \tag{5.15}$$

Catalyst [12]		MM30s	BM30
	$A_1[kmol/kgsPa]$	$2.139\ 10^{-9}$	$14.15\ 10^{-10}$
	$E_1[J/kmol]$	$1.879\ 10^8$	$1.16\ 10^8$
	A_2	0	$96.4\ 10^{-6}$
	E_2	0	$-2.5\ 10^7$
Average Temperature	$T_m[K]$	612.14	650.0
Diameter of the Catalyst Pellet	$d[m]$	0.0016	0.0015
Density of Catalyst Pellet	$\rho_P[kg/m^3]$	514.0	456.0
Average Radius of the Pores	$R_{pore}[m]$	$189.0\ 10^{-10}$	$185.0\ 10^{-10}$
Porosity	ϵ	0.75	0.5
Tortuosity	δ	2.5	5.0

Table 5.3: Properties of Selected Catalysts

Re denotes the particle Reynolds number:

$$Re = \frac{\rho v_0 d_p}{\mu} = \frac{G_m d_p}{\mu} \tag{5.16}$$

v_0 is the empty tube velocity of the gas and $G_m = v_0 \rho$ its mass velocity per unit cross-sectional area. The void fraction ϵ_{bed} of a fixed bed filled with spherical pellets is approximately 0.4. Similar to the Ergun-equation 5.14, the pressure drop equation for a fixed bed from VDI-Wärmeatlas chapter Le [72] is:

$$\Delta p = \mu \xi \frac{l}{d'} \frac{\rho}{2} \left(\frac{v_0}{\epsilon_{bed}}\right)^2 \tag{5.17}$$

The pressure drop parameter ξ is defined as

$$\xi = 2.2 \left(\frac{64.0}{Re} + \frac{1.8}{Re^{0.1}}\right) \tag{5.18}$$

with another definition of the particle Reynolds number

$$Re = \frac{\rho v_0 d'}{\epsilon_{bed} \mu} \qquad d' = \frac{2}{3} \frac{\epsilon_{bed}}{1 - \epsilon_{bed}} d_p \tag{5.19}$$

Both methods of pressure drop calculation deliver approximately the same results. In the subsequent reactor simulations the Ergun equation of will be employed.

5.5.3 Cost Calculation

The dehydrogenation plant consists essentially of reactors, heat exchangers and the hydrogen compressor. The latter is used for recycling hydrogen with the methylcyclohexane feed and is considered in detail in section 5.9. The following formula [69] describes the costs of the reactors:

$$\mathcal{K} = 8.4\$(5000 + \frac{1645V}{[m^3]}) \tag{5.20}$$

V denotes the volume of the reactor. The prefactor 8.4$ expresses material and installation costs as well as the index correction to normalise the cost to 1995 prices. Heat exchanger costs are estimated with a function which depends on the heat exchanger area A:

$$\mathcal{K} = 52.0 \cdot 23000\$ \left(\frac{A}{92.9[m^2]}\right)^{0.68} \tag{5.21}$$

Other cost calculation parameters have been assumed equal to those of the hydrogenation plant described in section 5.2 (19 *years* life time and 3% operating costs).

5.6 Fuel Cells

5.6.1 Electrochemical Processes in Fuel Cells

The standard reversible potential of a fuel cell is given by

$$U_0 = \frac{-\triangle G(T)}{nF} \tag{5.22}$$

The symbol n in the equation designates the number of elementary charges transferred in the redox reaction, e.g. $n = 2$ for CO_3^{2-}-ions (MCFC) and O^{2-}-ions (SOFC). The Faraday constant F equals 9.6485 $10^7 C/kmol$. U_0 is equal to 1.185V at the standard ambient temperature of 298 K and pressure of 101325 Pa. The efficiency of a fuel cell is linearly proportional to its cell voltage.

The dependence of the Gibbs potential on the temperature in the absence of phase transitions can be calculated with the following three thermodynamic equations:

$$\begin{aligned}
\triangle G(T) &= \triangle H(T) - T\triangle S \\
\triangle H(T) &= \triangle H_0 + \int_{T_0}^{T} \triangle C_p(T) dT \\
\triangle S(T) &= \triangle S_0 + \int_{T_0}^{T} \frac{\triangle C_p(T)}{T} dT
\end{aligned}$$

According to the Nernst equation the open circuit potential is given by

$$U = U_0 - \frac{RT}{nF} ln(K_{Nernst}) \tag{5.23}$$

K_{Nernst} is the fraction of the activities with the power of their stoichiometric coefficients of the reaction at the anode side and at the cathode side. For example K_{Nernst} in a solid oxide fuel cell (SOFC) is

$$K_{Nernst} = \frac{(p_{O^{2-}}/p)_{cat}(p_{H_2O}/p)_{an}}{(p_{O^{2-}}/p)_{an}(p_{O_2}/p)^{0.5}_{cat}(p_{H_2}/p)_{an}} = \frac{(p_{H_2O}/p)_{an}}{(p_{O_2}/p)^{0.5}_{cat}(p_{H_2}/p)_{an}} \tag{5.24}$$

It is assumed that the concentration of the O^{2-}-ions at the anode is equal to that at the cathode. In practice following losses occur:

- Anode and cathode overpotentials
- IR loss due to ohmic resistance across separating cell medium

Therefore real cell voltage is reduced to

$$U_{dc} = U - U_{Cat} - U_{IR} - U_{An} \tag{5.25}$$

To simplify calculation the aforementioned losses can be taken into account by multiplying the standard reversible potential with an efficiency factor ζ, which identifies the quality of the electrochemical process

$$U_{dc} = \zeta U_0 \tag{5.26}$$

5.6.2 Energy Balance in Fuel Cell Power Stations

To close the energy balance of a fuel cell power station, it is necessary to identify all the sources and dissipation of heat and energy. The input streams comprise hydrogen and air heated up to the operating temperature T of the fuel cell. In addition to their heat capacities the input streams also import the reaction enthalpy $\triangle H_0$. The exhaust streams exiting from both sides of the cell comprises the electrical power output P_{dc} and the remaining usable heat flux, caused by the entropy production of reaction, $T\triangle S$, and by the irreversible processes in the cell.

$$Q = \frac{dT\triangle S}{dt} + (1-\zeta)\frac{-d\triangle G(T)}{dt} \tag{5.27}$$

For high temperature fuel cells, this waste heat is very useful, since its temperature level is at the operating temperature of the fuel cell (SOFC 1000°C, MCFC 650°C).

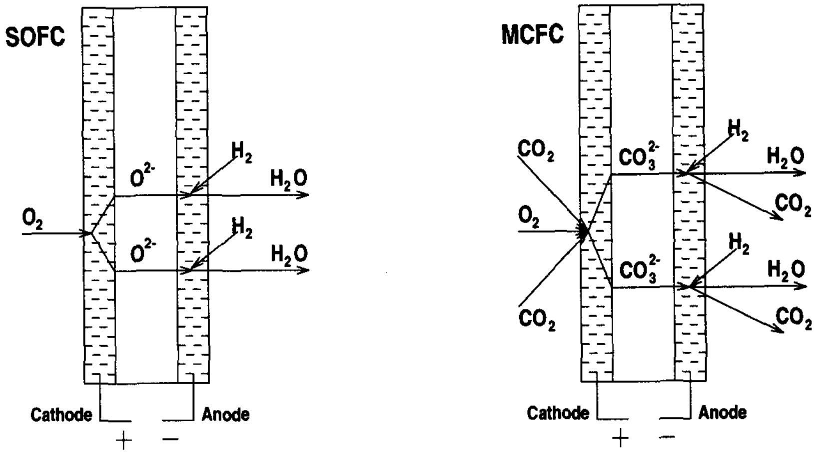


Figure 5.5: Electrochemical Processes in SOFC and MCFC

5.6.3 Solid Oxide Fuel Cells

On the left side of Figure 5.5 it is shown that solid oxide fuel cells (MCFC) operate with O^{2-}-ions. The oxygen is reduced to yield O^{2-}-ions at the cathode side and is combined with hydrogen to water at the anode side:

- Cathode: $\frac{1}{2}O_2 + 2e^- \longrightarrow O^{2-}$
- Anode: $H_2 + O^{2-} - 2e^- \longrightarrow H_2O$

For solid oxide fuel cells, ζ is between 0.78 and 0.88 [73]. In the MTH-system simulation of heat integration, a value of $\zeta = 0.82$ is assumed. This implies an efficiency $\eta_{dc} = 0.606$ of the fuel cell at a process temperature of 1250 K. With an efficiency of 0.96 for the dc/ac-converter (direct current $\rightarrow$ alternating current) a total efficiency $\eta_{ac} = 0.58$ of the fuel cell system is achievable.

5.6.4 Molten Carbonate Fuel Cells

Molten carbonate fuel cells (MCFC) need a large supply of carbon dioxide because they are operating with CO_3^{2-}-ions (right side of Figure 5.5). The main cell reactions are:

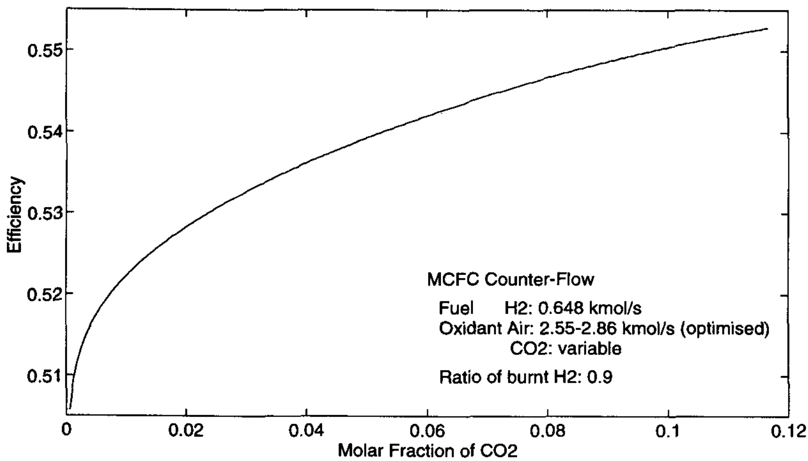


Figure 5.6: Efficiency of MCFC as Function of the available Carbon Dioxide

- Anode: $H_2 + CO_3^{2-} - 2e^- \longrightarrow H_2O + CO_2$
- Cathode: $\frac{1}{2}O_2 + CO_2 + 2e^- \longrightarrow CO_3^{2-}$

These equations show that the process needs as much carbon dioxide at the cathode side as hydrogen at the anode side. In practice carbon dioxide occurs in the output streams of both sides of the cell. At the fuel side, carbon dioxide is produced in the anodic reaction, and at the air side there is residual carbon dioxide which has not completely transferred through the cell membrane. The latter is lost from the system and must be replaced by a corresponding amount in the input stream. Therefore efficiency depends strongly on the available CO_2 from the combustion of the dehydrogenation byproducts. Nearly all carbon dioxide from the exhaust stream is recycled. Figure 5.7 shows the separation of the remaining hydrogen from the carbon dioxide using membrane separation (section 5.10) and the recycle of carbon dioxide to the anode side. The criticality of the cathode side CO_2 content to MCFC efficiency is shown in Figure 5.6. A sufficient partial pressure of CO_2 is needed to generate CO_3^{2-}-ions and utilise the high intrinsic efficiency of the molten carbonate fuel cell. Because of the limited quantity of available CO_2 from dehydrogenation byproducts, it is necessary to calculate the cell voltage (which is linearly

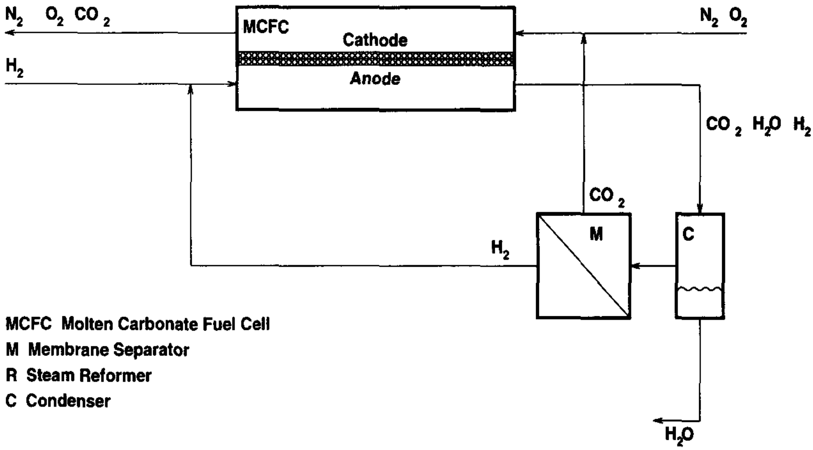


Figure 5.7: MCFC Plant Flow Sheet

proportional to the efficiency) more accurately than in the SOFC case.

$$K_{Nernst} = \frac{(p_{CO_2}/p)_{an}(p_{H_2O}/p)_{an}}{(p_{CO_2}/p)_{cat}(p_{O_2}/p)^{0.5}_{cat}(p_{H_2}/p)_{an}} \tag{5.28}$$

The calculation of overpotentials is performed with the data from J.R.Selman [74]. The cathode overpotential is

$$U_{Cat} = 7.50510^{-6}\Omega cm^2 \; i \; (p_{O_2})^{-0.43}_{cat}(p_{CO_2})^{-0.09}_{cat} \exp\frac{77.3 \; 10^6 J/kmol}{RT} \tag{5.29}$$

and the anode overpotential

$$U_{an} = 2.2710^{-5}\Omega cm^2 \; i \; (p_{H_2})^{-0.42}_{an}(p_{CO_2})^{-0.17}_{an}(p_{H_2O})^{-1}_{an} \exp\frac{53.5 \; 10^6 J/kmol}{RT} \tag{5.30}$$

where $i \approx 0.16 A/cm^2$ is the current density. The ohmic drop in the electrolyte is assumed to be $U_{IR} = 0.1V$.

5.6.5 Economics

Since fuel cells are not available at competitive prices today, cost calculations are based on future cost predictions. These future cost are assumed to be 1000 $\$/kW$ for MCFC and 1500 $\$/kW$ for SOFC [38] based on a power plant output of 1-100

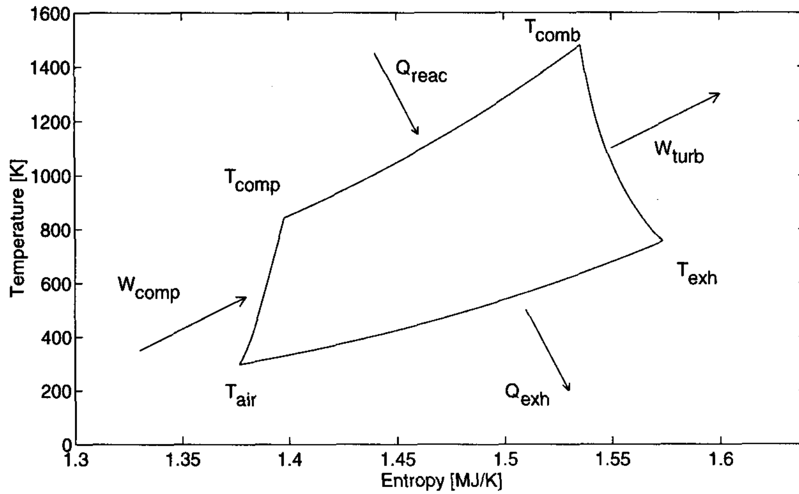


Figure 5.8: Temperature-Entropy Characteristic of a Single Stage Gas Turbine

MW. Other assumed costs are 600-780 $\$/kW$ for a 100 *MW* MCFC [75] and 1100 $\$/kW$ for SOFC [76]. Reference [77] gives a range of 1000-1500 $\$/kW$ for the fuel cell costs, which depends on the fuel used (natural gas and coal gas). This cost data of the year 1993 are normalised to 1995 with the CE-index. Annual operating costs are 3% of the investment costs. The estimated life time of fuel cells is 25 *years*. Like the electrolyser, fuel cells have high ground floor area requirements (67.5 m^2/MW). The investment costs are approximately linearly proportional to the power output (degression exponent 0.9).

5.7 Gas Turbine

5.7.1 Mechanism

In Figure 5.8 the thermodynamic process of a gas turbine is shown in a TS-plot (temperature-entropy). Entering air and gaseous fuel are compressed to combustion pressure with an isentropic efficiency η_{comp} compared with the ideal adiabatic process. In the isobaric combustion process the gas is heated up to the temperature

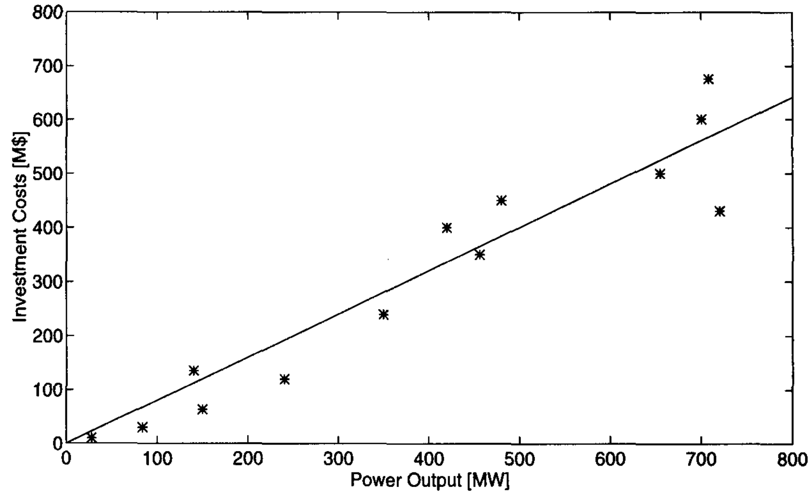


Figure 5.9: Investment Costs of Gas and Steam Turbine Plants

T_{comb} by the heat of the combustion reaction Q_{reac}. The hot gas stream expands in the turbine to atmospheric pressure. This irreversible expansion process works with an isentropic efficiency η_{turb}. The exhaust heat Q_{exh} can be used subsequently in a steam turbine. A fraction of the work of the turbine W_{turb} is used for the compression work W_{comp}. Therefore the remaining available mechanical work is:

$$available\ mechanical\ work = W_{turb} - W_{comp} \tag{5.31}$$

The following equations describe the thermodynamic process shown in Figure 5.8:

$$\begin{aligned}
T_{comp} &= \frac{T_{air}\pi^{\frac{\kappa-1}{\kappa}}}{\eta_{comp}} + T_{air}\left(1 - \frac{1}{\eta_{comp}}\right) && (5.32)\\
T_{exh} &= \eta_{turb}T_{comb}\pi^{-\frac{\kappa-1}{\kappa}} + T_{comb}\left(1 - \eta_{turb}\right) && (5.33)\\
W_{comp} &= \frac{C_{p_{air}}T_{air}\left(\pi^{\frac{\kappa-1}{\kappa}} - 1\right)}{\eta_{comp}} = C_{p_{air}}\left(T_{comp} - T_{air}\right) && (5.34)\\
W_{turb} &= C_{p_{exh}}T_{comb}\left(1 - \pi^{-\frac{\kappa-1}{\kappa}}\right)\eta_{turb} = C_{p_{exh}}\left(T_{comb} - T_{exh}\right) && (5.35)\\
Q_{reac} &= -\triangle H_0 - \int_{T_0}^{T_{comp}} \triangle C_p dT = C_{p_{air}}\left(T_{comb} - T_{comp}\right) && (5.36)
\end{aligned}$$

$\pi = \frac{p_{comb}}{p_{air}}$ denotes the ratio of combustion pressure to atmospheric pressures. $\kappa = \frac{C_p}{C_v}$ is approximately 1.4. To increase the efficiency of a gas turbine two methods are most commonly used:

- The combustion temperature is increased
- Two injection points permit a sequential combustion of the fuel with interstage expansion and an increase in the combustion pressure without using more air in the input stream or increasing combustion temperature.

In the simulation of the MTH-System including gas and steam turbines in section 7.2.4 both of these optimisation methods will be applied.

5.7.2 Parameters used for Simulation

The overall efficiency of a gas turbine depends mainly on two properties: the temperature of the gases at the outlet of combustion chamber, which limits the Carnot efficiency, and the isentropic efficiency of compression and expansion. The material properties of the turbine blades limit the maximum combustion temperature; current achievable temperatures are between 1450 K and 1500 K. In simulation, an isentropic efficiency of 0.88 is used for compression η_{comp} and expansion η_{turb}. Another parameter diminishing the output power is the electrical efficiency of the generator ($\eta_{elec} = 0.98$).

Figure 5.9 shows the cost of gas and steam turbines from contracts in the years 1994-1995 published in the Journal *Turbomachinery*. The costs of these turbines are linearly proportional to their output power (800 $\$/kW$). The life time of gas and steam turbines are 30 *years*. Because of seasonal use, low operating costs of only 3% of the investment costs are assumed.

5.8 Steam Turbine

5.8.1 Mechanism

Figure 5.10 shows the thermodynamic cycle of a condensing steam turbine. The feedwater is pumped at high pressure to the heat exchanger (step [3-4], pumping from the low condensing pressure to higher evaporation pressure), which heats up the

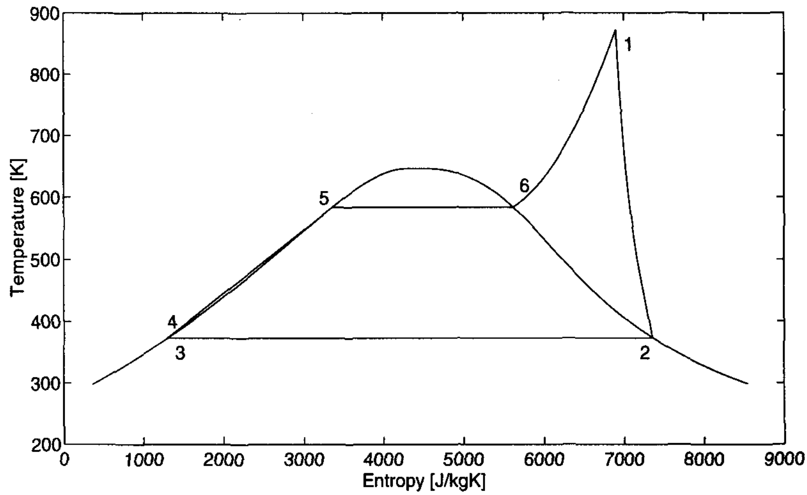


Figure 5.10: Thermodynamic Cycle of a Steam Turbine

[1-2] *Steam expansion*
[2-3] Condensing expanded steam to water
[3-4] Pumping feedwater with high pressure to the heat exchanger
[4-5] Heating up feedwater
[5-6] Vaporise feedwater to steam
[6-1] Superheat steam

feedwater (step [4-5]) to the boiling temperature. The boiler vaporises the feedwater (step [5-6]). The steam is superheated (step [6-1]) before it is expanded adiabatically in the turbine (step [1-2]) with the isentropic efficiency η_{turb}. A second superheating of the steam after first expansion constitutes a process alternative which often results in a higher overall efficiency. Another method to increase the overall efficiency is decreasing the condensing pressure at the step [2-3], which results in a lower condensing temperature. Evidently, the temperature of the cooling medium limits this decreasing of the condensing pressure. If the condensing pressure is equal to or higher than atmospheric pressure, the condensation of the steam would be unnecessary (noncondensing turbine without cooling tower). In this case the steam turbine cycle would be opened at between [2-3]. In a condensing turbine the steam/water cycle is closed, which makes it possible to use a lower condensing pressure than atmospheric pressure. The third way to optimise the overall efficiency, increasing the temperature of the superheated steam, is limited by material properties.

5.8.2 Parameters used for Simulation

The efficiencies of the feedwater pump η_{pump} and the isentropic expansion efficiency are 0.85. The generator has the same electrical efficiency $\eta_{elec} = 0.98$ as that of the gas turbine. The cost estimation parameter of steam turbines are supplied in section 5.7.2.

5.9 Compressor of Dehydrogenation Plant

A compressor is needed to recycle hydrogen to the input stream (methylcyclohexane) of the dehydrogenation plant. Because of its high energy (electricity) consumption this hydrogen compressor cannot be neglected. The mechanism is the same as in the air compression step of the gas turbine (section 5.7), given in the equations 5.32 and 5.34. The isentropic efficiency of compression η_{comp} is assumed to be 0.85 (lower than in the gas turbine) while electrical efficiency η_{elec} of the motor drive is 0.97. The cost data [69] of the compressor is based on its power (with a cost degression exponent of 0.8). As a part of the dehydrogenation plant, it has the same life time of 19 *years* and the same operating cost factor of 3% annually.

5.10 Membrane Separation of Hydrogen

The membrane modules shown in Figure 5.7 are used for separating the remaining hydrogen from the carbon dioxide in the exhaust stream of the molten carbonate fuel cells (MCFC). Without this hydrogen separation, the electrical efficiency of the whole system would be diminished significantly. The permeation mechanism of the Pd/Ag membrane separation method is considered in chapter 8. The costs of a composite-metal membrane modules (Pd/Ag on a porous support layer) are 3230 $\$/m^2$ [78]. The installation factor is estimated to be twice the module costs. Although these membrane separation modules are used only in seasonal operation, a pessimistic life time of 17 *years* is assumed. The operating costs are 3% of the investment cost per year. In addition a yearly replacement of 10% of the modules is taken into account.

Hydrogen separation from other gases is also a critical technology in the mobile application (chapter 2) of renewable fuels. Polymer electrolyte fuel cells (PEFC) operate with highly pure hydrogen. A major problem is the poisoning of the polymer electrolyte membrane by carbon monoxide impurities. The experimental part of this work (chapter 8) addresses the purification of hydrogen using Pd/Ag membranes.

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Chapter 6

Cost Basis for Plant, Inventory and Payback Strategy

6.1 Introduction

The purpose of this chapter is to provide the techniques and data of capital cost estimation. Unfortunately, actual cost data for each plant are not available and the cost change by the time. In addition, many cost data from literature are uncertain. In the systems analysis step of project planning, the factor (additional costs are accounted by multiplying the basic costs with specific factors) estimate technique is a powerful tool since cost information from detailed engineering is not yet available. Section 6.2 provides general techniques used in plant capital cost estimation. Together with informations on inflation (cost indices in section 6.2.2) and cost dependence on scale (section 6.2.3), the guidelines for capital cost estimation are given.

Moreover, the cost data of selected inputs are also provided: costs of input electricity (section 6.3), toluene price (section 6.4) and land costs (section 6.5). The capital and operating costs of the particular plants used in the MTH-System were considered in chapter 5.

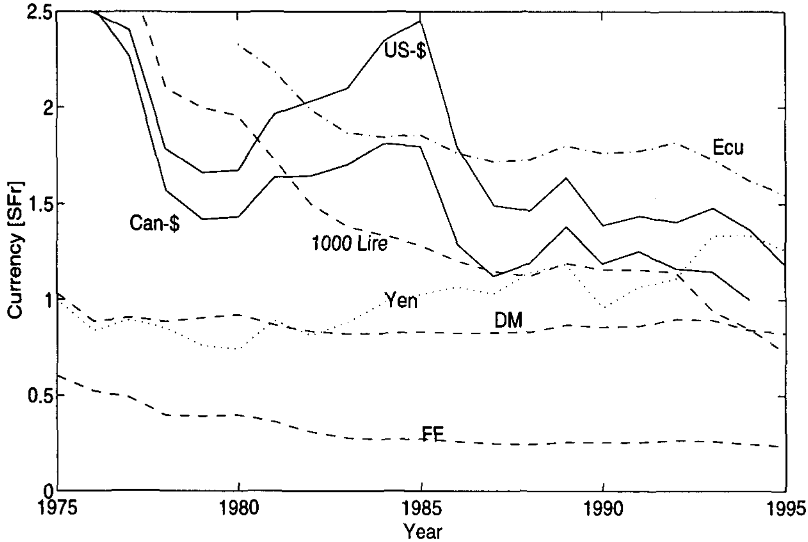

Figure 6.1: Currency Data

6.2 Costing Techniques

6.2.1 Currencies

To compare cost data of plants from different geographical sources (literature, data from manufacturer) currency data of each particular year are quite useful to transfer the cost data to the currency (US-$) which is the basis of the cost index data discussed in section 6.2.2. The currency data presented in Figure 6.1 were taken from the *Schweizerische Nationalbank* statistics [79]. They are normalised to Swiss Francs.

6.2.2 Cost Indices

Because of changing economic conditions, cost data will become obsolete with time. Cost indices allow old cost data to be updated. They reflect the change of costs of a certain types of equipment over time. If the cost at a referenced time in the

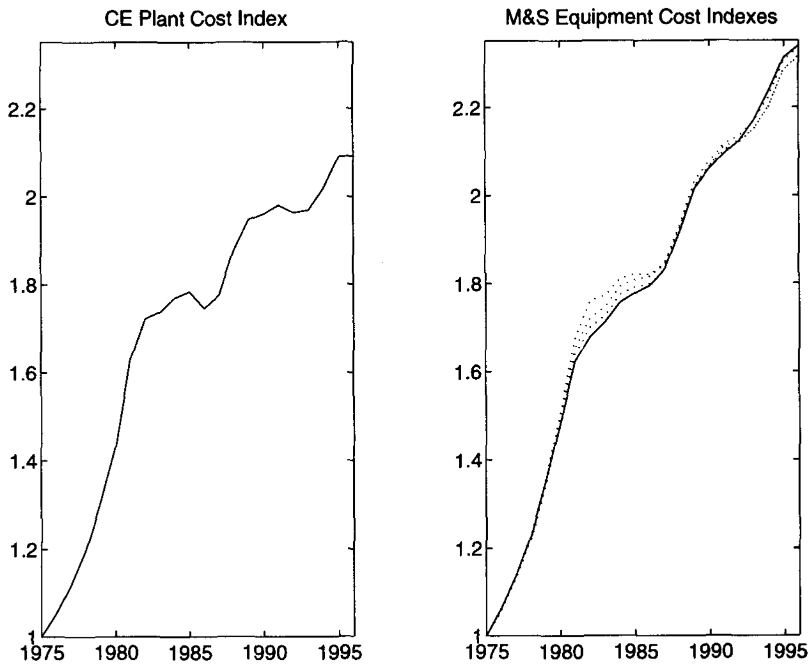

Figure 6.2: Cost Factors normalised for 1975

past is known, the present cost can be estimated with the cost indices. To estimate current cost, the old reference plant cost has been simply multiplied by the ratio of the present index value to the index of the year, in which the old reference plant cost was obtained.

$$Cost_{pres} = Cost_{ref} \frac{Index_{pres}}{Index_{ref}}$$

Table 6.1 shows the Chemical Engineering (CE) plant cost index and several Marshall and Swift (M&S) equipment cost indices. These indices are published every two months in the journal *Chemical Engineering*. The base year (for which the index value is 100) of the Chemical Engineering plant cost index is 1957-59 and that of the Marshall and Swift equipment cost indices is 1926. In Figure 6.2 the indices presented in Table 6.1 are shown as a function of time. The normalisation to 1 for the year 1975 shows the difference between the Chemical Engineering and the Marshall and Swift cost indices.

	CE plant cost index	M&S equipment cost index all industry	process industry	chemical industry	petrochem. industry
1975	182.4	444.3	450.0	447.6	470.9
1976	192.1	472.1	478.8	473.2	497.7
1977	204.1	505.4	509.0	507.1	535.9
1978	218.8	545.3	549.5	546.5	579.7
1979	238.7	599.4	606.3	599.3	637.3
1980	261.2	659.6	675.4	666.0	711.3
1981	297.0	721.3	744.9	733.8	790.5
1982	314.0	745.6	774.4	760.9	828.7
1983	316.9	760.8	785.7	772.6	834.4
1984	322.7	780.4	806.5	794.0	852.1
1985	325.3	789.6	813.4	801.4	857.4
1986	318.4	797.6	816.9	805.0	856.9
1987	323.8	813.6	830.4	819.2	866.2
1988	342.5	852.0	870.1	859.5	907.6
1989	355.4	895.1	914.2	904.5	950.7
1990	357.6	915.1	934.5	924.3	971.9
1991	361.3	930.6	951.8	940.8	993.4
1992	358.2	943.1	960.5	948.5	1000.2
1993	359.2	964.2	975.3	962.7	1012.4
1994	368.1	993.4	1000.2	984.8	1036.7
1995	381.1	1027.5	1037.4	1022.7	1075.4
1996	381.7	1039.2	1051.3	1036.2	1091.4

Table 6.1: Comparison of Cost Indices

6.2.3 Degression Exponents

The degression exponents (also called size or scale exponents) are used to estimate the cost of similar plants of different capacities. If the cost of a particular plant (reference) is known for one capacity, the cost of another plant with the same technology can be calculated with the following equation:

$$Cost_{plant} = Cost_{ref} \left(\frac{Capacity_{plant}}{Capacity_{ref}} \right)^{DegressionExponent}$$

A summary of degression (size) exponents was published in the journal *Chemical Engineering* [80] and in [69, 81].

6.2.4 Total Investment

The total investment consists of the following parts:

- equipment (basic plant, heat and mass transfer equipment, control)
- installation (section 6.2.8)
- plant start-up
- working capital
- land

The equipment cost serves as a basis of the calculation. It can be calculated from basic information (from industry, literature), adjusted by the factors and degression exponents defined in sections 6.2.2 and 6.2.3. The installation cost is often included in this basic information (electrolysis section 5.1.3, fuel cells section 5.6.5) or could be calculated with an installation factor (multiple of equipment cost provided by [69] Appendix 1). The total plant cost is the sum of equipment and installation cost. The plant start-up cost lies between 5 and 10% of the total plant cost [69].

Chemical plants in operation need a working capital, because the invoices (raw materials, utilities) accumulated during operation must be paid before the product is sold. This working capital amounts to 10-20% of the total plant cost [69, 82]. The two main contributions to the working capital in the MTH-System are the toluene inventory and the input electricity, which are calculated separately. Further raw material is not required, the working capital only consists of wages, maintenance and operating supplies. Therefore a low working capital of 5% of the total plant costs can be expected in the MTH-System.

6.2.5 Life Time of Chemical Plants

The estimated life times of chemical plants lie between 9 and 13 *years* (midpoint 11 *years*) and petrochemical plant between 13 and 19 *years* (midpoint 16 *years*) [41]. Based on the fact that each chemical plant in the MTH-system is only a half year in operation, a life time of 19 *years* can be expected, provided corrosion problems during standby are not excessive.

6.2.6 Straight Line Depreciation

After the life time T_{life} of a plant the investment credit has to be paid off. The fraction of capital which could be saved is designates as salvage value, including working capital, land and scrap value of the plant. The difference between investment capital $\mathcal{K}_{inv}$ and salvage value $\mathcal{K}_{salv}$ has to be paid back during the plant life. Straight line depreciation provides paying back the same amount per time.

$$Depreciation = \frac{\mathcal{K}_{inv} - \mathcal{K}_{salv}}{T_{life}} \tag{6.1}$$

In practice often credit pay back is accelerated at the beginning of the life period. One of these rapid depreciation methods is the double declining balance. The depreciation per year is always twice that of the straight line depreciation of the remainder. Figure 6.3 shows different depreciation methods. These methods do not include the problem of the sinking interest and the high cost of capital at the beginning of the plant life. For simple estimation, a straight line depreciation with a constant average interest rate is the easiest method, as used in the sensitivity analyses, chapter 3.

6.2.7 Sinking Fund Method

During the pay back period, investment funds are diminishing. The cost of interest will be lower because it is linearly proportional to the credit. The assumption of a continuous compound interest with an interest rate of R_I leads to an incremental interest dI of a fund F at the time t during the time period dt.

$$dI = R_I F(t) dt \tag{6.2}$$

If the time t $[year]$ is not too long (e.g. $t = 1 year$) and interest rate not too high (e.g. $R_I = 0.05 year^{-1}$), the rate R_I of the continuous interest is comparable to the simple interest (5% annually):

$$F(t = 1 year) = e^{R_I t} F(0) \approx F(0) + R_I F(0) \qquad first\ order$$

The interest rate R_I is chosen as constant in time, because a prediction over 10 or 20 years is uncertain. The fund will be incremented by the interest and decreased by the pay back $P(t)dt$

$$dF = dI - P(t) dt \tag{6.3}$$

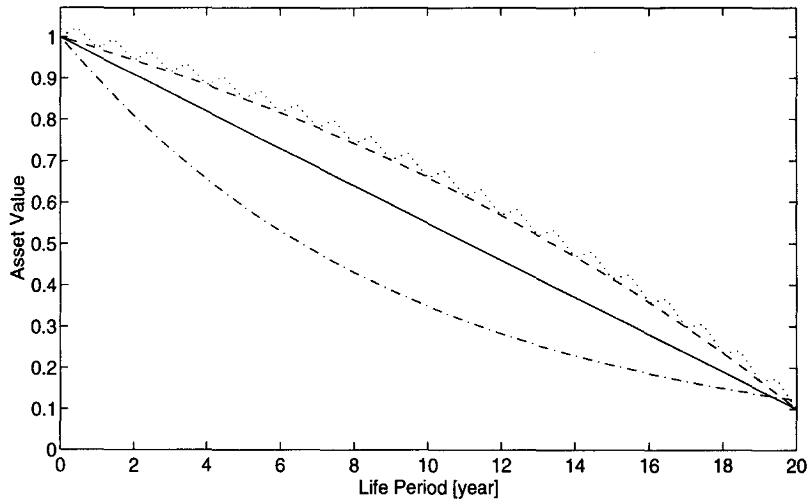

Figure 6.3: Depreciation Methods

——— Straight Line
– · – · – Double Declining Balance
- - - - - - Sinking Fund Method with constant payback
· · · · · · · Sinking Fund Method with rectangular payback function

The previous two equation leads to a first order linear differential equation.

$$\frac{dF}{dt} = R_I F(t) - P(t) \tag{6.4}$$

The general solution of this equation is

$$F(t) = e^{R_I t}\left(F_0 - \int_0^t P(t')e^{-R_I t'}dt'\right) \tag{6.5}$$

At time $t = 0$, $F(t)$ is equal to F_0. Therefore the integration constant F_0 is the total cost of the installed plant including interest during installation at the beginning (start-up) of the plant life.

6.2.8 Installation Cost

Before plant start up at the time $t = 0$, the payback function $P(t)$ is negative due to expenses e.g. construction, during the installation time T_{inst}. Accumulating the

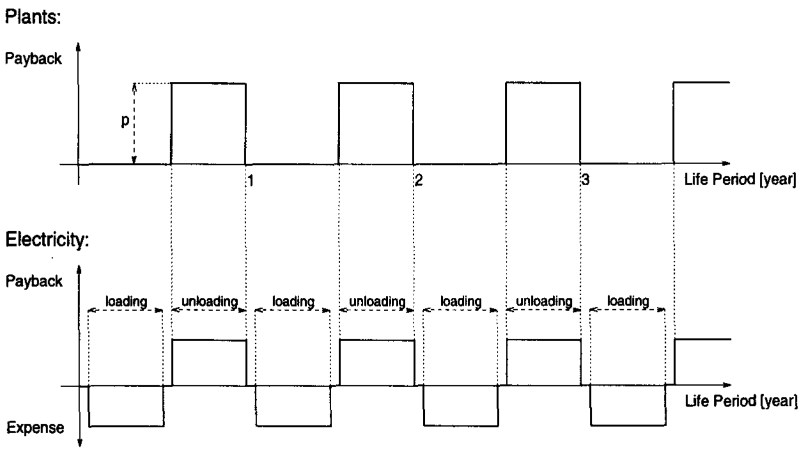

Figure 6.4: Rectangular Payback Function

interest and expenses over the installation time gives the total cost of the installed plant

$$F_0 = F(0) = -\int_{-T_{inst}}^{0} P(t)e^{-R_I t}dt \tag{6.6}$$

Assuming constant expenses F'/T_{inst} during the installation time results in

$$F_0 = \int_{-T_{inst}}^{0} \frac{F'}{T_{inst}} e^{-R_I t} dt = \frac{F'}{R_I T_{inst}}\left(e^{R_I T_{inst}} - 1\right) \tag{6.7}$$

In many cases the installation costs are included in the investment cost data or could be added with a factor.

6.2.9 Payback Strategy

If the payback is constant with time $P(t) = p$, the fund $F(t)$ of equation 6.5 results in:

$$F(t) = e^{R_I t}\left(F_0 - \left(-\frac{pe^{-R_I t}}{R_I} + \frac{p}{R_I}\right)\right) = e^{R_I t}\left(F_0 - \frac{p}{R_I}\right) + \frac{p}{R_I} \tag{6.8}$$

The depreciation is very slow at the beginning of the life time. Most of the payback in this period is used by the high interest. At the end of the life time, the sinking fund method accelerates the diminishing of the fund. In Figure 6.3 the sinking fund

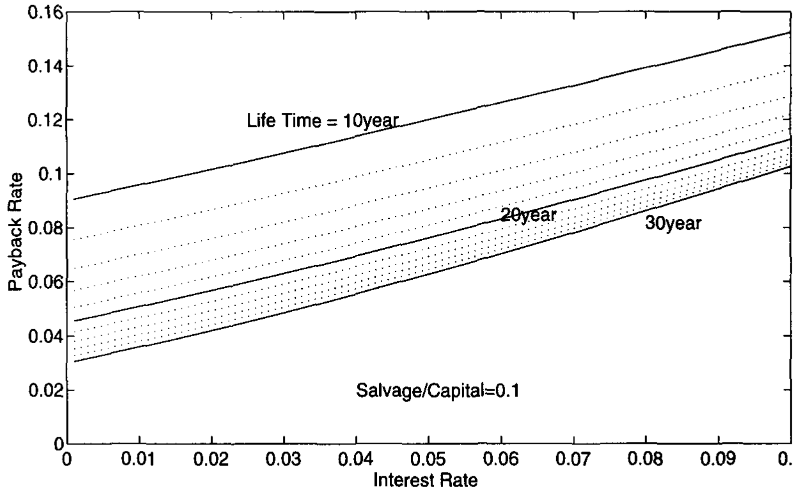

Figure 6.5: Payback Rate as a Function of the Interest Rate for Several Life Times

method with constant payback is compared with faster methods (straight line and double declining)

A constant payback function $P(t)$ is only justified if a constant income is expected. The MTH-System produces electricity only in the winter during the unloading time. Therefore the payback function $P(t)$ for the MTH-System is rectangular, zero at loading and equal to p at unloading, as shown in the upper function in Figure 6.4. This rectangular function could be represented with a sum of Heavyside step functions:

$$P(t) = p \sum_{y=1}^{T_{life}} \left(H(y - T_{unload}) - H(y) \right) \tag{6.9}$$

Inserted in equation 6.5 the fund $F(t)$ looks as follows:

$$F(t) = e^{R_I t} \left(F_0 - p \sum_{y=1}^{T_{life}} \int_{y-T_{unload}}^{y<t} e^{-R_I t} dt \right) \tag{6.10}$$

with the integrals:

$$\int_{y-T_{unload}}^{y} e^{-R_I t} dt = - \frac{e^{-R_I t}}{R_I} \Bigg|_{t=y-T_{unload}}^{t=y} = - \frac{e^{-R_I y}}{R_I} + \frac{e^{-R_I (y-T_{unload})}}{R_I} \tag{6.11}$$

The behavior of this special kind of sinking fund method with rectangular payback function is also shown in Figure 6.3.

The value of the payback constant p must be chosen so that $F(t = T_{life})$ should be equal to the salvage value. This extraordinary boundary condition enables the calculation of the constant p (capital costs per unloading time) of each plant.

$$p = \frac{e^{R_I T_{life}} F_0 - F(T_{life})}{e^{R_I T_{life}} \sum_{y=1}^{T_{life}} \int_{y-T_{unload}}^{y} e^{-R_I t} dt} \tag{6.12}$$

Figure 6.5 shows the relation between interest rate and capital cost per year as a fraction of the investment capital for several life times. In Figures 6.3 and 6.5, the salvage value is assumed to be 10% of the investment capital. For example, for a plant life time of 16 *years* with an interest rate of 8.5%, a pay back rate of 10% is obtained. The payback function $P(t)$ in equation 6.9 is used for all capital cost contributions in the MTH-System (plants, storage tanks, land). Another situation is given in the case of input electricity, shown in the lower part of Figure 6.4 and described in section 6.3. In the MTH-System the salvage value is assumed to be zero, except the toluene inventory, which has a constant value over time.

6.3 Costs of Input Electricity

As discussed in the sensitivity analyses (chapter 3) the cost and availability of the input electricity represents the major uncertainty in the cost estimation of the MTH-System. Conventional production costs of electricity amount to 0.05-0.10 $\$/kWh$ [83, 84, 85]. Excess summer electricity from hydropower is much cheaper: in Switzerland 0.02-0.04 $\$/kWh$ [43], the marginal cost of electricity production in Canada is 0.015 $\$/kWh$ [86].

During the loading time in the summer, cheap electricity is purchased. The expenses for electricity every year have to be paid back during the unloading time. Therefore the fund $F(t)$ of the input electricity costs is zero at $t = 0$ and should be also zero at the beginning of every operating year. This means the payback function $P(t)$ is negative during the loading time and positive during the unloading time. This special kind of payback is shown in the lower function in Figure 6.4. Calculated with the sinking fund method the objective function kWh-costs (winter electricity) can be split into two parts, the contributions of the input electricity costs

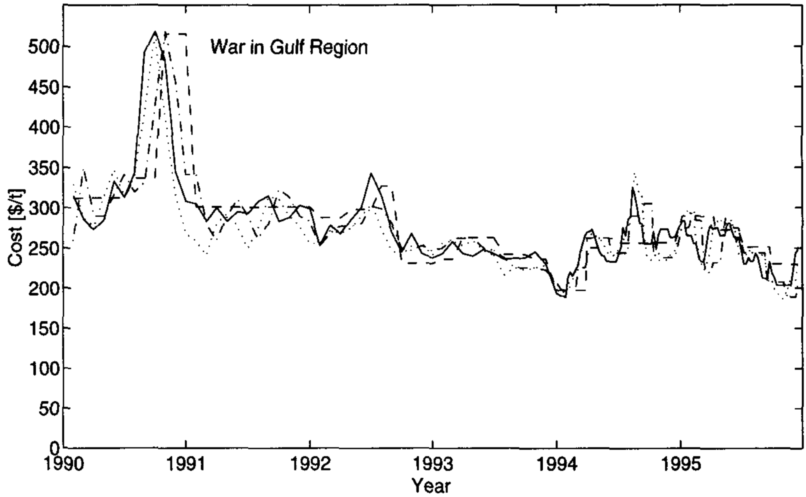

Figure 6.6: Toluene Prices

······· US Spot Market
— · — · — US Contract
——— European Spot Market
- - - - - European Contract

and the specific plant costs $\mathcal{K}_{plant}$ per kWh winter electricity.

$$\begin{aligned}\mathcal{K}_{kWhwinter} &= \frac{\mathcal{K}_{kWhsummer}}{\eta_{tot}}\frac{\int_{\Delta T+T_{load}}^{\Delta T} e^{-R_I t}dt}{\int_{1year-T_{unload}}^{1year} e^{-R_I t}dt} + \mathcal{K}_{plant} \\ &= \frac{\mathcal{K}_{kWhsummer}}{\eta_{tot}}\frac{-e^{-R_I(\Delta T+T_{load})}+e^{-R_I\Delta T}}{-e^{-R_I(1year)}+e^{-R_I(1year-T_{unload})}} + \mathcal{K}_{plant} \\ &= \frac{\mathcal{K}_{kWhsummer}}{\eta_{tot}}1.0253 + \mathcal{K}_{plant}\end{aligned} \tag{6.13}$$

Assuming an interest rate of 5%, a loading time $T_{load} = 3200 hours$ and a unloading time $T_{load} = 4800 hours$ the interest factor of the input electricity costs is equal to 1.0253. The gaps between the loading and the unloading time are assumed to have an equal duration $\Delta T = 1year - T_{load} - T_{unload}$. The total efficiency of the system η_{tot} takes losses in the storage process into account.

6.4 Toluene Costs

In the MTH-System toluene is used in large quantities as hydrogen carrier. The average cost of toluene in US-$ per ton was nearly constant over the last few years. The data in Figure 6.6 are taken from the price reports, which are published regularly in *Chemical Week*. The peak at the end of the year 1990 was caused by the Gulf War. Therefore, it is reasonable to build up the average cost over the time period after April 1991:

US Contract	256 ± 30 $/t	free-on-board
US Spot Market	257 ± 29 $/t	free-on-board
European Contract	262 ± 32 $/t	delivered
European Spot Market	261 ± 29 $/t	free-on-board

The differences between the mean values are very small. The cost of toluene produced on a contract basis may be lower than the market prices above. But for estimation purpose for a Swiss location, the value from the European contract market is selected.

During operation, the value of the toluene inventory is nearly conserved. This means that the salvage value is equal to the initial investment and that only interest must be paid. The operating costs depend on the amount of byproducts produced by dehydrogenation (and hydrogenation) reaction. Thus toluene makeup is required after every MTH-System cycle.

6.5 Land Costs

The land requirement of the MTH-System is relatively high compared with conventional power plants, because the storage tanks need a large area. In Switzerland the land prices are relatively high. The development of the prices of land for industrial use [87, 88, 89] is given in Figure 6.7. A price assumption of 300 SFr/m^2 for the required area is reasonable. In other European countries the prices are much lower, e.g. Germany 28-43 DM/m^2 [90].

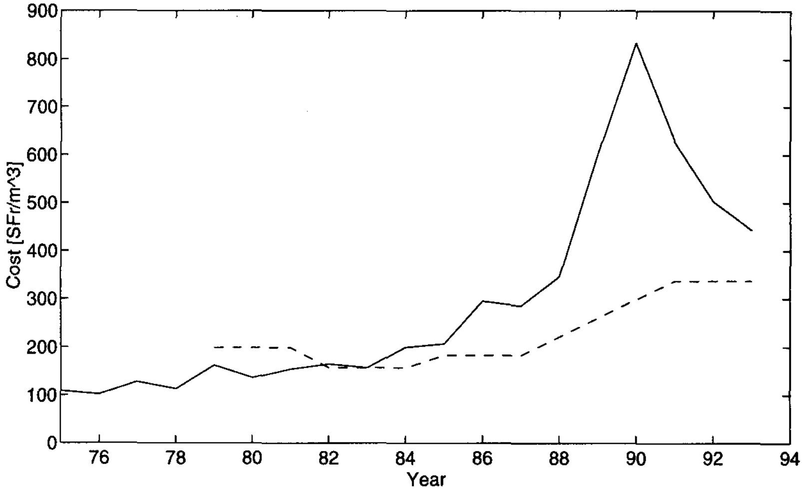

Figure 6.7: Land Cost in Switzerland (SFr = 0.85$, 1995)

——— Canton Zürich

- - - - - - Canton Basel Landschaft

Prices today in Canton Bern: 150-200 SFr/m^2

6.6 Summary

The costing of plant, land and toluene inventory were estimated for Swiss location. Payback strategies were considered for the unique situation of a petrochemical plant generating electricity during winter period (4800 *hours*) only. The sinking fund method is chosen as depreciation strategy so that a yearly constant payback pattern during the life time is guaranteed.

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Chapter 7

Simulation of Summer and Winter Processes

7.1 Summer Process

The flowsheet of the summer process of the MTH-System is shown in Figure 7.1. The sensitivity analyses has shown that the *technical* parameters of the summer process are economically not so important as those of the winter process. However, the summer process includes some *economic* parameters, which strongly influence the total costs and the ecological relevance of the MTH-System. One of them is the cost of the electrolysis, identified in the sensitivity analyses in chapter 3. The latter showed the investment cost of the electrolysis to be one of the most important economic parameters, with the hydrogenation plant being less important for the cost of output electricity.

The technical benefit of hydrogenation arises from the waste heat available from the exothermic reaction, which may be used for separation of the byproducts produced in the dehydrogenation step. Because the heat balance in the winter process is thermodynamically nearly closed, heat is unavailable during that period for a separation process, without diminishing the efficiency of the total system. Therefore it is more efficient to separate the byproducts in summer rather than in winter. During summer enough heat at a sufficiently high temperature level of $250°C$ becomes available. The problems with purification of the toluene from byproducts are discussed in section 5.3.

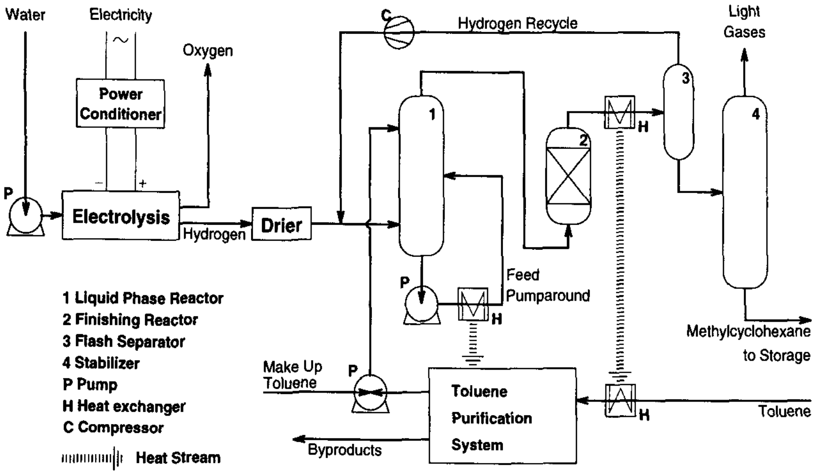


Figure 7.1: Summer Process - Electrolysis, Toluene Purification and Hydrogenation

It is most likely too expensive to convert the overheads from the distillation back to toluene by isomerisation. If they have no value for gasoline use, they have to be completely oxidised. So they contribute to carbon emissions for electricity produced ($\simeq 50 g_{CO_2}/kWh$, assuming 2% byproducts).

7.2 Winter Process

7.2.1 Introduction

The optimisation of the objective function kWh-costs for seasonal storage of electricity results in a decision making problem. The decision tree is shown in Figure 7.2. The conventional approach comprises electricity production from fossil sources during the winter months without storing any summer electricity. Hydropower storage is a strong competitor to the MTH-System, since it offers the additional advantage of peak power production which has a higher economic value than the constant power production in the MTH-System. The three major alternatives are shown in the middle of the decision tree in Figure 7.2. It has been argued before that the MTH-System represents the cheapest way to store electricity on a seasonal basis via

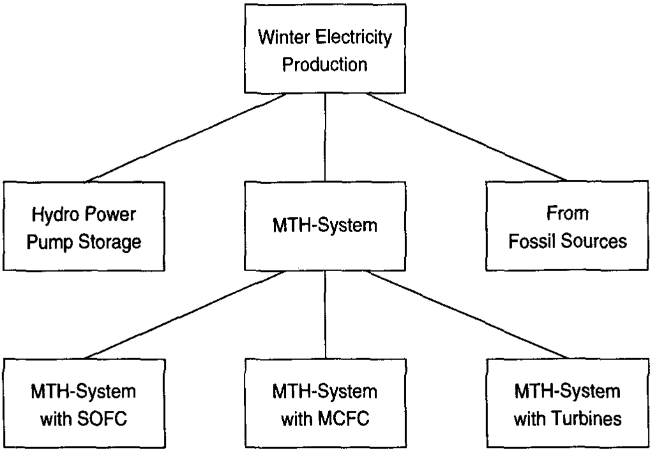


Figure 7.2: Decision Tree for Winter Electricity Production

hydrogen production [35].

The three process alternatives of the MTH-System refer to the reelectrification of the hydrogen. These reelectrification alternatives are considered in detail in the next sections:

MTH-SOFC MTH-System with solid oxide fuel cells (section 7.2.2)

MTH-MCFC MTH-System with molten carbonate fuel cells (section 7.2.3)

MTH-Turbines MTH-System with gas- and steam turbines (section 7.2.4)

Low temperature fuel cells (less than $400°C$) are excluded because it is impossible to use their waste heat in the dehydrogenation plant, which would result in a low overall efficiency.

The calculation of the kWh-costs (objective function) for each process alternative requires simulation and economic estimation. The capital cost calculations employ a sinking fund depreciation with a continuous compound yearly interest of 5%.

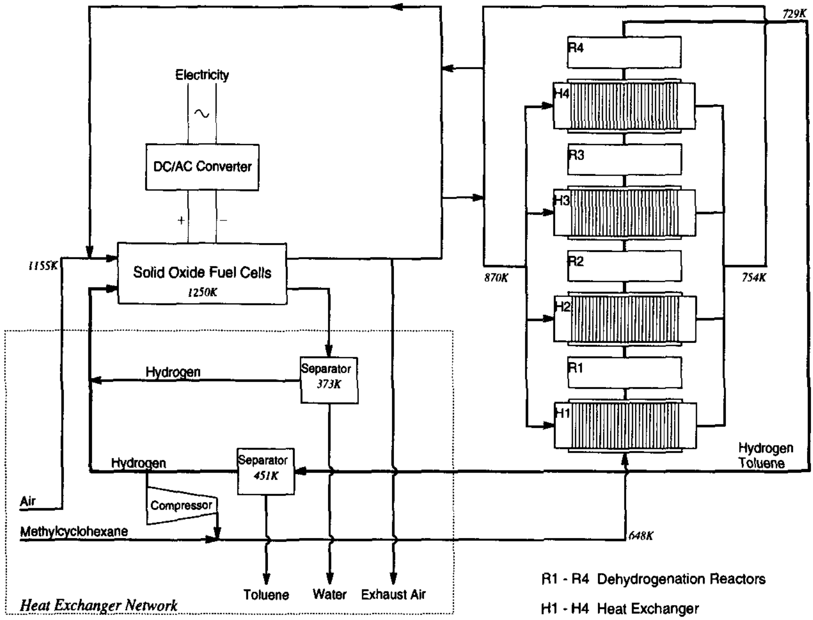


Figure 7.3: Flowsheet of Winter Process combining Dehydrogenation with SOFC

7.2.2 MTH-System with Solid Oxide Fuel Cells

As pointed out in section 5.6.3 the efficiency of the cell process ζ in solid oxide fuel cells is assumed to be 0.82 [73]. Therefore the electrical (direct current dc) efficiency is $\eta_{dc} = 0.61$. A fuel cell system efficiency of 0.96 has to take losses in the fuel cell equipment e.g. dc/ac-converter into account. Multiplied with the direct current efficiency η_{dc}, a total efficiency of $\eta_{pp} = 0.58$ is achievable. A part of the electricity produced is used for the supply of the hydrogen compressor. The remaining energy fraction $1 - \eta_{dc} = 0.39$ dissipates as heat from the irreversible cell reaction. The temperature level of this heat is very high, at the process temperature of $1000°C$. This heat is transferred to the heat exchangers of the dehydrogenation plant.

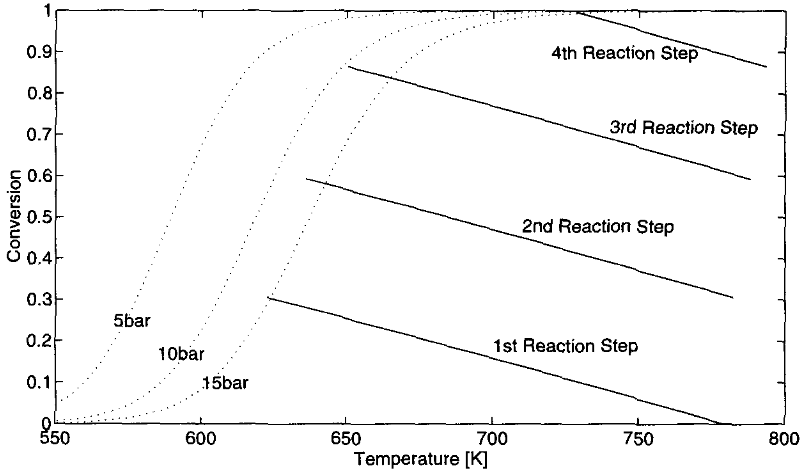


Figure 7.4: Four Reaction Step of Dehydrogenation

The conversion in the four adiabatic reaction step from input (right) to output (left) are shown as a function of the temperature. The dehydrogenation of methylcyclohexane reaches nearly the equilibrium of the pressure at the particular output. The equilibrium curves are shown as dotted lines for different pressures.

Dehydrogenation Plant

The dehydrogenation plant consists of four reaction steps in series operated adiabatically. Each reaction step contains a cross-flow heat exchanger and four fixed bed reactors with a length of 2.42 m and a diameter of 1.17 m. The fixed bed reactors are filled with 1.6mm diameter spherical catalyst particles. Kinetics for the reaction were taken from R.H.Manser [12], section 5.5.1. Figure 7.4 shows the four reaction steps of dehydrogenation of methylcyclohexane to toluene with 99% conversion. The drop in pressure, from 16 *bar* at the feed to 5.2 *bar* after the last dehydrogenation step, shifts the equilibrium to lower temperatures. Some examples of equilibrium curves are shown as dotted lines in Figure 7.4.

The four heat exchangers are heated by a part of the hot air stream from the fuel cells. The splitting ratio of this hot air stream allows regulation of the conversion to 99%. After heating up the feed for the reactors the heating stream is split into two parts (see flowsheet Figure 7.3). One fraction of this stream leaves the cycle going

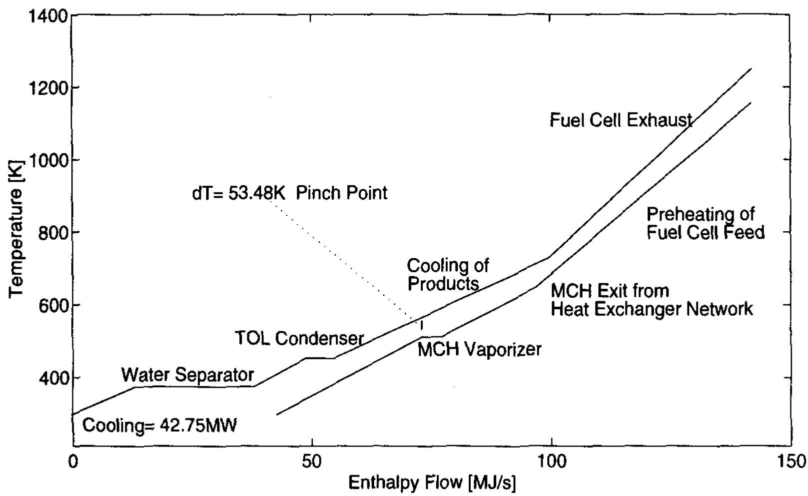


Figure 7.5: Pinch Analysis of the Heat Exchanger Network

back to the fuel cells, the other part returns to the reactors mixed with hot air from the fuel cells. A fraction of the hydrogen produced has to be recycled to the feed stream in order to avoid deactivation of the catalysts. This arrangement of heating streams enables the transfer of the high temperature heat to a lower temperature level with minimal losses.

Heat Exchanger Network

Pinch analysis [91] is the suitable method for analysing the heat exchanger network outlined in Figure 7.3 by balancing with respect to temperature level the heat transfer processes between output streams providing heat (reactor products, fuel cell exhaust; total available heat 143 MJ/s) and input streams accepting heat (MCH feed, fuel and air to the fuel cell; total heat requirement 100 MJ/s). The purpose of this pinch analysis was to determine the total heat exchange of the heat exchanger network. In the cold composite curve the heat requirement for all input streams are added for each temperature increment (lower curve in Figure 7.5). The same addition is used for the hot composite curve, which contains the heat supply of the output streams to the heat exchanger network. The results (composite curves) presented in Figure 7.5 show *that the methylcyclohexane (MCH) feed is preheated* to the reactor temperature by heat rejected from the reactor products. The pinch point reflects the minimal temperature difference between the methylcyclohexane (MCH) feed vaporiser and the reaction product cooling. The hydrogen and the air are passed to the fuel cell and raised to a temperature of $1155K$ with exhaust air from the fuel cell. It is assumed in the calculations that 4% of the exchanged heat in the heat exchanger network would be lost. The pinch analysis shows that the preheating of the input streams needs no additional heat from the fuel cell. There are enough heat streams at sufficient temperature levels available for preheating the input streams. Therefore a total efficiency of 0.58 in the fuel cells could be reached. Most of the required cooling is caused by the condensing water from the fuel cell reaction exhaust.

Cost Estimates from MTH-SOFC Simulation

The overall efficiency of this system alternative reaches 0.399, with a winter efficiency of 0.549. The output electricity costs amount to 0.262 $\$/kWh$. In terms of equation 6.13 the costs of the output electricity are estimated from the following equation:

$$\mathcal{K}_{kWh_{winter}} = \frac{\mathcal{K}_{kWh_{summer}}}{0.399} 1.025 + 0.187\$/kWh \qquad (7.1)$$

While the first term expresses the cost contribution of the input electricity, multiplied with the interest factor 1.025, the specific plant cost is 0.187 \$/kWh.

7.2.3 MTH-System with Molten Carbonate Fuel Cells

These fuel cells operate also at a very high temperature ($650°C$), which makes the heat integration of the dehydrogenation feasible. The main problem of integrating molten carbonate fuel cells in the MTH-System lies in its use of CO_3^{2-} as transfer ions. This implies a nearly closed recycle of CO_2. The remaining hydrogen in the exhaust stream of the fuel side of the cell must be separated from CO_2 and water. Then CO_2 is transferred to the input stream to the fuel cells air side (Figure 7.6). During the electrochemical reaction in the cell, CO_2 diffuses in form of CO_3^{2-} ions through the carbonate matrix to the fuel side of the cell. It is too difficult to separate the remaining CO_2 from nitrogen and oxygen in the stream leaving from the air side of the cell. Thus the remaining CO_2 is lost from the system. A lower loss of CO_2

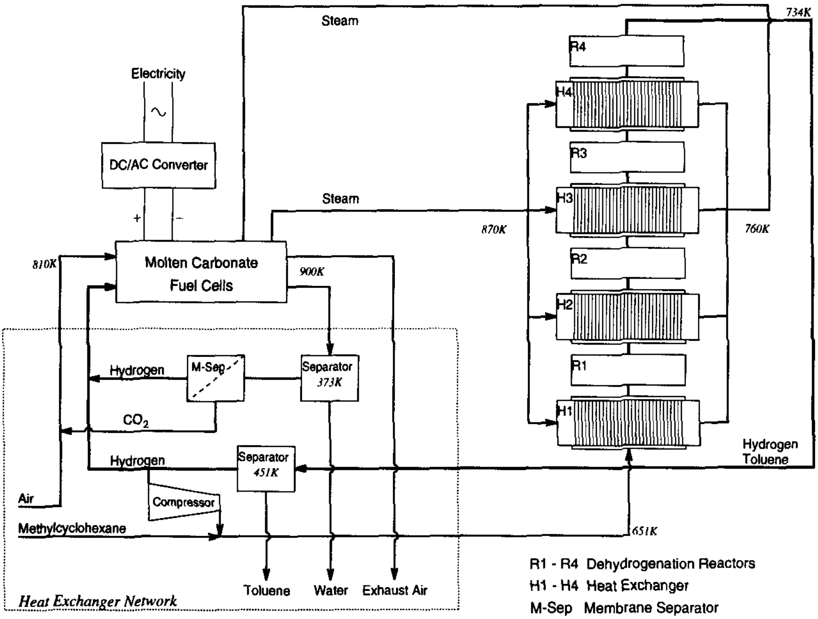


Figure 7.6: Flowsheet of Winter Process combining Dehydrogenation with MCFC

implies a lower partial pressure of CO_2 on the air side of the fuel cell, which results in a lower cell voltage and a lower efficiency. To close the CO_2 balance of the system, the loss of CO_2 from the system is equal to the available CO_2 from the combustion of the byproducts produced in the dehydrogenation step. The available CO_2 is produced only in limited quantity. Therefore the efficiency of the molten carbonate fuel cells is significantly lower than that of the solid oxide fuel cells and depends on the available CO_2 from the oxidised byproducts. The numerical calculation of the efficiency is given in section 5.6.4. The efficiency of the dc/ac-converter is 0.96, equal to that in the solid oxide fuel cells.

Dehydrogenation

By virtue of the similarity between the MTH-System with solid oxide fuel cells and the MTH-System with molten carbonate fuel cells, the dehydrogenation plant also consists of four reaction steps with a cross-flow heat exchanger and four fixed bed

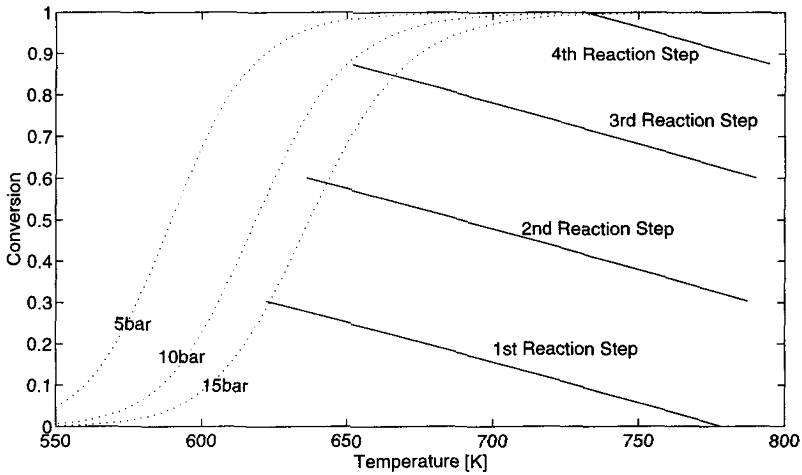


Figure 7.7: Conversion in Four Reaction Steps of Dehydrogenation heated from MCFC

reactors (length 2.42 m and diameter 1.17 m). The kinetics for the reaction are described in section 5.5.1. Figure 7.7 shows the four reaction steps of the adiabatic dehydrogenation with interstage heat exchange to satisfy the endothermic heat of reaction. Steam produced with the waste heat from the molten carbonate fuel cells supplies the heat required for the dehydrogenation plant.

Heat Exchanger Network

The heat exchanger network resembles that of the MTH-System with SOFC described in section 7.2.2. In the cold composite curve of the pinch analysis in Figure 7.8, the heat requirements for all input streams are added for each temperature increment. The same addition is done for the hot composite curve, which contains the heat supply of the output streams to the heat exchanger network. The MCH-feed is preheated to the reactor temperature of 651 K by heat rejected from the reactor products. The temperature difference at the pinch point exceeds that in the MTH-System with SOFC. The hydrogen and the air are passed to the fuel cell and raised to a temperature of 810 K with exhaust air from the fuel cell. Losses of 4% in the heat exchanger network are taken into account.

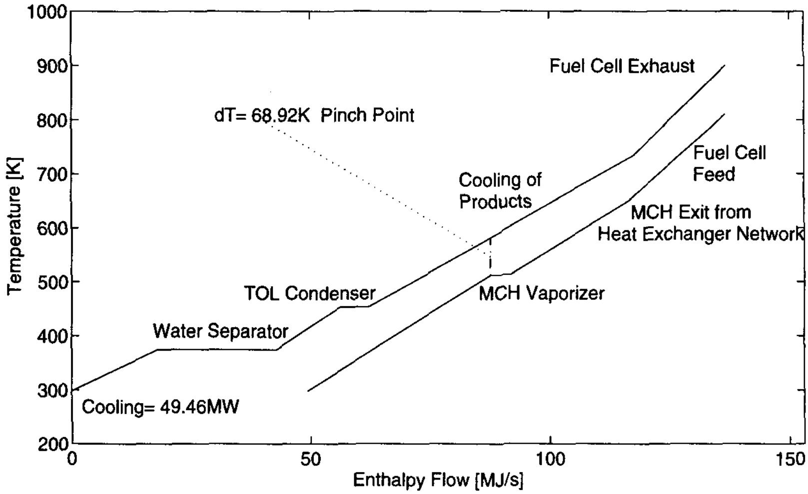


Figure 7.8: Pinch Analysis of the Heat Exchanger Network for MTH-MCFC

Because of the lower efficiency (more waste heat available than in the SOFC case) of the molten carbonate fuel cells, the heat balance of the system closes more easily. This fact also results in the higher temperature difference at the pinch point.

Cost Estimates from MTH-MCFC Simulation

Even though molten carbonate fuel cells will have lower investment costs (1000 $\$/kW$ [38]) than solid oxide fuel cells (1500 $\$/kW$ [38]) based on mature technology, the costs of the output electricity is higher, amounting to 0.296 $\$/kWh$, Table 7.1. This is a result of the lower overall efficiency of 0.332. Therefore the cost of one kWh of winter electricity produced with the MTH-System with MCFC amounts to

$$\mathcal{K}_{kWh_{winter}} = \frac{\mathcal{K}_{kWh_{summer}}}{0.332} 1.0253 + 0.206\$/kWh \tag{7.2}$$

7.2.4 MTH-System with Gas and Steam Turbines

Figure 7.9 shows the complete winter process of the MTH-System with turbine technology. It consists mainly of the gas turbine, dehydrogenation plant, steam turbine

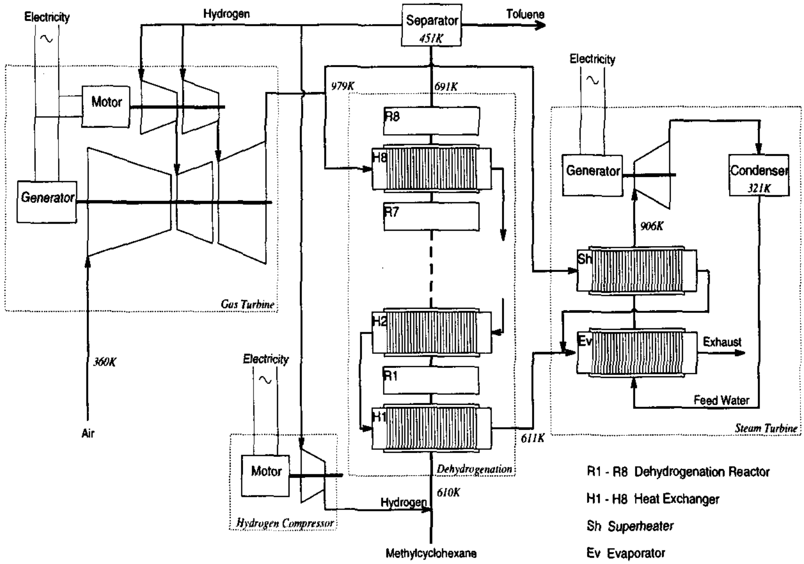


Figure 7.9: Integration of Gas and Steam Turbine in the MTH-Winter Process

and hydrogen compressor. The hydrogen produced in the dehydrogenation reactors is injected into the gas turbine. One part of the exhaust gases (80%) passes to the dehydrogenation plant to supply heat for the endothermic reaction. Because of the lower temperature level of this heat (compared with SOFC and MCFC), eight steps of heat exchanger and adiabatic reactor are necessary to dehydrogenate the methylcyclohexane. The rest (20%) is supplied to the superheater of the steam turbine. After heating the dehydrogenation reactors and superheating steam, the exhaust gases enter into the evaporator of the steam turbine to preheat and vaporise the feedwater. Recirculating a part of the produced hydrogen to the methylcyclohexane feed requires a hydrogen compressor. While gas and steam turbines are producing electricity, the hydrogen compressor consumes part of it.

The flow of the air/exhaust through the system gas turbine - dehydrogenation plant - steam turbine plant is shown in Figure 7.10. First, the air and the hydrogen fuel are compressed in the gas turbine. After the first injection and combustion of hydrogen and subsequent expansion, the remaining hydrogen is injected for a second combustion and expansion to atmospheric pressure. Most of the mechanical work

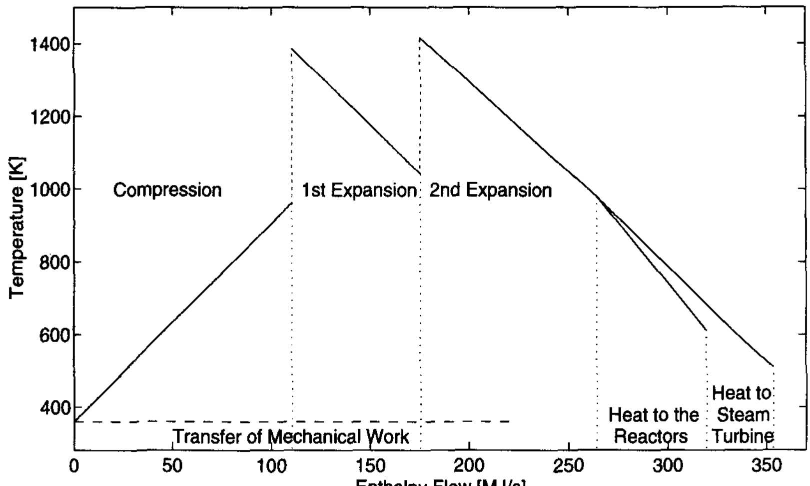


Figure 7.10: Thermodynamic Overview of the MTH-Turbine System

of the expansion parts of the gas turbine gets utilised for the air compression. This transfer of mechanical work is marked with a dashed line in Figure 7.10 (length: twice as the compression work). The mechanical work that is not used by the compression of the air is available for electricity production. At medium temperature, the heat of the exhaust from the gas turbine is split up and transferred to the dehydrogenation plant (80%) and to the superheater (20%). The remaining heat at low temperature supplies the evaporator of the steam turbine.

Gas Turbine

A gas turbine with two injection points was used in the simulation. After partial pressure reduction (1st expansion in Figure 7.10) of the combustion gases, the second part of the available hydrogen is injected to the turbine. Then the combustion gases are expanded further (2nd expansion in Figure 7.10) to atmospheric pressure. Figure 7.11 shows the TS-plot of the gas turbine. The exhaust temperature of the turbine exceeds that in normal operation, e.g. gas turbine in a combined cycle plant. This high temperature level of 979 K is necessary to supply the dehydrogenation reactors with heat.

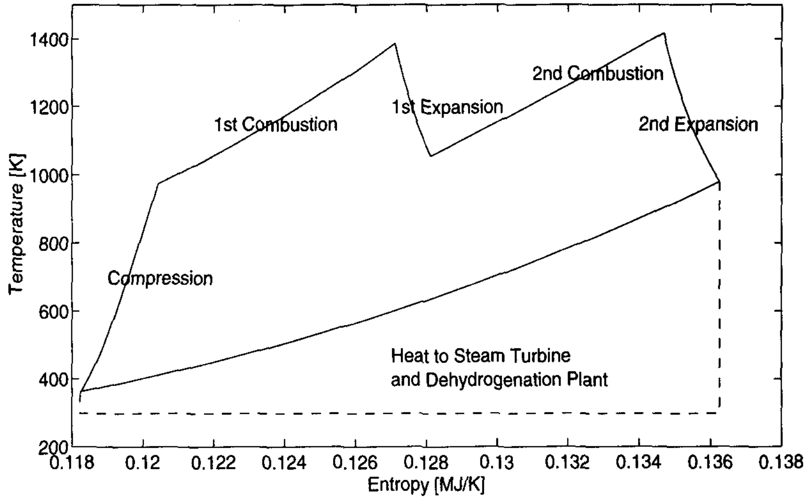


Figure 7.11: Gas Turbine with two Injection Points

Dehydrogenation

Eight adiabatic dehydrogenation reactors in series are capable of converting nearly all of the methylcyclohexane to toluene. The operation of these eight reactors is shown in Figure 7.12. The reactors consist of a relatively shallow fixed bed (0.2-0.3 m) with a cross-section of 21 m^2 which may be arranged in a radial flow reactor. Because kinetics, and not equilibrium limits the reaction rate in the last reactor (Figure 7.12 shows the gaps between the equilibrium curve and the conversions at the reactor outputs), it has a deeper fixed bed with a depth of 1.2 m to convert nearly all of the methylcyclohexane. The dotted lines represent the equilibrium of the dehydrogenation reaction at different pressure. Methylcyclohexane is fed to the dehydrogenation plant together with hydrogen (ratio 1:4) at a pressure of 5.5 bar. The product stream leaves the plant at a pressure of 5.1 bar. The reason for using eight instead of four reaction steps (as used in the fuel cell cases) is a lower temperature level of the available heat. The reactors are operated at lower temperatures (compare Figure 7.12 with Figure 7.7). In addition, the pressure of the feed stream is adjusted to only 5.5 bar instead of 16 bar, to achieve high equilibrium conversion at lower temperatures.

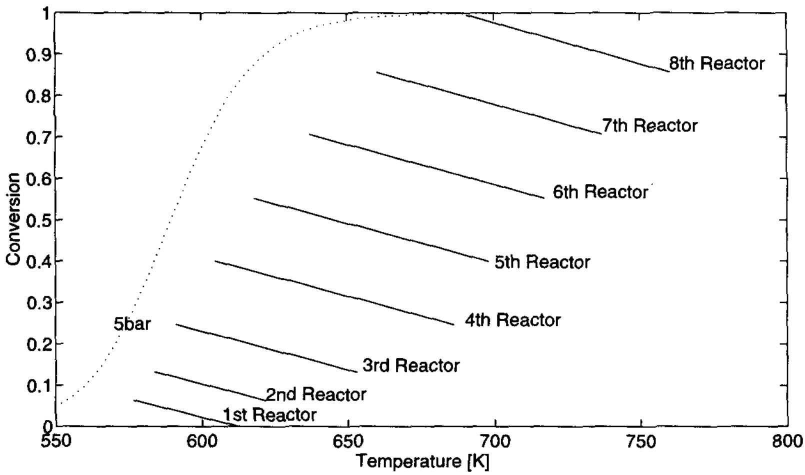


Figure 7.12: Conversion in Eight Dehydrogenation Reactors heated with Exhaust from the Gas Turbine

Steam Turbine

The lower part of Figure 7.13 shows the enthalpy-entropy diagram of the steam turbine cycle. The upper one shows the temperature-entropy (TS) plot. The dotted line on both parts of Figure 7.13 represents the saturation line of steam and water.

Feedwater (9.5 kg/s) is pumped at 35 bar to the evaporator. After evaporation it is superheated to a temperature of 906 K. Finally the dry steam is expanded to a pressure of 0.1 bar. This low pressure implies a low condensing temperature of 321 K.

Preheating

In Figure 7.14 heat exchanges are shown in the pinch analysis representation. Methylcyclohexane (MCH) feed is preheated (lower curve in Figure 7.14 left) by the product stream containing toluene and hydrogen (upper curve). Hydrogen is removed from the product stream at the toluene (TOL) condenser. The right side of Figure 7.14 shows the pinch analysis of the heat exchange to the steam turbine. The hot stream

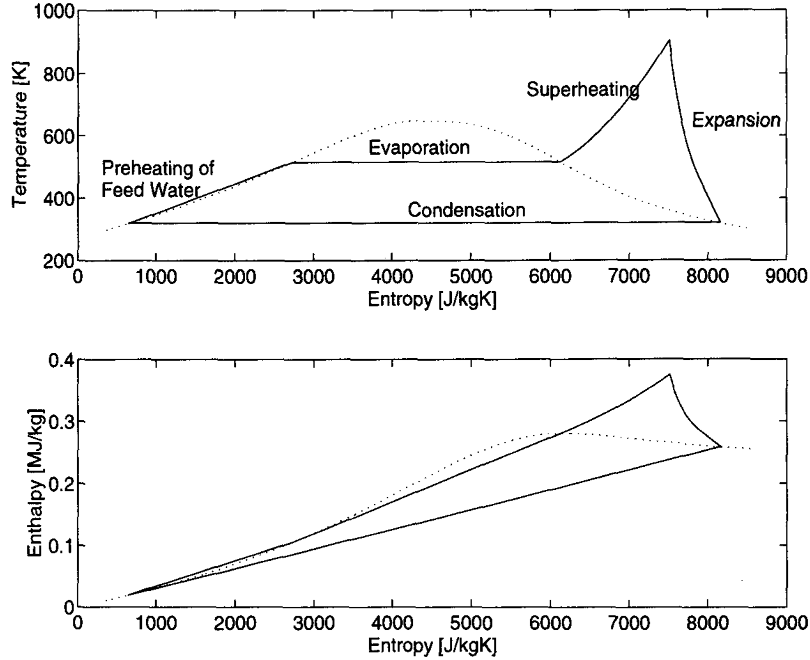
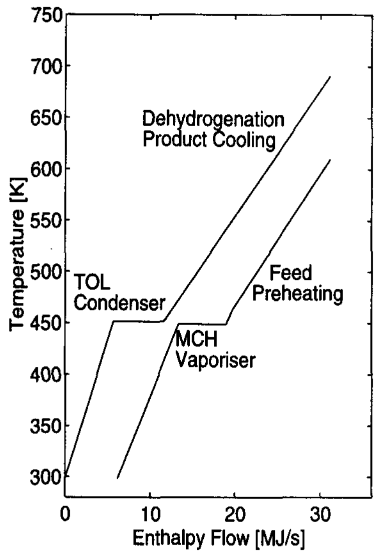


Figure 7.13: Steam Turbine with Decreased Condensing Pressure

contains a part (20%) of the hot exhaust gases from the gas turbine at a temperature of 979 K and the whole exhaust stream from the gas turbine at lower temperature of 611 K including the heat of water condensation in the combustion product of the gas turbine. The heat requirements of the steam turbine are shown in the lower curve of the right side in Figure 7.14. It contains the preheating of the feedwater, its vaporisation and the superheating of the steam.

Cost Estimates from MTH-Turbines Combination

The integration of gas and steam turbines for electricity production in the winter process of the MTH-System leads to a total system efficiency of 24.8%. The winter process itself has an efficiency of 34.3%. Because the investment costs of the gas- and steam turbine process are relatively low, the total cost is 0.361 $\$/kWh$ for the



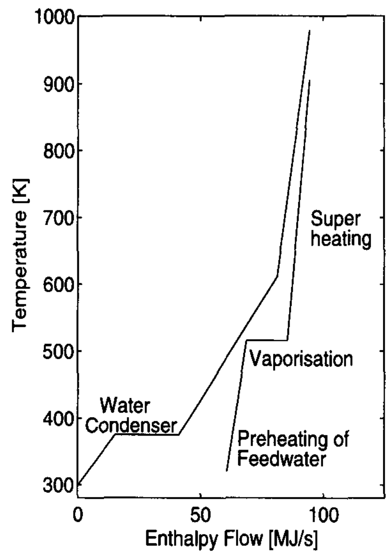


Figure 7.14: Heat Exchange in the MTH-Turbines System

left side: preheating of methylcyclohexane with the reaction products, right side: heat transfer of the gas turbine exhaust to the steam turbine.

stored winter electricity. The costs of the output electricity as a function of the summer electricity costs are expressed by the following equation:

$$\mathcal{K}_{kWhwinter} = \frac{\mathcal{K}_{kWhsummer}}{0.248} 1.0253 + 0.241\$/kWh \tag{7.3}$$

7.3 Economic Comparison of MTH-Alternatives

The values given in Table 7.1 are based on a byproduct rate of 2% and a price of 0.26 $\$/kg$ for the makeup toluene. Since both summer process and input electricity (320 MW at 3200 hours) are equal for each design alternative presented in Table 7.1, power output becomes proportional to winter efficiency as well as to total efficiency. The MTH-System with solid oxide fuel cells shows the highest overall efficiency of 0.40. But it also represents the alternative with the highest total annual costs (107 $M\$/year$). Nevertheless lowest specific electricity costs (0.26 $\$/kWh$) are reached. According to the optimisation of the objective function kWh-costs, the MTH-System with solid oxide fuel cells is the optimal alternative. On the other hand, the assumptions on fuel cell's specific investment cost are uncertain, because they are based on predictions (MCFC: 1000 $\$/kW$ and SOFC: 1500 $\$/kW$ [38]).

MTH-System with	SOFC	MCFC	Turbines
Power Output $[MW]$	85.1	70.9	53.0
Total Efficiency	0.40	0.33	0.25
Winter Efficiency	0.55	0.46	0.34
Total Investment $[M\$]$	699	645	582
Annual Plant Capital Costs $[M\$/year]$	44.6	40.8	35.6
Annual Working Capital Costs $[M\$/year]$	1.6	1.5	1.3
Annual Land Costs $[M\$/year]$	1.4	1.4	1.4
Annual Operating Costs $[M\$/year]$	28.7	26.5	22.9
Annual Input Electricity $[M\$/year]$	30.6	30.6	30.6
Total Annual Costs $[M\$/year]$	106.9	100.8	91.8
Specific kWh-Costs $[\$/kWh]$	0.26	0.30	0.36

Table 7.1: Economic Comparison of Winter Electricity Production Alternatives Investigated

This is a typical case of decision making under uncertainty, since the probabilities (cost and efficiency) of future fuel cell development are unknown. Today, the MTH-System combined with gas- and steam turbine process represents the only industrially realizable technology.

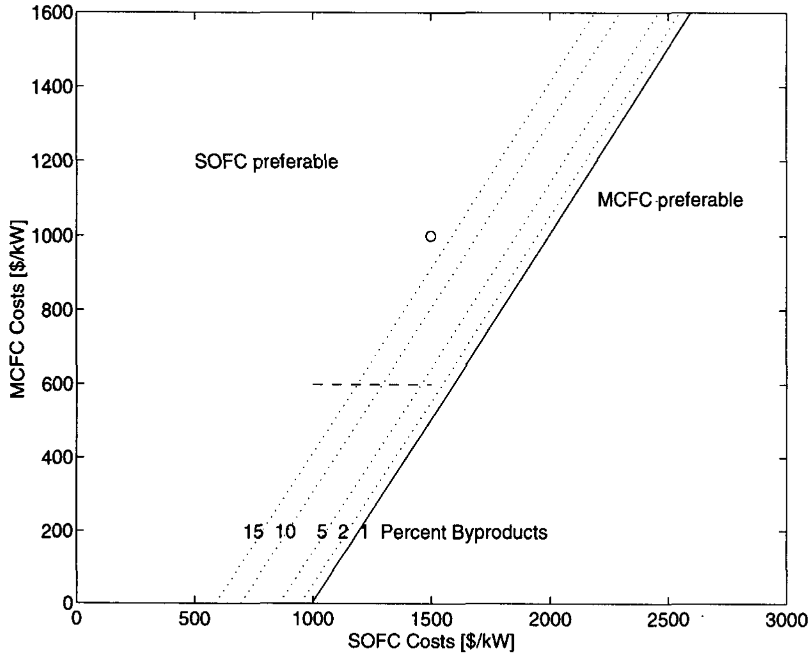


Figure 7.15: Decision Lines due to kWh-Costs Minimisation

The future cost estimates are taken from: - - - - - Blomen, Mugerwa [92]; o Srinivasan et al. [38] assumptions in section 5.6.5

7.4 SOFC versus MCFC

The molten carbonate fuel cell shows a lower efficiency that depends strongly on the available CO_2 from the byproducts. To reach the optimal decision, the influence of input parameter changes dI on the kWh-costs must be considered via the approach of the sensitivity analyses (chapter 3):

$$d\mathcal{K}_{kWh} = \nabla\mathcal{K}_{kWh} \cdot \mathbf{dI} = \sum_i \frac{\partial\mathcal{K}_{kWh}}{\partial I_i} dI_i \tag{7.4}$$

$\nabla\mathcal{K}_{kWh}$ denotes the gradient deduced from the sensitivity analyses in chapter 3. Focusing on changes in the fuel cell investment costs $I_{K_{FC}}$ and efficiency $I_{\eta_{FC}}$ results in

$$\mathcal{K}_{kWh} = \mathcal{K}_{kWh}^{ref} + \frac{\partial\mathcal{K}_{kWh}}{\partial I_{K_{FC}}} dI_{K_{FC}} + \frac{\partial\mathcal{K}_{kWh}}{\partial I_{\eta_{FC}}} dI_{\eta_{FC}} \tag{7.5}$$

	MTH-SOFC	Hydro-Project	
Summer Energy to Storage $[GWh/year]$	1024	1090	1480
Winter Energy from Storage $[GWh/year]$	410	1040	1040
Storage Efficiency	0.40	0.95	0.70
Investment $[M\$]$	699	2300	2300
Annual Costs $[M\$/year]$	107	219	215
kWh-Costs $[\$/kWh]$	0.26	0.21	0.22

Table 7.2: Economic Comparison of the MTH-System with a new Hydropower Project

The MTH-System with solid oxide fuel cells (SOFC) with an efficiency of 0.58 and specific investment costs of 1500 $\$/kW$ serves as the reference case. To compare MCFC and SOFC integrated into the MTH-System, it is necessary to calculate the decision line of equal kWh-costs in a plot of MCFC versus SOFC specific investment costs (Figure 7.15). The decision line, which depends on the available byproducts, follows the equation:

$$\frac{\partial K_{kWh}}{\partial I_{K_{SOFC}}} dI_{K_{SOFC}} = \frac{\partial K_{kWh}}{\partial I_{K_{MCFC}}} dI_{K_{MCFC}} + \frac{\partial K_{kWh}}{\partial I_{\eta_{MCFC}}} dI_{\eta_{MCFC}} \tag{7.6}$$

The term containing the SOFC efficiency η_{SOFC} vanishes because the latter remains constant and serves as the reference value. The last term in the linear equation 7.6 is a constant, which depends only on the MCFC efficiency η_{MCFC}, or equivalently, on the available CO_2 from the oxidised byproducts. Figure 7.15 shows the decision between SOFC and MCFC. A cost estimation pair (MCFC and SOFC investment costs) on the right-hand side of the decision line means that MCFC is preferable in the MTH-System from an economic viewpoint, and on the left-hand side that SOFC is preferable. For example the assumption in section 5.6.5, 1000 $\$/kW$ for MCFC and 1500 $\$/kW$ for SOFC [38], lies on the left-hand side of the decision line (designated by $\circ$ in Figure 7.15). Therefore the SOFC integration in the MTH-System is superior to the MCFC, even though this technology is more expensive.

7.5 Comparison with Conventional Alternatives including a CO_2-Tax

The MTH-System alternatives should be compared economically with other methods of winter electricity production shown in Figure 7.2. Economic analyses show that electricity from new hydro power plants (Grimsel West) costs 0.21 $\$/kWh$ [35], which is comparable to the best alternative of the MTH-Systems (MTH-SOFC) with 0.26 $\$/kWh$, listed in Table 7.2. In spite of the lower efficiency of the MTH-System, 0.40 versus 0.95 for hydropower production, the relatively lower specific investment allows the decentralised MTH-System to provide electricity at about the same cost as a new hydropower project. The efficiency of 0.95 results for a project in which hydraulic pump storage and hydropower storage are combined in a system of several lakes and water sources. For pure hydropower pump storage an efficiency of 0.7 is more realistic. This efficiency is equal to the product of the efficiencies of particular production steps: motor drive $\eta_{motor} = 0.96$, pump $\eta_{pump} = 0.85$, water losses $\eta_{loss} = 0.99$, Pelton turbine $\eta_{Pelton} = 0.9$, generator $\eta_{elec} = 0.85$ The results based on the same plant show that the influence of the lower efficiency on the output electricity costs (0.22 $\$/kWh$) is insignificant.

However, the MTH-System (50 g_{CO_2}/kWh) must also compete with conventional fossil-fuelled power plants, which suffer the disadvantage of producing CO_2 in large quantities (300-800 g_{CO_2}/kWh). In consequence, governments in different countries are considering regulating CO_2-emissions by a carbon tax. This tax should internalise the cost of damages caused to the environment. The suggestions for carbon taxes range between 2 $\$/t_{CO_2}$ and 100 $\$/t_{CO_2}$ [93].

Gas turbines, coal power plant and gas-fed fuel cells represents alternatives to the MTH-project for the production of winter electricity. The fact that the fossil-fuelled power plants produce more CO_2 could be taken into account with a theoretical CO_2-tax or a general energy tax on imported fuels and electricity from not renewable sources. For simplicity, the following considerations employ a CO_2-tax. Same assumptions for the economical relevant parameters must be used as in the MTH-System. Therefore the operating time lasts 4800 *hours* per year in winter and the total annual operating costs amount to 15% of the investment costs (interest rate 5%, depreciation 5%, maintenance 5%). All of the alternative plants are combined cycle plants. This gives rise to the relatively high efficiencies.

The specific investment costs of the gas turbine (combined cycle plant) are assumed to be 800 $\$/kW$ at an efficiency of 58% [94]. For fuel cells the same future cost predictions as in section 7.3 are assumed (MCFC: 1000 $\$/kW$ and SOFC: 1500 $\$/kW$). The feed gas costs 0.019 $\$/kWh$ [95]. The electrical efficiencies of the fuel cells integrated in combined cycle plants are 70% (MCFC) and 80% (SOFC) [73]. The combined coal gasification power plant with a net power efficiency of 45% costs

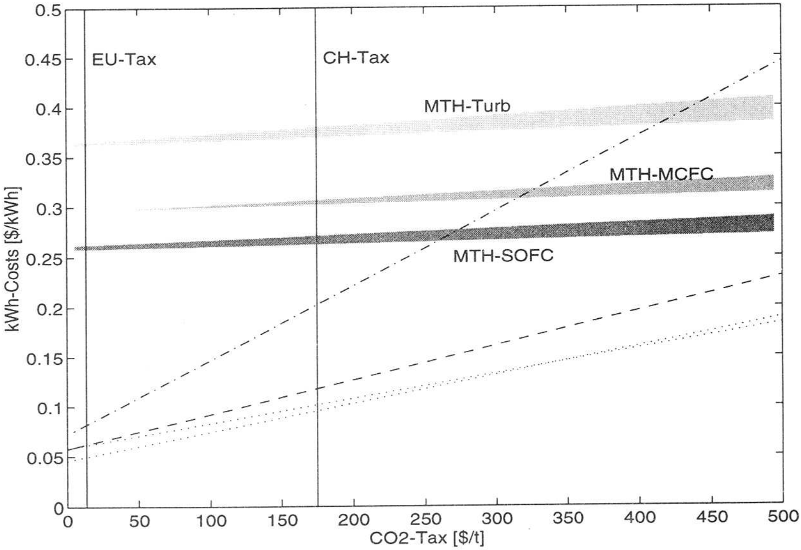


Figure 7.16: Comparison of Conventional Electricity Costs (Mature Technology) as a Function of a CO_2-Tax and the MTH Storage Systems

shade: MTH-Projects (Byproducts 1-2%)
- - - - - - Gas Turbine
— · — · — Coal Power Plant
· · · · · · · Fuel Cells fed with Gas
——— Tax Proposal (EU and Switzerland)

1830 $\$/kW$ [96]. The price of the coal on the import market is 0.054 $\$/kg$ [97].

The production rate of byproducts in the MTH-project lies between 1 and 2% (Table 7.1 refers to 2% assumed byproducts). This constitutes the only CO_2-source of electricity production with the MTH-System, assuming that the input electricity is produced from renewable energy sources (hydropower).

The kWh-costs as a function of a CO_2-tax for the several alternatives appear in Figure 7.16. The steep increase of kWh-costs of the combined coal gasification power plant depending on the CO_2-tax results from low efficiency and high carbon content of coal. Therefore those plants do not provide serious competition in an electricity market regulated by a CO_2-tax. The MTH-System alternatives must compete with combined cycle plants based on gas turbines or fuel cells (dotted lines in Figure

7.16). It is evident that the MTH-System would be economically competitive to the other alternatives only if an energy tax comparable to a CO_2-tax of more than 600 $\$/t_{CO_2}$ were to be introduced.

An economic analysis by the Paul Scherrer Institute calculates the marginal CO_2-tax to pursue the recommendations of the Toronto conference (i.e. 50% reduction of CO_2-emissions by the year 2050). To reach this goal in Switzerland, average costs of 270-350 SFr/ton_{CO_2} are necessary [98]. On the other hand, the EU proposed a tax of $13.3\$/t_{CO_2}$ (=9.4ecu) [99], and the Swiss government a maximum tax of $175\$/t_{CO_2}$ (=$210SFr$) [100]. However, it is uncertain whether these taxes will be implemented in the near future. Even with implementation, conventional base load winter electricity production costs would be one third of those of the MTH-System; however, summer hydroelectricity is not stored.

The comparison with the hydro power pump storage shows that the MTH-System competes economically on a seasonal storage basis (i.e. when the duration of the winter process is 4800 hours). But the hydropower pump storage carries the advantage of short term electricity production and storage (instead of the constant power during 4800 hours from the MTH-System) which has a higher economic value.

7.6 Best-Case Study

The cost data of many plants described in chapter 5 are uncertain. To estimate the potential of the MTH-System in a long-term future (20-50 years), some optimistic technical and economic assumptions are made for the best-case analysis:

- Pure MCH feed to the dehydrogenation plant eliminates the hydrogen compressor, which saves investment and electricity in the winter process
- Higher efficiency of SOFC $\eta = 0.65$ ($\zeta = 0.88$ [73])
- Higher efficiency of electrolyser $\eta = 0.75$ (LHV) 4.0 $kWh/m_n^3H_2$ [40]
- Lower SOFC costs 1100 $\$/kW$ [76]
- Lower electrolyser costs 250 $\$/kW$ [40]
- Insignificant amount of byproducts; the toluene purification will be obsolete

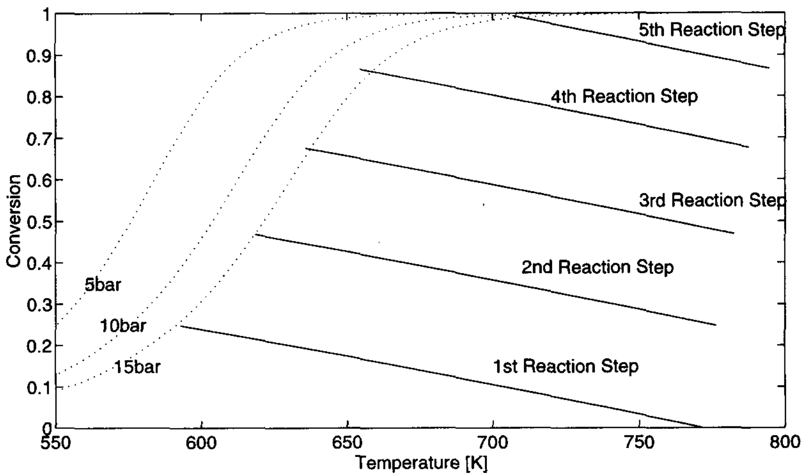


Figure 7.17: Five Reaction Steps of Dehydrogenation

- Lower heat loss in the heat and mass transfer equipment (1% instead of 4%)

The flowsheet of this plant remains the same as in the SOFC case (shown in Figure 7.3), but without the hydrogen compressor and the recycle of hydrogen to the dehydrogenation plant.

7.6.1 Modelling of the Dehydrogenation Plant

Because of the lower heat capacity of the feed (pure MCH without additional hydrogen), the dehydrogenation plant consists of five reaction steps. Each reaction step contains a cross-flow heat exchanger and four fixed bed reactors with a height of 2 m and a diameter of 1.15 m.

7.6.2 Heat Exchanger Network

It is assumed that only 1% of the exchanged heat in the heat exchanger of the dehydrogenation plant is lost. The results (Composite Curve) presented in Figure

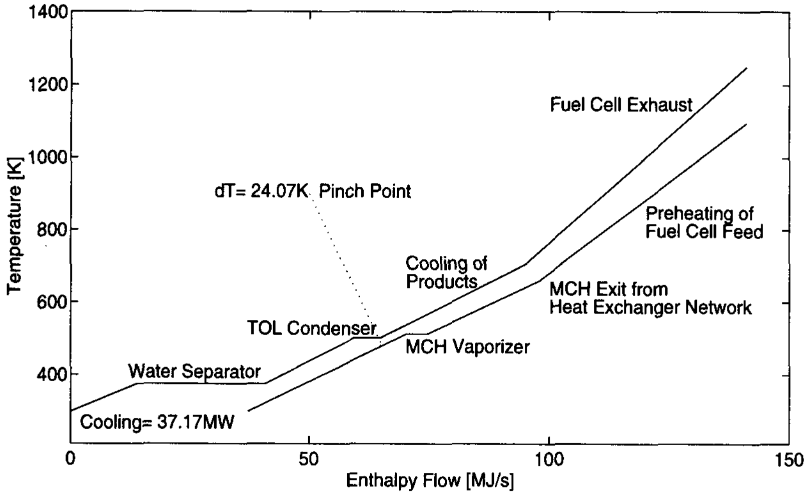


Figure 7.18: Pinch Analysis of the Heat Exchanger Network

7.18 show that heat rejected from the reactor products preheats the MCH-feed to the reactor temperature. The temperature difference at the pinch point (between the methylcyclohexane feed vaporiser and the reaction product cooling) is much smaller than that in the MTH-System with SOFC, Figure 7.5 in section 7.2.2. The hydrogen and the air are passed to the fuel cell and raised to a temperature of 1175 K with exhaust air from the fuel cell.

Even though the fuel cell exhibits a very high efficiency ($\eta_{pp} = 0.65$) and does not produce much heat, the heat balance can be closed with the assumption that only 1% of the transferred heat would be lost.

7.6.3 Results

The overall efficiency of this system alternative comes to 0.475 with a winter efficiency of 0.625. The output electricity costs amount to 0.166 $\$/kWh$. According to equation 6.13 the lowest possible costs of winter electricity produced with the MTH-System are:

$$\mathcal{K}_{kWhwinter} = \frac{\mathcal{K}_{kWhsummer}}{0.475} 1.0253 + 0.103\$/kWh \tag{7.7}$$

These output electricity costs lie in an economically reasonable range for winter electricity. With increasing importance of seasonal storage of electricity due to the enhanced use of renewable energy primary sources like solar energy, the MTH-System may stand an economic chance in a long-term future.

Leer - Vide - Empty

Chapter 8

Experimental Part: Pd-Ag Membranes for Hydrogen Separation

8.1 Introduction

In hydrogen energy applications where purity is important, e.g. in fuel cells, hydrogen separation represents a critical technology. The growing significance of membranes arises from their property of separating mixtures with an energy-efficient process. Membranes can conveniently be up- and downsized and their investment costs are mainly linear to plant capacity. For practical use, the membrane has to be installed in a suitable module. The prevention of leakages in the membrane and its module is a major problem of membrane technology development. Additional problems such as durability, regenerability and costs in relation to other system components have to be solved too.

A highly efficient way to separate high purity hydrogen from other gases are palladium based membranes, e.g. *Pd-Ag*, *Pd-Cu*, based on their application by Johnson-Matthey for 99.9999% purity of the produced hydrogen in the electronics industry. These metallic membranes have no pores and are impermeable for gases except hydrogen.

Hydrogen H_2 is dissociated catalytically into two H^+-ions and electrons at the upstream side of the membrane and recombines as gaseous H_2 at the downstream

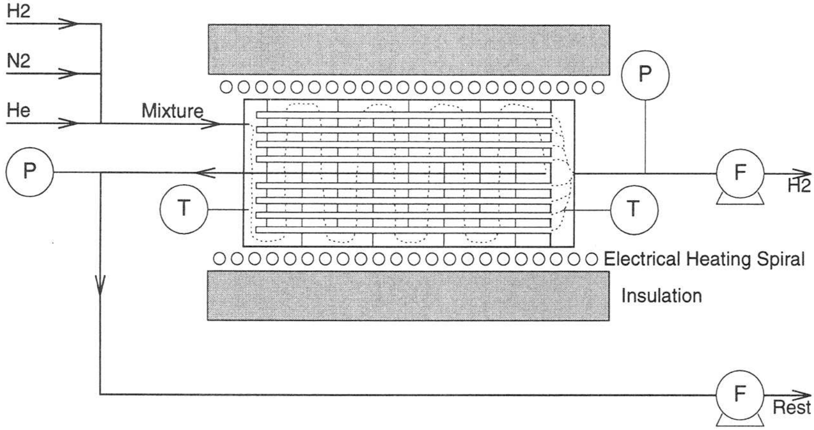


Figure 8.1: Multitube Membrane Module with Electrical Heating

side. The H^+-ions pass easily through the metal-hydrogen matrix of the membrane by diffusion. A part of the hydrogen atoms is incorporated in the metal lattice during the diffusion process, causing a change in the lattice structure and creating stresses in the membrane. A critical temperature of $320°C$ has to be exceeded for optimum operation.

Recent work in literature considers the separation of hydrogen from methylcyclohexane and toluene in membrane reactors [101] where deactivation and regeneration of in situ membranes was shown. The ex situ foil membrane approach was used [102] to exceed equilibrium in the dehydrogenation reaction studied.

The economics of the practical use of metal membrane reactors for industrial use was investigated [78] with membrane investment costs of 300 $\$/ft^2$. For zero emission vehicles using reformer hydrogen production to fuel cells, membrane cost and fuel cell system costs were estimated to be approximately equal.

The purpose of this chapter is to compare permeation measurements with membrane modules suitable for ex situ applications. Both tubular membranes and composites are investigated, the latter to reduce costs since only 7 μm membrane thicknesses are used compared to 65 μm for the tubes.

8.2 Experimental Setup

Figure 8.1 shows the experimental setup with an installed multi-tube membrane module. The module is heated up by an electrical heating spiral, which is thermally insulated. Temperature and pressure data are taken at both the high and low pressure sides of the membrane module. The several inputs allow different gas mixtures for testing the membrane module. *The module itself consists of Pd-Ag* tubes installed similarly to a cross-flow heat exchanger. On the shell-side, cross-flow of the gas mixture is induced by baffles. This prevents short circuiting and non optimal separation of the entering hydrogen rich mixture. The separation efficiency is maximised. After shell-side passage, the mixture with unseparated hydrogen leaves the module through the tube at its central axis. From the inner side of the tubes, the separated hydrogen exits the membrane module. Gas flow-meters measure the two output streams from the module.

8.3 Multi-Tube Membrane Modules

8.3.1 Preliminary Work

The initial membrane module consists of 10 $Pd\text{-}Ag_{23\%}$ tubes with a length of 240 mm. The outer diameter of these tubes is $3mm$ and the wall thickness 100 μm. Therefore the total separation area amounts to 0.0226 m^2. Material costs alone for this module are about 106 \$ with palladium costs of 4 $\$/g$ [103]. Figure 8.2 shows the permeation measurements for pure hydrogen at different pressures on both sides of the membrane without a sweep gas on the downstream side to maintain hydrogen purity. These data are taken at a temperature of 526 K. The permeation rate of hydrogen depends approximately linearly on the square root pressure difference $\sqrt{p_{up}} - \sqrt{p_{down}}$ across the membrane thickness t_{memb}.

8.3.2 Optimised Multi-Tube Membrane Module

This membrane module has the same outside dimensions and construction as the preliminary membrane module described in section 8.3.1, but with a much higher permeation rate. It consists of 34 $Pd\text{-}Ag_{23\%}$ tubes with a length of 245 mm.

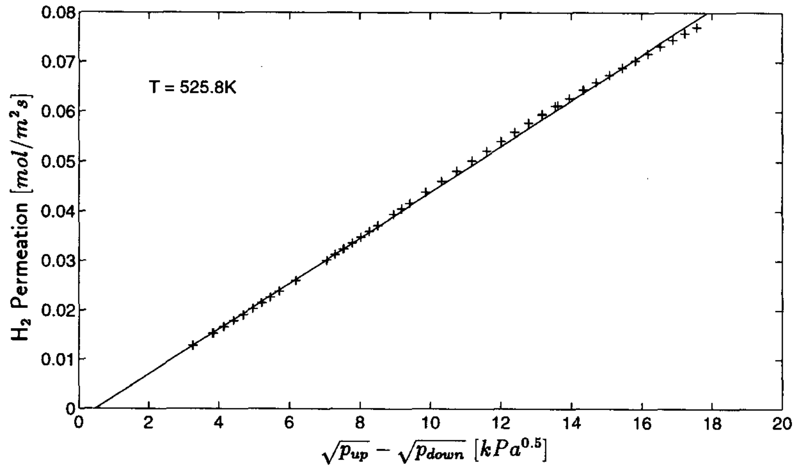


Figure 8.2: Pressure Dependence of Hydrogen Permeation, 10 $Pd\text{-}Ag_{23\%}$ Tubes

The diameter of these tubes is 1.6 mm and the wall thickness 65 μm. The total membrane area amounts to 0.0418 m^2. Material costs alone for this module are about 126 \$. Results of pure hydrogen permeation rates at different temperatures are presented in Figure 8.3. It is obvious from these plots that the permeation rate at a specific temperature depends linearly on the square root pressure difference, $\sqrt{p_{up}} - \sqrt{p_{down}}$. The permeation rate depends also on the temperature.

Separation of Hydrogen from Mixtures

By installing baffles in the membrane module, a high hydrogen permeation rate is obtained. It was possible to direct the inlet gas mixture properly from tube to tube along the baffles. If the gas were mixed in the whole module, the hydrogen permeation rate through the membrane would be lower. The data labelled + in Figure 8.4 signify the permeation rates at the entrance and $\times$ at exit. The solid lines represent the calculated values between entrance and exit.

Hydrogen separation experiments were also performed using a reformate gas with the following composition: 3% CO, 20% CO_2, 42% H_2, 35% N_2.

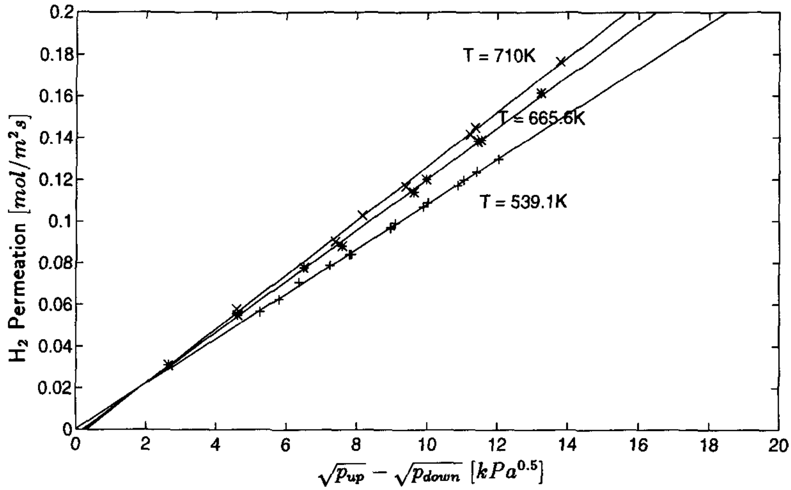


Figure 8.3: Pressure Dependence of Hydrogen Permeation, 34 $Pd\text{-}Ag_{23\%}$ Tubes

Temperature $[K]$	Total Pressure $[kPa]$	H_2-flow $[mol/m^2s]$	expected H_2-flow $[mol/m^2s]$	CO $[ppm]$
611	614	0.0081	0.0098	< 5
613	627	0.0175	0.0231	< 5
611	812	0.0221	0.0260	< 5
612	810	0.0148	0.0162	< 5
611	713	0.0133	0.0152	< 5
611	719	0.0199	0.0246	< 5
654	713	0.0146	0.0158	< 10
655	720	0.0216	0.0247	< 10

Table 8.1: Results of Experiments with a Reformate Gas

The second column of Table 8.1 lists the total pressure at the membrane upstream side. To calculate the partial pressure p_{up} of hydrogen in the feed, the total pressure has to be multiplied with the molar fraction 0.42 of H_2 in the reformate gas. The pressure on the downstream side of the membrane was atmospheric in all experiments.

The measured permeation rate (H_2-flow in Table 8.1) is lower than the expected

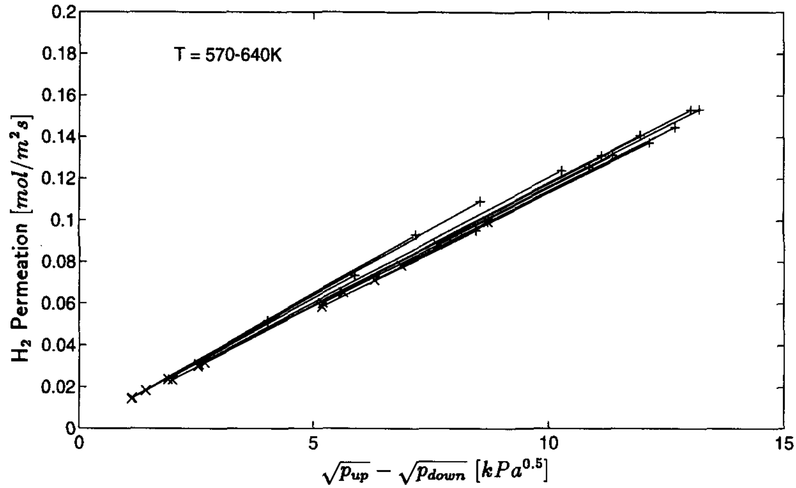


Figure 8.4: Different Experiments of Hydrogen Separation from Mixtures

+ entrance, x exit, the lines represent the calculated permeation rates taking into account the decreasing hydrogen partial pressure between entrance and exit of the module

permeation according to equation 8.3. The diminishing influence of the carbon monoxide CO in the feed gas will be considered in section 8.5.

Temperature Dependence of the Permeation Rate

Figure 8.5 shows the hydrogen permeation rate as function of the temperature T in the module. The data points shown in the plot are the measured values with error bars at the square root pressure difference of $\sqrt{p_{up}} - \sqrt{p_{down}} = 10\ \sqrt{kPa}$. An equation for the temperature dependence of the hydrogen permeation rate from the literature [101] is

$$F = 3.82\ 10^{-8} mols^{-1}m^{-1}Pa^{-0.5}\ e^{\frac{-261K}{T}}\ \frac{\sqrt{p_{up}} - \sqrt{p_{down}}}{t_{memb}} \tag{8.1}$$

t_{memb} denotes the thickness of the membrane. This approximation is plotted as dotted line in Figure 8.5 and compares to the results of the measurements. However, it does not fit the data well. Therefore the data are fitted again with the χ^2-minimisation method:

$$\chi^2 = \sum_{i=1}^{N} \frac{(f_i^{est} - f_i^{exp})^2}{\sigma_i^2} \tag{8.2}$$

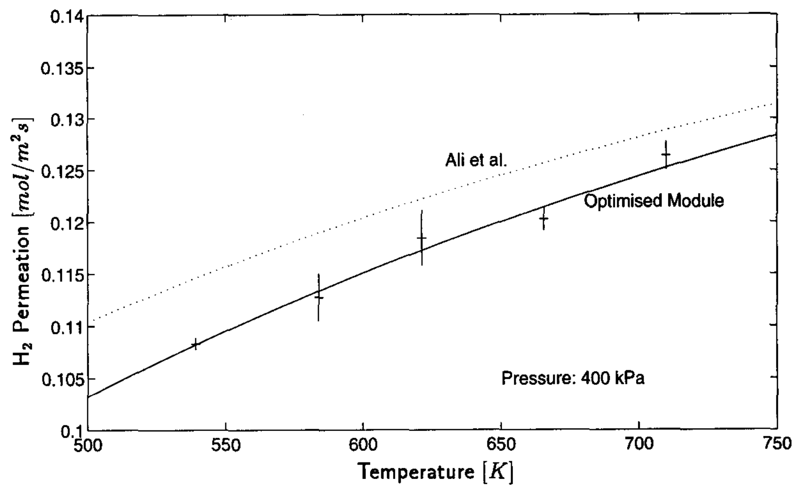


Figure 8.5: Temperature Dependence of Hydrogen Permeation

The sum χ^2 is the least square fit which weighs the experimental data points f_i^{exp} with their deviation σ_i. The f_i^{est} is the estimated value for the data point i calculated with the model (fitting function). Fitting the data points with χ^2-minimisation correlates with the equation

$$F = 4.08\ 10^{-8} mol s^{-1} m^{-1} Pa^{-0.5} e^{\frac{-327K}{T}} \frac{\sqrt{p_{up}} - \sqrt{p_{down}}}{t_{memb}} \tag{8.3}$$

which is plotted as a solid line in Figure 8.5. The χ^2 at this minimum is 2.09. From the comparison with χ^2 distribution for $N - 2 = 3$ degrees of freedom, it follows that the equation 8.3 fits the data well.

8.4 Composite Membranes

The selective layer and the support layer of a composite membrane consist of different materials. A porous ceramic tube forms the support layer. A very thin *Pd-Ag* layer with a thickness t_{memb} of $7\mu m$ is deposited on this support layer. Figure 8.7 shows the structure of such a composite membrane.

The total pressure drop across the composite membrane for a particular hydrogen permeation flow rate equals the sum of the pressure drop across the *Pd-Ag* layer

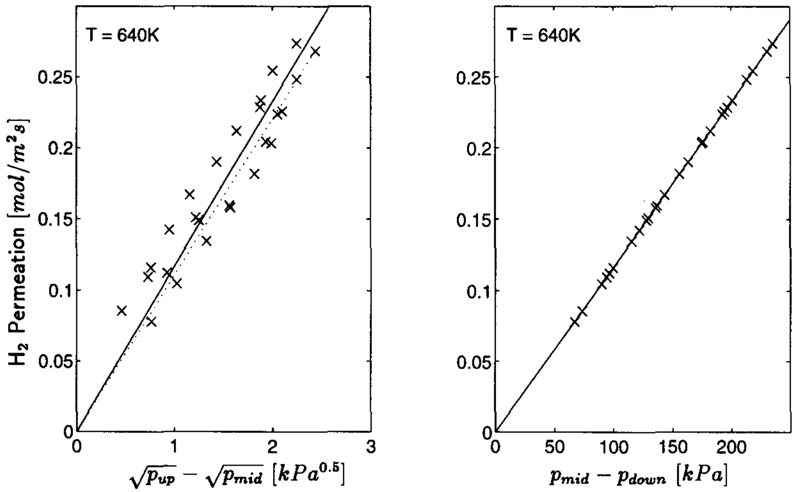


Figure 8.6: Hydrogen Flow through a Composite Membrane

left side: H_2-flow through the *Pd-Ag* layer of the composite membrane, right side: flow through the ceramic support layer.

$\triangle p_{met}$ and that across the porous ceramic layer $\triangle p_{cer}$:

$$\begin{aligned} \triangle p &= \triangle p_{met} + \triangle p_{cer} \\ \triangle p_{met} &= p_{up} - p_{mid} \\ \triangle p_{cer} &= p_{mid} - p_{down} \end{aligned} \tag{8.4}$$

where p_{up} means the partial pressure of hydrogen at the upstream side of the membrane. p_{mid} and p_{down} denote the pressures of the purified hydrogen between the two layers and at the exit of the porous ceramic tube.

The pressure drop across the porous ceramic layer is a function of the flow rate F. Because of the similarity between porous media and fixed beds (Ergun-equation 5.14 in section 5.5.2) the pressure drop consists of a laminar part (linearly proportional to the flow rate) and a turbulent part (quadratic term):

$$\triangle p_{cer} = k_1 F + k_2 F^2 \tag{8.5}$$

The pressure drop across the the *Pd-Ag* layer with the thickness t_{memb} could be described with the following equation:

$$\frac{\sqrt{p_{up}} - \sqrt{p_{mid}}}{t_{memb}} = k_3 F \tag{8.6}$$

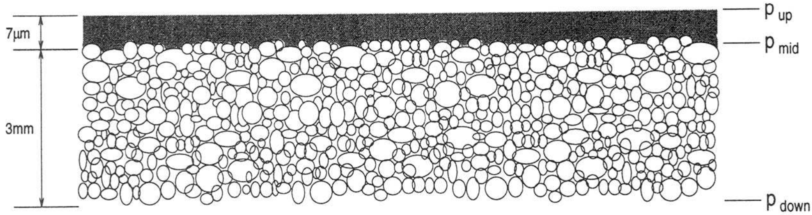


Figure 8.7: Structure of the Composite Membrane

If this *Pd-Ag* layer has the same activity as the membranes described in section 8.3.2 the parameter k_3 should fit the equation 8.3.

Fitting the experimental data with equations 8.4, 8.5 and 8.6 shows that the laminar part in equation 8.5 is dominating. Because the parameter k_2 is very small, the quadratic term in equation 8.5 remains negligible. Therefore the flow rate F is linearly proportional to the pressure drop across the porous ceramic layer (very small pores cause a Reynolds number $Re \ll 1$). This linear dependence is shown on the right side in Figure 8.6. The flow rate F through the selective *Pd-Ag* layer depends linearly on the square root pressure difference $\sqrt{p_{up}} - \sqrt{p_{mid}}$ across the thickness t_{memb} of the *Pd-Ag* layer. The fitted parameter k_3 (solid line in Figure 8.6 left) is not significantly different from the product of the preexponential factor and the exponential function in equation 8.3. The dotted line in Figure 8.6 shows the expected permeation flow rate from the latter equation.

Approximately 2/3 of the total pressure drop is caused by the porous ceramics. Only 1/3 of the total pressure drop is available across the selective *Pd-Ag* layer. Therefore a *Pd-Ag* layer which is less thick than the used $7\mu m$ improves the hydrogen permeation flow rate F only insignificantly. In other words, the pressure drop across the porous ceramic support layer limits the potential of this membrane.

8.5 Separation of Hydrogen from Carbon Monoxide

The chemical adsorption of carbon monoxide CO on the surface of the *Pd-Ag* membrane diminishes the permeation rate significantly. To examine this effect, the per-

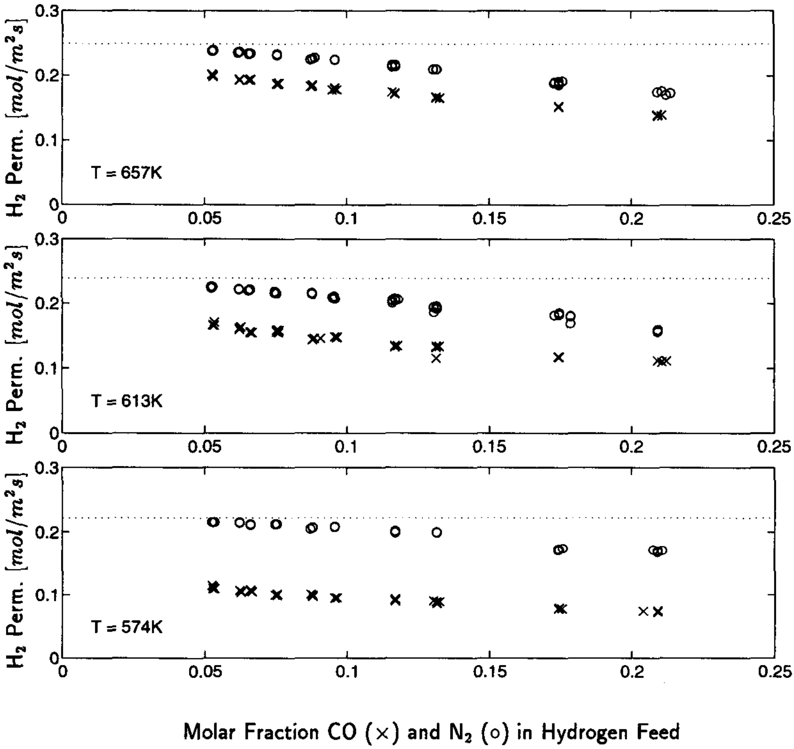


Figure 8.8: Influence of Carbon Monoxide on the Permeation (Single Tube)

meation through a single membrane tube with a diameter of 1.6 mm, a wall thickness $t_{memb} = 65\ \mu m$ and a length of 232 mm is measured. The pressure upstream of the membrane is 1000 kPa.

The data designated with $\times$ in Figure 8.8 show the effect of CO on the hydrogen permeation rate at different temperatures. In each plot of Figure 8.8 the permeation rate of pure hydrogen in the input stream serves as reference value (dotted line). For comparison the influence of an inert gas (nitrogen N_2) is also measured. The lower permeation rate in the nitrogen case (compared with pure hydrogen) is caused by the lower partial pressure of the hydrogen in the input stream. The lower partial pressure cannot explain the lower permeation rate in the CO case, because it is

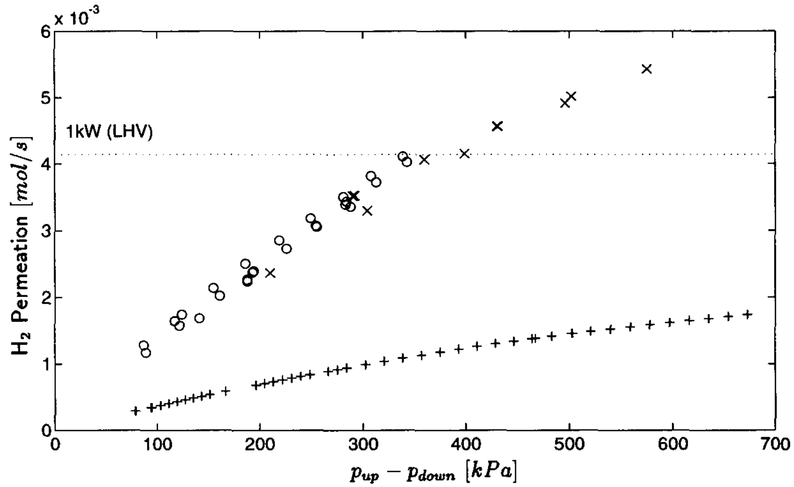


Figure 8.9: Total Permeation Rates of Membrane Modules with the same Volume

+	Initial Membrane Module ($0.0226m^2$ $26gPd-Ag$) at $526K$
×	Optimised Membrane Module ($0.0418m^2$ $32gPd-Ag$) at $538K$
o	Composite Membrane ($0.0150m^2$ $1.3gPd-Ag$) at $640K$

much lower than for nitrogen; it is caused by binding of CO on Pd. With increasing temperature the chemisorption of carbon monoxide CO and its influence on the permeation rate becomes smaller.

8.6 Costs of Membranes compared to Catalyst Costs

For commercial applications, the ratio of membrane material costs to catalyst costs of about 1 is desirable. For 1 kW capacity of the new module, this ratio is \$126/\$7 = 18/1 when catalyst costs are 100 $\$/kg$. Since permeation rates would be halved using gas mixtures instead of pure hydrogen as in Figure 8.9, this ratio increases to about 40/1. The incentive for using a composite membrane of 7 μm thickness in future work is compelling, the ratio would then decrease to 2/1.

8.7 Conclusion

The improvement in the hydrogen permeation of the optimised membrane module (data designated with $\times$) and the composite membrane (designated with $\circ$) compared with the initial membrane module (+) is shown in Figure 8.9. All the modules have the same volumetric size of 1.14 dm^3. The goal of 1 kW hydrogen power is reached with the optimised membrane module as well as with the composite membrane. 1 kW power means a hydrogen flow of 0.00414 mol/s based on the lower heating value (LHV) of 241.8 kJ/mol (dotted line in Figure 8.9). The total permeation rate of the composite membrane is approximately 10% lower than those of the optimised membrane module because of the higher operating temperature of 640 K used with the latter in the experimental data shown in Figure 8.9.

Further experiments on the optimised membrane module have shown that carbon monoxide CO is not completely separated from CO/H_2 mixtures due to leakages through the membrane. A CO content of 5-10 ppm has to be tolerated. The composite membrane was totally unsuitable for CO separation due to substantial leaks through or around the membrane. Further development work is required.

The low content of palladium Pd (1.3 g) makes the composite membrane module economically interesting, compared with the other two modules which contains 26 and 32 g palladium and silver. Palladium is a relatively expensive raw material (4 $\$/g$ [103]).

A disadvantage of the composite membrane is its high pressure drop across the porous ceramic support layer ($\approx$2/3 of the total pressure drop). This fact makes further improvement of this membrane difficult. A possibility to reduce the pressure drop across the porous ceramic support layer is the use of graded porous ceramics (small pores at the *Pd-Ag* layer and bigger pores in the rest of the mechanic support layer).

Chapter 9

Conclusions

This final section summarises the conclusions given at the end of the previous chapters. In addition, some ideas for further research are suggested. Section 2.5 describes the major problems of mobile applications using a range-extender system. Overall efficiency was estimated at 28%, which in a full fuel cycle analysis is comparable to Otto engines, but the system costs were too high due to the use of *Pd-Ag* membranes. Cost-efficient solutions for hydrogen purification are urgently needed.

9.1 MTH-System Analysis

The calculated costs of winter electricity produced with the MTH-System depend significantly on the input parameters employed. It was shown in chapters 3 and 4, how sensitivity analyses and exergy considerations detect the critical points in the system and targets the simulation step of the systems analysis. These analyses conclude that the influence of the power plant investment costs to the total costs of produced electricity is small. As a consequence, the costs of this technology are less important compared with their technical features like efficiency and the available waste heat at a high temperature level.

By using simulation and economic considerations, it was possible to calculate with more accuracy the efficiencies and costs of the three alternatives for producing electricity from hydrogen than in the first estimate (section 3.2) used as reference point for the sensitivity analyses:

1. MTH-System with solid oxide fuel cells SOFC:
   0.26 $\$/kWh$ ($\eta_{tot} = 0.40$)

2. MTH-System with molten carbonate fuel cells MCFC:
   0.30 $\$/kWh$ ($\eta_{tot} = 0.33$)

3. MTH-System with gas and steam turbines:
   0.36 $\$/kWh$ ($\eta_{tot} = 0.25$)

These cost and efficiency data are based on mature technology for 1000 GWh of summer electricity to storage with a 85 MW output in winter for the MTH-SOFC option. Table 7.1 shows further details on these three alternatives, whereas Table 7.2 compares the economics of the MTH-System with a new hydropower project in Switzerland. The 'best case' study in section 7.6 estimated the maximum potential of the MTH-System. The maximum efficiency of the MTH-System is $\eta_{tot} = 0.48$ with the lowest possible costs of 0.17 $\$/kWh$ for the output electricity.

Compared with today's conventional electricity production costs from fossil fuels (0.05-0.1 $\$/kWh$) the electricity produced by the MTH-System is expensive. This economic disadvantage is compensated by the low CO_2 emissions, 75-85% lower than the best natural gas combined cycle plant. The potential introduction of an energy tax (CO_2-tax) in the near future cannot compensate the economic disadvantages of the MTH-System. In addition, it will be difficult to introduce high energy taxes in a deregulated future electricity market in Europe. However, the hydrogen-photovoltaic study of reference [18] gives a comparable price (0.225 $\$/kWh$) for their output electricity. Its assumptions of future costs and efficiencies of hydrogen storage and conversion plants are comparable to those of the best case study presented in section 7.6.

The additional benefit of the MTH-System as energy reserve, which guarantees a strategic independence from foreign imports of energy in a crisis, cannot easily be taken into account in this cost calculation.

9.2 Hydrogen Separation Membranes

In the experimental part, two types of *Pd-Ag* membranes and their practical aspects and applications were tested: the multitube membrane module and the composite membrane. Further research with a single membrane tube addressed the influence of carbon monoxide CO on the hydrogen permeation rate through *Pd-Ag* membranes.

A major problem of membrane applications is the sealing, especially in the case of *Pd-Ag* membranes, which are heated up to 320-400°C with upstream pressures of 10-15 *bar*. With the composite membrane, it was not possible to suppress leaking below the value of *100 ppm* CO in the purified hydrogen for a reformate feed gas with 3% CO. Significant CO separation (less than 10 *ppm* in the purified hydrogen) was tested with the optimised multitube membrane module (Table 8.1 in section 8.3.2).

From data analysis of the hydrogen permeation rate experiments at different pressure conditions, an inherent limitation of the composite membrane was deduced. Two thirds of the pressure drop is lost over the ceramic support layer of the composite membrane. However, this loss of pressure is well compensated by the economic benefit of its low palladium content.

The decrease of the hydrogen permeation by CO in the feed gas (section 8.5) is partially offset by operating temperatures above 350°C. Operating in this temperature range is advisable anyway because temperatures below 320°C give rise to stress in the metal-hydride lattice and may damage the sealing or the membrane.

9.3 Future Outlook

In today's European electricity market, the MTH-System is not economically competitive . The economics of the MTH-System in other locations e.g. Canada, Brazil could be considered for niche markets with the methods and data used in this work. In the near term future, the imminent deregulation of the electricity market implies a decrease of the summer electricity prices, the most significant parameter in the MTH-System economic analysis. Since hydraulic pump storage is limited by the sites remaining and ecological arguments the nearly carbon free MTH-System is a valuable alternative. However, it is hardly competitive with energy from fossil sources, even with significant energy taxes. In the medium to long term future, seasonal storage of electricity could play a critical role in the energy economy due to an increasing utilisation of renewable energies such as wind or solar.

Membrane applications will have an increasing importance in future, provided the costs are reduced. Especially in hydrogen energy systems, palladium based membranes are a key technology to provide CO-free hydrogen (chapter 2). In addition, *Pd-Ag* membranes are also used for energy efficient hydrogen separation in the petrochemical industry. This important application of *Pd-Ag* membranes does not depend on the introduction of hydrogen as an energy carrier. Therefore further research to improve the permeation and sealing of the composite membrane is needed. Additional questions of membrane durability and regenerability have to be addressed before applications are seriously considered. New materials, a *Pd-Ta-Pd* sandwich [104], promise much higher permeation rates.

The methods developed in this thesis to analyse the MTH-System could be adapted to other energy storage and transportation systems, e.g. methanol in transportation applications, provided the CO_2-hydrogenation step is commercially proven to close the carbon neutral cycle.

Appendix A

Nomenclature

A	area $[m]$
C_p	heat capacity $[JK^{-1}]$
D_{eff}	effective diffusivity $[m^2/s]$
D_{AB}	bulk diffusivity $[m^2/s]$
$D_{Knudsen}$	Knudsen diffusivity $[m^2/s]$
t_{memb}	membrane thickness $[m]$
d_p	diameter of the spherical catalyst pellet $[m]$
F	permeation flow rate $[mol/m^2s]$
f_k	friction factor [-]
G	Gibbs potential $[J]$
$G_m = v_0\rho$	mass velocity $[kg/m^2s]$
H	enthalpy $[J]$
I	economical input parameter
$\mathcal{K}_{kWh}$	costs of output electricity $[\$/kWh]$
$\mathcal{K}$	cost $[\$]$
l	length of fixed bed $[m]$
M	molecular weight $[kg/kmol]$
p	pressure $[Pa]$
P	output of the power plant $[W]$
r	reaction rate
$R = 8314.5J/Kkmol$	gas constant
Re	Reynolds number [-]

R_{pore}	average radius of the pores $[m]$
S	entropy $[JK^{-1}]$
T	temperature $[K]$
T_m	average temperature $[K]$
U	voltage $[V]$
v_0	empty tube velocity $[m/s]$
V	volume $[m^3]$
W	work $[W]$
δ	catalyst tortuosity factor [-]
ϵ	catalyst porosity [-]
ϵ_{bed}	bed void fraction [-]
η	efficiency [-]
$\kappa = \frac{C_p}{C_v}$	≈ 1.4
μ	viscosity of fluid $[Pas]=[kg/ms]$
$\pi = \frac{p_{comb}}{p_{air}}$	pressure ratio [-]
Φ	Thiele modulus
ρ	density of fluid $[kg/m^3]$
ρ_p	density of catalyst pellet $[kg/m^3]$
τ	exergetic temperature [-]
ξ	pressure drop parameter
ζ	efficiency in relation to the reversible cell

Subscripts and Superscripts

ac	alternating current
air	input air and feed
an	anode
cat	cathode
cer	ceramic
coke	coked (catalyst)
comb	combustion
comp	compression
dc	direct current
dhy	dehydrogenation

$diff$	diffusion
eff	effective
el	electrolysis
$elec$	electrical
env	environment
eq	equilibrium
exh	exhaust
FC	fuel cell
$fuel$	fuel
HHV	higher heating value
hyd	hydrogenation
IR	ohmic drop
kWh	kWh kilowatthour
LHV	lower heating value
met	metal
MCH	methylcyclohexane
$MCFC$	molten carbonate fuel cell
pp	power plant (fuel cell)
$pump$	feedwater pump
$reac$	reaction
ref	reference
$SOFC$	solid oxide fuel cell
$theo$	theoretical
TOL	toluene
tot	total
$turb$	turbine expansion

Symbols

$\triangle$	difference of reactants and products
∇	Nabla operator
$\prod$	product

Leer - Vide - Empty

Appendix B

Simulation Results

B.1 Summer Process of the MTH-System

```
Initialisation Values

Electricity  = 3.2e+08 kW
Temp. Feed   = 648.281 K
Temp. Heat Medium    = 869.875 K
feedH2  = 0.87 kmol/s
airoutAr= 0.0976185 kmol/s
airoutN2= 8.39616 kmol/s
airoutO2= 0.536671 kmol/s
pfeed   = 1.6e+06 Pa
pairout = 100000 Pa


Electrolyser

tempin [K]    = 300
tempreac [K] = 300
tempout [K]  = 300
Efficieny Power Conditioner = 0.97
          of Cells          = 0.714286
Power Consumption [kWh/m^3] = 4.2

Streams: [kmol/s]
  IN:  H2O = 0.95649
  OUT: H2  = 0.95649        O2  = 0.478245

Investment [$] = 2.08211e+08
Lifetime [year] = 30
Land Require [m^2] = 16551.7
Capital Cost [$/year]   = 1.49325e+07
Operating Cost [$/year] = 1.24926e+07


Byproduct Separation

Streams: [kmol/s]
   IN:   TOL = 0.318798
         MCH = 0.00318511
   OUT:  TOL = 0.313951
         MCH = 0.00159256
```

```
   C7 Waste   = 0.00643966
   makeupTOL = 0.00643966

Massflow [ton/hour] = 106.874
Investment Cost [$] = 1.3881e+07
Lifetime [year] = 19
Land [m^2] = 585.986
Capital Cost [$/year]    = 1.26111e+06
Operating Cost [$/year] = 416429
Electricity [W] = 19631.5

Qwaste [W] = 2.51191e+07
```

Hydrogenation Reactor

```
tempin [K]    = 300
tempreac [K] = 550
tempout [K]   = 300
minimal Pressure [Pa] = 2.64511e+06

Streams: [kmol/s]
  IN:  H2   = 0.95649        TOL = 0.318798       MCH = 0.00318511
  OUT: H2   = 0.00105204        TOL = 0.000318798        MCH = 0.321664

Massbalance: [kg/s]
  IN:  H2   = 1.92828        TOL = 29.3744       MCH = 0.31274
     total = 31.6154
  OUT: H2   = 0.00212092        TOL = 0.0293744        MCH = 31.5836
     total = 31.6151

Energybalance: [J/s]=[W]
  Qfeed    = 145620
  Qinside = 2.60028e+07
  Qprod    = 2.40619e+07
  Qtank    = 110325
  Qreac    = 6.71908e+07
  Qext     = 4.11881e+07
   Balance Reactor = 0
   Balance Total    = -0.948783

Massflow [ton/hour] = 113.815
Electricity [kW] = 1.70723e+06
Catalyst Cost [$/hour] = 307.302
Investment [$] = 1.82533e+07
Lifetime [year] = 19
Land Require [m^2] = 121.945
Capital Cost [$/year]    = 1.65834e+06
Operating Cost [$/year] = 547599
     + Catalyst [$/year] = 983365
```

Tank

```
Space [m^3]             = 520000 = 26 x 20000
minimal Space [m^3]  = 475416
Investment Costs [$] = 1.2339e+08
Land [m^2]             = 86666.7
Inventory [kmol]  MCH: 3.70557e+06  TOL: 3672.55
Out [kmol/s]  MCH: 0.214443  TOL: 0.000212532
Investment [$] = 1.2339e+08
Lifetime [year] = 65
Capital Cost [$/year]    = 7.15205e+06
Operating Cost [$/year] = 2.64407e+06
Land Require [m^2] = 86666.7
Toluene Investment  [$] = 8.88611e+07
Capital Cost Toluene [$/year]          = 4.49388e+06
Operating Cost (Byproducts) [$/year] = 1.77722e+06
```

B.2 Winter Process of the MTH-System with Solid Oxide Fuel Cells

Hydrogen Compressor

```
Streams: [kmol/s]
  IN = OUT: O2  = 0
            N2  = 0
            Ar  = 0
            H2  = 0.87
            CH4 = 0
            CO2 = 0

Massbalance: [kg/s]
  IN = OUT: O2  = 0
            N2  = 0
            Ar  = 0
            H2  = 1.75392
            CH4 = 0
            CO2 = 0
     total  = 1.75392

Inlet Temperature of Gas [K]   = 453.9
Inlet Pressure of Gas [Pa]     = 537650
Outlet Temperature of Gas [K]  = 648.281
Outlet Pressure of Gas [Pa]    = 1.6e+06

Energybalance: [J/s]=[W]
  Qin        = 3.95417e+06       (298.15K -> 453.9K)
  Qout       = 8.90634e+06       (298.15K -> 648.281K)
  Wcomp       = 4.95217e+06       (453.9K -> 648.281K)
  elec        = 5.10533e+06
  Qloss       = 153160
  balance  4.95217e+06 = 4.95217e+06

Investment [$] = 6.32279e+06
Lifetime [year] = 19
Land Require [m^2] = 9.90434
Capital Cost [$/year]   = 574436
Operating Cost [$/year] = 189684
```

Heat Exchanger 1

```
numbank = 30   numtube = 200    dbank = 0.07m    dtube = 0.07m
din = 0.036m    dout = 0.0424m    length = 3m

HeatBalance [W]:
   Inside= 1.18909e+07   Outside= 1.19002e+07
   Heat Require [W] = 1.19004e+07
   Heat Transfercoef. [W/m^2K] = 50.2906
Tempbegin [K] = 869.875     Tempend [K] = 770.503
Pressure (Out) [Pa] Begin= 100000   End= 99561.7    Diff=  438.305
Pressure (Tube) [Pa] Begin= 1.6e+06   End= 1.6e+06   Diff=  3.2999
Temp. Product [K] = 778.592
Heat Exchange Area [m^2] = 21.7238

Investment [$] = 445272
Lifetime [year] = 22
Land Require [m^2] = 4.34476
Capital Cost [$/year]   = 37187.1
Operating Cost [$/year] = 13358.2
```

Dehydrogenation Step 1

```
Number of Reactor = 4
din = 1.17m    length = 2.42m

Heat Balance per Reactor [W]: Reac= 3.5361e+06   Inside= -3.52532e+06
```

```
Mass Balance per Reactor [kg]: In= 5.7073   Out= 5.70732
 In  [kmol/s]: MCH= 0.0536107  TOL= 5.3133e-05  H2= 0.2175
 Out [kmol/s]: MCH= 0.0372626  TOL= 0.0164013  H2= 0.266544
 Massvelocity [kg/sm^2] = 5.30846        LHSV [1/hr]  = 9.51688

Conversion = 0.30563           (Equilibrium at 0.307709 )
Pressure (Tube) [Pa] Begin= 1.6e+06   End= 1.45532e+06   Diff=  144681
Temp. Product [K] = 622.577

Investment [$] = 312743
Lifetime [year] = 22
Land Require [m^2] = 21.9024
Capital Cost [$/year]   = 26118.9
Operating Cost [$/year] = 9382.3    + Catalyst [$/year] = 312219
```

Heat Exchanger 2

```
numbank = 70   numtube = 200     dbank = 0.07m     dtube = 0.07m
din = 0.036m    dout = 0.0424m    length = 3m

HeatBalance [W]:
   Inside= 1.44703e+07   Outside= 1.44872e+07
   Heat Require [W] = 1.4487e+07
   Heat Transfercoef. [W/m^2K] = 26.2054
Tempbegin [K] = 869.875    Tempend [K] = 748.62
Pressure (Out) [Pa] Begin= 100000   End= 98973.4   Diff=  1026.57
Pressure (Tube) [Pa] Begin= 1.45532e+06   End= 1.45531e+06   Diff=  0.977184
Temp. Product [K] = 782.156
Heat Exchange Area [m^2] = 50.6888

Investment [$] = 792227
Lifetime [year] = 22
Land Require [m^2] = 10.1378
Capital Cost [$/year]   = 66163.2
Operating Cost [$/year] = 23766.8
```

Dehydrogenation Step 2

```
Number of Reactor = 4
din = 1.17m     length = 2.42m

Heat Balance per Reactor [W]: Reac= 3.33952e+06   Inside= -3.33054e+06

Mass Balance per Reactor [kg]: In= 5.70732   Out= 5.70734
 In  [kmol/s]: MCH= 0.0372626  TOL= 0.0164013  H2= 0.266544
 Out [kmol/s]: MCH= 0.0218233  TOL= 0.0318406  H2= 0.312862
 Massvelocity [kg/sm^2] = 5.30847        LHSV [1/hr]  = 9.02747

Conversion = 0.593334           (Equilibrium at 0.599335 )
Pressure (Tube) [Pa] Begin= 1.45531e+06   End= 1.26424e+06   Diff=  191070
Temp. Product [K] = 635.778

Investment [$] = 312743
Lifetime [year] = 22
Land Require [m^2] = 21.9024
Capital Cost [$/year]   = 26118.9
Operating Cost [$/year] = 9382.3    + Catalyst [$/year] = 312219
```

Heat Exchanger 3

```
numbank = 80   numtube = 200     dbank = 0.07m     dtube = 0.07m
din = 0.036m    dout = 0.0424m    length = 3m

HeatBalance [W]:
   Inside= 1.38974e+07   Outside= 1.39118e+07
   Heat Require [W] = 1.39116e+07
   Heat Transfercoef. [W/m^2K] = 23.5732
Tempbegin [K] = 869.875    Tempend [K] = 753.496
Pressure (Out) [Pa] Begin= 100000   End= 98820.1   Diff=  1179.91
Pressure (Tube) [Pa] Begin= 1.26424e+06   End= 1.26424e+06   Diff=  1.04093
Temp. Product [K] = 787.925
Heat Exchange Area [m^2] = 57.9301

Investment [$] = 867529
```

```
Lifetime [year] = 22
Land Require [m^2] = 11.586
Capital Cost [$/year]   = 72452.1
Operating Cost [$/year] = 26025.9
```

Dehydrogenation Step 3

```
Number of Reactors = 4
din = 1.17m    length = 2.42m

Heat Balance per Reactor [W]: Reac= 3.15464e+06   Inside= -3.14664e+06

Mass Balance per Reactor [kg]: In= 5.70734   Out= 5.70735
 In  [kmol/s]: MCH= 0.0218233  TOL= 0.0318406  H2= 0.312862
 Out [kmol/s]: MCH= 0.00723871  TOL= 0.0464251  H2= 0.356616
 Massvelocity [kg/sm^2] = 5.30849       LHSV [1/hr]  = 8.56528

Conversion = 0.86511          (Equilibrium at 0.878876 )
Pressure (Tube) [Pa] Begin= 1.26424e+06   End= 998862   Diff=  265382
Temp. Product [K] = 650.534

Investment [$] = 312743
Lifetime [year] = 22
Land Require [m^2] = 21.9024
Capital Cost [$/year]   = 26118.9
Operating Cost [$/year] = 9382.3    + Catalyst [$/year] = 312219
```

Heat Exchanger 4

```
numbank = 90   numtube = 200     dbank = 0.07m    dtube = 0.07m
din = 0.036m    dout = 0.0424m    length = 3m

HeatBalance [W]:
   Inside= 1.31509e+07   Outside= 1.31627e+07
   Heat Require [W] = 1.31626e+07
   Heat Transfercoef. [W/m^2K] = 21.3324
Tempbegin [K] = 869.875    Tempend [K] = 759.837
Pressure (Out) [Pa] Begin= 100000   End= 98664   Diff=  1336.01
Pressure (Tube) [Pa] Begin= 998862   End= 998861   Diff=  1.22434
Temp. Product [K] = 793.612
Heat Exchange Area [m^2] = 65.1714

Investment [$] = 939870
Lifetime [year] = 22
Land Require [m^2] = 13.0343
Capital Cost [$/year]   = 78493.7
Operating Cost [$/year] = 28196.1
```

Dehydrogenation Step 4

```
Number of Reactors = 4
din = 1.17m
length = 2.42m

Heat Balance per Reactor [W]: Reac= 1.52224e+06   Inside= -1.51721e+06

Mass Balance per Reactor [kg]: In= 5.70735   Out= 5.70736
 In  [kmol/s]: MCH= 0.00723871  TOL= 0.0464251  H2= 0.356616
 Out [kmol/s]: MCH= 0.000201084  TOL= 0.0534628  H2= 0.377729
 Massvelocity [kg/sm^2] = 5.3085       LHSV [1/hr]  = 8.12866

Conversion = 0.996253          (Equilibrium at 0.999725 )
Pressure (Tube) [Pa] Begin= 998861   End= 537650   Diff=  461211
Temp. Product [K] = 728.595

Investment [$] = 312743
Lifetime [year] = 22
Land Require [m^2] = 21.9024
Capital Cost [$/year]   = 26118.9
Operating Cost [$/year] = 9382.3    + Catalyst [$/year] = 312219
```

```
Summary Dehydrogenation

Investment [$] = 1.06187e+07
Land Require [m^2] = 136.617
Capital Cost [$/year]   = 933208
Operating Cost [$/year] = 318560    + Catalyst [$/year] = 1.24888e+06


Fuel Cells

Inlet Temperature of Air [K]        = 1083.71
Outlet Temperature of Air [K]       = 1083.71
Inlet Temperature of Fuel [K]       = 1155
Exhaust Temperature [K]             = 1155
Inlet Temperature of Steam [K]      = 0
Outlet Temperature of Steam [K]     = 0
Temperature of Streams to Cell [K] = 1083.71
Temperature Inside Cell [K]         = 1250

Streams: [kmol/s]
  IN:  air      O2  = 0.967049
                N2  = 10.1159
                Ar  = 0.117613
                CO2 = 0
       fuel     H2  = 0.712128
                H2O = 0
                CH4 = 0
                CO2 = 0
  OUT: air      O2  = 0.646591
                N2  = 10.1159
                Ar  = 0.117613
                CO2 = 0
       exhaust H2  = 0.0712128
                H2O = 0.640916
                CH4 = 0
                CO2 = 0
  STEAM:        H2O = 0

Massbalance: [kg/s]
  IN:  air      O2  = 30.9446
                N2  = 283.376
                Ar  = 4.69839
                CO2 = 0
       fuel     H2  = 1.43565
                H2O = 0
                CH4 = 0
                CO2 = 0
  OUT: air      O2  = 20.6903
                N2  = 283.376
                Ar  = 4.69839
                CO2 = 0
       exhaust H2  = 0.143565
                H2O = 11.5461
                CH4 = 0
                CO2 = 0
  IN total  = 320.454
  OUT total = 320.454

Energybalance: [J/s]=[W]
  effcell   = 0.82
  effsyst   = 0.606402
  heatvalue =  1.54973e+08
  hr        =  -4.76989e+06
  T*sr      =  -9.72767e+06
  wrev      =  1.14605e+08
  elec      =  9.39761e+07
  heat      =  6.57672e+07
  Qcell     = 6.61947e+07       (1083.71K -> 1250K)
  Qair      = 0        (1083.71K -> 1083.71K)
  Qfuel     = -1.55307e+06      (1155K -> 1083.71K)
  Qexhaust  = 2.8694e+06      (1250K -> 1155K)
  Qoutair   = 6.06545e+07       (1250K -> 1083.71K)
  Qreflux   = 0        (1250K -> 1083.71K)
  Qsteam    = 0        (0K -> 0K)
  Qrest     = heat-Qcell-Qreflux-Qsteam = -427511

Investment [$] = 1.49845e+08
Lifetime [year] = 25
Land Require [m^2] = 6343.39
```

```
Capital Cost [$/year]   = 1.17011e+07
Operating Cost [$/year] = 7.49225e+06
```

<u>Dehydrogenation Heat Exchange</u>

```
Heat Require Heat Exchanger [W] = 5.34614e+07
  Heater1 [W] = 1.19004e+07
  Heater2 [W] = 1.4487e+07
  Heater3 [W] = 1.39116e+07
  Heater4 [W] = 1.31625e+07
Heat Supply Fuel Cell        [W] = 5.55756e+07
Heat Loss                    [W] = 2.11423e+06
Rest for Heat Ex. Network    [W] = 1.12556e+06

Preheating of feed (liquid, vaporisation, gas)
  Qlfeed     [W] = 1.11737e+07        (298.15K -> 512.871K)
  condMCH    [W] = 4.1362e+06
  Qgfeed     [W] = 7.62096e+06        (512.871K -> 648.281K)
  total      [W] = 2.29308e+07        (298.15K -> 648.281K)

Cooling of Product (gas, condensation, liquid)
  Qgproduct [W] = 2.35252e+07         (728.595K -> 453.9K)
  condTOL   [W] = 6.15343e+06
  Qlproduct [W] = 8.955e+06         (453.9K -> 298.15K)
  total     [W] = 3.86336e+07         (728.595K -> 298.15K)

Heat Exchanger Network
  Request [W] = 9.91956e+07
          Qair    5.8169e+07
          Qfuel   1.80957e+07
          Qgfeed  7.62096e+06
          Qlfeed  1.11737e+07
          condMCH 4.1362e+06
  Supply [W]  = 1.28168e+08
        Qexhaust  2.8694e+06
        Qoutair   6.06545e+07
        Qgproduct 2.35252e+07
        Qlproduct 8.955e+06
        condTOL   6.15343e+06
        condH2O   2.60102e+07
  Rest    [W] = 2.89722e+07

  Gas Heater: transfercoef. [W/m^2K] = 50.0
              dT [K] = 57
              area [m^2] = 2674.02
              cost [$] = 1.17485e+07
              capital costs [$/year]   = 1.14319e+06
              operating costs [$/year] = 352454
              land [m^2] = 534.804
  Evaporator: transfercoef. [W/m^2K] = 70.0
              dT [K] = 55.0
              area [m^2] = 1074.34
              cost [$] = 6.31953e+06
              capital costs [$/year]   = 614924
              operating costs [$/year] = 189586
              land [m^2] = 214.868
  Liq Heater: transfercoef. [W/m^2K] = 150.0
              dT [K] = 55.0
              area [m^2] = 1354.39
              cost [$] = 7.39765e+06
              capital costs [$/year]   = 719831
              operating costs [$/year] = 221930
              land [m^2] = 270.877
```

<u>Streams</u>

```
Netout    :    Temperature = 1155 [K]
      Ar= 0.02 kmol/s
      N2= 1.72 kmol/s
      O2= 0.43 kmol/s
   Enthalpy = 5.8169e+07 [W]

Cellin    :    Temperature = 1083.71 [K]
      Ar= 0.117618 kmol/s
      N2= 10.1162 kmol/s
      O2= 0.966671 kmol/s
   Enthalpy = 2.71514e+08 [W]
```

```
Cellout    :     Temperature = 1250 [K]
      Ar= 0.117613 kmol/s
      N2= 10.1159 kmol/s
      O2= 0.646591 kmol/s
   Enthalpy = 3.23962e+08 [W]

Netin      :     Temperature = 1250 [K]
      Ar= 0.0199941 kmol/s
      N2= 1.7197 kmol/s
      O2= 0.10992 kmol/s
   Enthalpy = 5.50735e+07 [W]

Reflux     :     Temperature = 1066.2 [K]
      Ar= 0.0976185 kmol/s
      N2= 8.39616 kmol/s
      O2= 0.536671 kmol/s
   Enthalpy = 2.13313e+08 [W]

Reac begin:      Temperature = 869.875 [K]
      Ar= 0.163999 kmol/s
      N2= 14.1056 kmol/s
      O2= 0.901607 kmol/s
   Enthalpy = 2.61607e+08 [W]

Reac end   :     Temperature = 753.644 [K]
      Ar= 0.163999 kmol/s
      N2= 14.1056 kmol/s
      O2= 0.901607 kmol/s
   Enthalpy = 2.06029e+08 [W]

Fuel Cell feed     :     Temperature = 1155 [K]
      H2 = 0.712128 kmol/s
      H2O= 0 kmol/s
   Enthalpy (heat) = 1.80957e+07 [W]
   Enthalpy (comb) = 1.72207e+08 [W]

Fuel Cell Exhaust :     Temperature = 1250 [K]
      H2 = 0.0712128 kmol/s
      H2O= 0.640916 kmol/s
   Enthalpy (heat) = 2.36889e+07 [W]
   Enthalpy (comb) = 1.72207e+07 [W]

Stream Balances:
   2.71482e+08 = 2.71514e+08
   5.55771e+07 = 5.55756e+07
```

<u>Economics</u>

```
Total Electricity Output [W] = 8.51117e+07
Winter Efficiency = 0.549202
Total Efficiency = 0.398961

Land Require [m^2] = 111427
Land Investment [$]  = 2.83247e+07
Plant Investment [$] = 6.38525e+08
Working Capital [$]  = 3.19263e+07
Total Investment [$] = 6.98776e+08

Land Capital Cost [$/year]       = 1.43244e+06
Plant Capital Cost [$/year]      = 4.46101e+07
Working Capital Cost [$/year]    = 1.61457e+06
Total Operating Cost [$/year]    = 2.86568e+07
Input Electricity Cost [$/year] = 3.06115e+07
                 Total [$/year] = 1.06926e+08
Specific Costs [$/kWh]: Land        = 0.00350626
                        Capital     = 0.109195
                        Working Cap = 0.00395209
                        Operating   = 0.0701451        Plant costs = 0.186799
                        Input Elec = 0.0749298

 kWh-costs [$/kWh] = 0.261728
```

B.3 Winter Process of the MTH-System with Molten Carbonate Fuel Cells

Hydrogen Compressor

```
Streams: [kmol/s]
  IN = OUT: O2  = 0
            N2  = 0
            Ar  = 0
            H2  = 0.87
            CH4 = 0
            CO2 = 0

Massbalance: [kg/s]
  IN = OUT: O2  = 0
            N2  = 0
            Ar  = 0
            H2  = 1.75392
            CH4 = 0
            CO2 = 0
     total  = 1.75392

Inlet Temperature of Gas [K]   = 452.94
Inlet Pressure of Gas [Pa]     = 527860
Outlet Temperature of Gas [K]  = 650.727
Outlet Pressure of Gas [Pa]    = 1.6e+06

Energybalance: [J/s]=[W]
  Qin       = 3.92979e+06        (298.15K -> 452.94K)
  Qout      = 8.96885e+06        (298.15K -> 650.727K)
  Wcomp      = 5.03907e+06        (452.94K -> 650.727K)
  elec       = 5.19491e+06
  Qloss      = 155847
  balance  5.03907e+06 = 5.03907e+06

Investment [$] = 6.4114e+06
Lifetime [year] = 19
Land Require [m^2] = 10.0781
Capital Cost [$/year]    = 582486
Operating Cost [$/year] = 192342
```

Heat Exchanger 1

```
numbank = 30   numtube = 140    dbank = 0.07m    dtube = 0.07m
din = 0.036m    dout = 0.0424m    length = 3m

HeatBalance [W]:
   Inside= 1.15774e+07   Outside= 1.1584e+07
   Heat Require [W] = 1.15844e+07
   Heat Transfercoef. [W/m^2K] = 67.7438
Tempbegin [K] = 870     Tempend [K] = 778.663
Pressure (Out) [Pa] Begin= 100000   End= 99578.2   Diff=  421.83
Pressure (Tube) [Pa] Begin= 1.6e+06   End= 1.59999e+06   Diff=  6.15074
Temp. Product [K] = 777.529
Heat Exchange Area [m^2] = 15.2067

Investment [$] = 349375
Lifetime [year] = 22
Land Require [m^2] = 3.04133
Capital Cost [$/year]    = 29178.2
Operating Cost [$/year] = 10481.3
```

Dehydrogenation Step 1

```
Number of Reactor = 4
din = 1.17m    length = 2.42m

Heat Balance per Reactor [W]: Reac= 3.51369e+06   Inside= -3.50309e+06
```

```
Mass Balance per Reactor [kg]: In= 5.7073   Out= 5.70732
 In  [kmol/s]: MCH= 0.0536107  TOL= 5.3133e-05  H2= 0.2175
 Out [kmol/s]: MCH= 0.0373662  TOL= 0.0162977  H2= 0.266234
 Massvelocity [kg/sm^2] = 5.30846        LHSV [1/hr]  = 9.51688

Conversion = 0.303699           (Equilibrium at 0.305756 )
Pressure (Tube) [Pa] Begin= 1.59999e+06   End= 1.4555e+06   Diff=  144494
Temp. Product [K] = 622.438

Investment [$] = 312743
Lifetime [year] = 22
Land Require [m^2] = 21.9024
Capital Cost [$/year]   = 26118.9
Operating Cost [$/year] = 9382.3    + Catalyst [$/year] = 312219
```

Heat Exchanger 2

```
numbank = 120   numtube = 140     dbank = 0.07m     dtube = 0.07m
din = 0.036m    dout = 0.0424m    length = 3m

HeatBalance [W]:
   Inside= 1.49664e+07   Outside= 1.49824e+07
   Heat Require [W] = 1.49821e+07
   Heat Transfercoef. [W/m^2K] = 22.808
Tempbegin [K] = 870     Tempend [K] = 751.342
Pressure (Out) [Pa] Begin= 100000   End= 98299.2   Diff=  1700.79
Pressure (Tube) [Pa] Begin= 1.4555e+06   End= 1.4555e+06   Diff=  0.715695
Temp. Product [K] = 787.24
Heat Exchange Area [m^2] = 60.8266

Investment [$] = 896794
Lifetime [year] = 22
Land Require [m^2] = 12.1653
Capital Cost [$/year]   = 74896.2
Operating Cost [$/year] = 26903.8
```

Dehydrogenation Step 2

```
Number of Reactor = 4
din = 1.17m     length = 2.42m

Heat Balance per Reactor [W]: Reac= 3.44999e+06   Inside= -3.4403e+06

Mass Balance per Reactor [kg]: In= 5.70732   Out= 5.70734
 In  [kmol/s]: MCH= 0.0373662  TOL= 0.0162977  H2= 0.266234
 Out [kmol/s]: MCH= 0.0214162  TOL= 0.0322477  H2= 0.314084
 Massvelocity [kg/sm^2] = 5.30847        LHSV [1/hr]  = 9.03058

Conversion = 0.60092            (Equilibrium at 0.606964 )
Pressure (Tube) [Pa] Begin= 1.4555e+06   End= 1.26356e+06   Diff=  191939
Temp. Product [K] = 636.276

Investment [$] = 312743
Lifetime [year] = 22
Land Require [m^2] = 21.9024
Capital Cost [$/year]   = 26118.9
Operating Cost [$/year] = 9382.3    + Catalyst [$/year] = 312219
```

Heat Exchanger 3

```
numbank = 150   numtube = 140     dbank = 0.07m     dtube = 0.07m
din = 0.036m    dout = 0.0424m    length = 3m

HeatBalance [W]:
   Inside= 1.40451e+07   Outside= 1.40553e+07
   Heat Require [W] = 1.4055e+07
   Heat Transfercoef. [W/m^2K] = 17.8819
Tempbegin [K] = 870     Tempend [K] = 758.819
Pressure (Out) [Pa] Begin= 100000   End= 97853.2   Diff=  2146.82
Pressure (Tube) [Pa] Begin= 1.26356e+06   End= 1.26356e+06   Diff=  0.516801
Temp. Product [K] = 789.93
Heat Exchange Area [m^2] = 76.0333

Investment [$] = 1.04374e+06
```

```
Lifetime [year] = 22
Land Require [m^2] = 15.2067
Capital Cost [$/year]   = 87168.3
Operating Cost [$/year] = 31312.2
```

Dehydrogenation Step 3

```
Number of Reactors = 4
din = 1.17m    length = 2.42m

Heat Balance per Reactor [W]: Reac= 3.1732e+06   Inside= -3.16502e+06

Mass Balance per Reactor [kg]: In= 5.70734   Out= 5.70735
 In  [kmol/s]: MCH= 0.0214162  TOL= 0.0322477  H2= 0.314084
 Out [kmol/s]: MCH= 0.00674579  TOL= 0.0469181  H2= 0.358095
 Massvelocity [kg/sm^2] = 5.30849        LHSV [1/hr]  = 8.55309

Conversion = 0.874295           (Equilibrium at 0.887848 )
Pressure (Tube) [Pa] Begin= 1.26356e+06   End= 996171   Diff=  267389
Temp. Product [K] = 651.852

Investment [$] = 312743
Lifetime [year] = 22
Land Require [m^2] = 21.9024
Capital Cost [$/year]   = 26118.9
Operating Cost [$/year] = 9382.3    + Catalyst [$/year] = 312219
```

Heat Exchanger 4

```
numbank = 150   numtube = 140     dbank = 0.07m     dtube = 0.07m
din = 0.036m    dout = 0.0424m    length = 3m

HeatBalance [W]:
   Inside= 1.31211e+07   Outside= 1.31301e+07
   Heat Require [W] = 1.31298e+07
   Heat Transfercoef. [W/m^2K] = 17.8247
Tempbegin [K] = 870     Tempend [K] = 766.263
Pressure (Out) [Pa] Begin= 100000   End= 97841.9    Diff=  2158.1
Pressure (Tube) [Pa] Begin= 996171   End= 996170    Diff=  0.679991
Temp. Product [K] = 794.526
Heat Exchange Area [m^2] = 76.0333

Investment [$] = 1.04374e+06
Lifetime [year] = 22
Land Require [m^2] = 15.2067
Capital Cost [$/year]   = 87168.3
Operating Cost [$/year] = 31312.2
```

Dehydrogenation Step 4

```
Number of Reactors = 4
din = 1.17m
length = 2.42m

Heat Balance per Reactor [W]: Reac= 1.42466e+06   Inside= -1.41987e+06

Mass Balance per Reactor [kg]: In= 5.70735   Out= 5.70736
 In  [kmol/s]: MCH= 0.00674579  TOL= 0.0469181  H2= 0.358095
 Out [kmol/s]: MCH= 0.000159286  TOL= 0.0535046  H2= 0.377854
 Massvelocity [kg/sm^2] = 5.3085        LHSV [1/hr]  = 8.11391

Conversion = 0.997032           (Equilibrium at 0.999786 )
Pressure (Tube) [Pa] Begin= 996170   End= 527860   Diff=  468310
Temp. Product [K] = 733.756

Investment [$] = 312743
Lifetime [year] = 22
Land Require [m^2] = 21.9024
Capital Cost [$/year]   = 26118.9
Operating Cost [$/year] = 9382.3    + Catalyst [$/year] = 312219
```

```
Summary Dehydrogenation

Investment [$] = 1.0996e+07
Land Require [m^2] = 143.308
Capital Cost [$/year]   = 965373
Operating Cost [$/year] = 329881    + Catalyst [$/year] = 1.24888e+06


Fuel Cells

Inlet Temperature of Air [K]       = 298.15
Outlet Temperature of Air [K]      = 298.15
Inlet Temperature of Fuel [K]      = 298.15
Exhaust Temperature [K]            = 298.15
Inlet Temperature of Steam [K]     = 759.523
Outlet Temperature of Steam [K]    = 870
Temperature of Streams to Cell [K] = 810
Temperature Inside Cell [K]        = 900

Streams: [kmol/s]
  IN:  air      O2  = 0.496332
                N2  = 1.98533
                Ar  = 0.0230852
                CO2 = 0.627853
       fuel     H2  = 0.664256
                H2O = 0
                CH4 = 0
                CO2 = 0
  OUT: air      O2  = 0.197417
                N2  = 1.98533
                Ar  = 0.0230852
                CO2 = 0.030022
       exhaust H2  = 0.0664256
                H2O = 0.597831
                CH4 = 0
                CO2 = 0.597831
  STEAM:        H2O = 13

Massbalance: [kg/s]
  IN:  air      O2  = 15.8821
                N2  = 55.615
                Ar  = 0.922208
                CO2 = 27.6318
       fuel     H2  = 1.33914
                H2O = 0
                CH4 = 0
                CO2 = 0
  OUT: air      O2  = 6.31713
                N2  = 55.615
                Ar  = 0.922208
                CO2 = 1.32127
       exhaust H2  = 0.133914
                H2O = 10.7699
                CH4 = 0
                CO2 = 26.3105
  IN total  = 101.39
  OUT total = 101.39

Energybalance: [J/s]=[W]
  effcell   = 0.671581
  effsyst   = 0.550575
  heatvalue =  1.44555e+08
  hr        =  -3.21632e+06
  T*sr      =  -5.48076e+06
  wrev      =  1.18509e+08
  elec      =  7.95887e+07

  heat      =  6.81832e+07
  Qcell     = 1.19666e+07        (810K -> 900K)
  Qair      = 5.33757e+07        (298.15K -> 810K)
  Qfuel     = 9.97063e+06        (298.15K -> 810K)
  Qexhaust  = 3.10217e+07        (900K -> 298.15K)
  Qoutair   = 4.10748e+07        (900K -> 298.15K)
  Qreflux   = 0         (900K -> 810K)
  Qsteam    = 5.5872e+07        (759.523K -> 870K)

  Qrest     = heat-Qcell-Qreflux-Qsteam = 344608
```

Nr	burnratio	effcell	E	H2	H2O	CO2
0	0.09	0.635838	0.653176	0.604473	0.0597831	0.030022
1	0.18	0.686334	0.705048	0.54469	0.119566	0.0898051
2	0.27	0.696089	0.715069	0.484907	0.179349	0.149588
3	0.36	0.697055	0.716061	0.425124	0.239132	0.209371
4	0.45	0.69414	0.713066	0.365341	0.298915	0.269154
5	0.54	0.68852	0.707294	0.305558	0.358698	0.328937
6	0.63	0.680209	0.698756	0.245775	0.418482	0.38872
7	0.72	0.668365	0.686589	0.185992	0.478265	0.448504
8	0.81	0.65057	0.668309	0.126209	0.538048	0.508287
9	0.9	0.618693	0.635562	0.0664256	0.597831	0.56807
	0.9	0.671581		0.0664256	0.597831	0.030022

```
Flowsheet:
      H2  =       0.0664256                              0.664256
      H2O =       0.597831                                0
   +--CO2 =       0.597831                                0
   |                          -----------------
   |              exhaust     |  |  |  |  |  |  |        fuel
   |              <<<<<<<<<<<<<  <  <  <  <  <  <<<<<<<<<<<<<
   |                          |  |  |  |  |  |  |
   |                          |::|::|::|::|::|::|  number of cells = 10
   |                          |  |  |  |  |  |  |
   |              >>>>>>>>>>>>>  >  >  >  >  >  >>>>>>>>>>>>>
   |              air         |  |  |  |  |  |  |      outair
   |                          -----------------
   | O2  =        0.496332                              0.197417
   | N2  =        1.98533                               1.98533
   +->CO2 =       0.627853                              0.030022
       ^
       |
   byproducts
```

Investment [$] = 8.46027e+07
Lifetime [year] = 25
Land Require [m^2] = 5372.23
Capital Cost [$/year]   = 6.60648e+06
Operating Cost [$/year] = 4.23014e+06

Membrane Separation

Membrane Thickness [m] = 2.5e-05
Membrane Area   [m^2] = 2000
Operating Temperature [K] = 550
presin   [Pa] = 100000
pressep [Pa] = 6000
presdrop [Pa] = 94000
Hydrogen Separation Ratio = 0.343833

```
Streams: [kmol/s]
  IN:  H2  = 0.0664256
       TOL = 0
       MCH = 0
       H2O = 0
       CO2 = 0.597831
       CO  = 0
       Ar  = 0
       N2  = 0
       O2  = 0
  OUT: H2  = 0.0435863
       TOL = 0
       MCH = 0
       H2O = 0
       CO2 = 0.597831
       CO  = 0
       Ar  = 0
       N2  = 0
       O2  = 0
  SEP: H2  = 0.0228393
       TOL = 0
       MCH = 0
       H2O = 0
       CO2 = 0
       CO  = 0
       Ar  = 0
       N2  = 0
       O2  = 0
```

```
Investment [$] = 1.2916e+07
Lifetime [year] = 17
Land Require [m^2] = 50
Capital Cost [$/year]   = 1.25679e+06
Operating Cost [$/year] = 387480    + Catalyst [$/year] = 645800
```

Membrane Evac

```
Streams: [kmol/s]
  IN = OUT: O2  = 0
            N2  = 0
            Ar  = 0
            H2  = 0.0228393
            CH4 = 0
            CO2 = 0

Massbalance: [kg/s]
  IN = OUT: O2  = 0
            N2  = 0
            Ar  = 0
            H2  = 0.0460441
            CH4 = 0
            CO2 = 0
      total  = 0.0460441

Inlet Temperature of Gas [K]   = 298.15
Inlet Pressure of Gas [Pa]     = 6000
Outlet Temperature of Gas [K]  = 729.654
Outlet Pressure of Gas [Pa]    = 100000

Energybalance: [J/s]=[W]
  Qin        = 0        (298.15K -> 298.15K)
  Qout       = 288532        (298.15K -> 729.654K)
  Wcomp       = 288532        (298.15K -> 729.654K)
  elec        = 297456
  Qloss       = 8923.67
  balance  288532 = 288532

Investment [$] = 394899
Lifetime [year] = 19
Land Require [m^2] = 0.577064
Capital Cost [$/year]   = 35877.2
Operating Cost [$/year] = 11847
```

Dehydrogenation Heat Exchange

```
Heat Require Heat Exchanger [W] = 5.37512e+07
  Heater1 [W] = 1.15844e+07
  Heater2 [W] = 1.49821e+07
  Heater3 [W] = 1.4055e+07
  Heater4 [W] = 1.31298e+07
Heat Supply Fuel Cell          [W] = 5.5872e+07
Heat Loss                      [W] = 2.12075e+06

Preheating of feed (liquid, vaporisation, gas)
  Qlfeed     [W] = 1.11737e+07          (298.15K -> 512.871K)
  condMCH    [W] = 4.1362e+06
  Qgfeed     [W] = 7.77129e+06          (512.871K -> 650.727K)
  total      [W] = 2.30812e+07          (298.15K -> 650.727K)

Cooling of Product (gas, condensation, liquid)
  Qgproduct [W] = 2.40775e+07          (733.756K -> 452.94K)
  condTOL   [W] = 6.16981e+06
  Qlproduct [W] = 8.89644e+06          (452.94K -> 298.15K)
  total     [W] = 3.91437e+07          (733.756K -> 298.15K)

Heat Exchanger Network
  Request [W] = 8.71544e+07
          Qair    5.33757e+07
          Qfuel   1.06976e+07
          Qgfeed  7.77129e+06
          Qlfeed  1.11737e+07
          condMCH 4.1362e+06
  Supply [W]  = 1.37271e+08
        Qexhaust  3.10217e+07
        Qoutair   4.10748e+07
```

```
        Qgproduct 2.40775e+07
        Qlproduct 8.89644e+06
        condTOL   6.16981e+06
        condH20   2.60306e+07
  Rest     [W] = 5.01164e+07

  Gas Heater: transfercoef. [W/m^2K] = 50.0
              dT [K] = 57
              area [m^2] = 2726.77
              cost [$] = 1.19056e+07
              capital costs [$/year]   = 1.15848e+06
              operating costs [$/year] = 357167
              land [m^2] = 545.354
  Evaporator: transfercoef. [W/m^2K] = 70.0
              dT [K] = 55.0
              area [m^2] = 1074.34
              cost [$] = 6.31953e+06
              capital costs [$/year]   = 614924
              operating costs [$/year] = 189586
              land [m^2] = 214.868
  Liq Heater: transfercoef. [W/m^2K] = 150.0
              dT [K] = 55.0
              area [m^2] = 1354.39
              cost [$] = 7.39765e+06
              capital costs [$/year]   = 719831
              operating costs [$/year] = 221930
              land [m^2] = 270.877
```

Streams

```
Netout    :     Temperature = 810 [K]
      Ar= 0.0230852 kmol/s
      N2= 1.98533 kmol/s
      O2= 0.496332 kmol/s
     CO2= 0.627853 kmol/s
   Enthalpy = 5.33757e+07 [W]

Cellin    :     Temperature = 810 [K]
      Ar= 0.0230852 kmol/s
      N2= 1.98533 kmol/s
      O2= 0.496332 kmol/s
     CO2= 0.627853 kmol/s
   Enthalpy = 5.33757e+07 [W]

Cellout   :     Temperature = 900 [K]
      Ar= 0.0230852 kmol/s
      N2= 1.98533 kmol/s
      O2= 0.197417 kmol/s
     CO2= 0.030022 kmol/s
   Enthalpy = 4.10748e+07 [W]

Netin     :     Temperature = 900 [K]
      Ar= 0.0230852 kmol/s
      N2= 1.98533 kmol/s
      O2= 0.197417 kmol/s
     CO2= 0.030022 kmol/s
   Enthalpy = 4.10748e+07 [W]

Reac begin:     Temperature = 870 [K]
     H2O= 13 kmol/s
   Enthalpy = 2.69451e+08 [W]

Reac end  :     Temperature = 759.523 [K]
     H2O= 13 kmol/s
   Enthalpy = 2.13579e+08 [W]

Fuel Cell feed    :     Temperature = 810 [K]
      H2 = 0.712686 kmol/s
      H2O= 0 kmol/s
      CO2= 0 kmol/s
   Enthalpy (heat) = 1.06976e+07 [W]
   Enthalpy (comb) = 1.72342e+08 [W]

Fuel Cell Exhaust :     Temperature = 900 [K]
      H2 = 0.0664256 kmol/s
      H2O= 0.597831 kmol/s
      CO2= 0.597831 kmol/s
   Enthalpy (heat) = 3.10217e+07 [W]
   Enthalpy (comb) = 1.6063e+07 [W]
```

```
Economics

Total Electricity Output [W] = 7.09127e+07
Winter Efficiency = 0.457222
Total Efficiency = 0.332403

Land Require [m^2] = 110524
Land Investment [$]  = 2.80951e+07
Plant Investment [$] = 5.87128e+08
Working Capital [$]  = 2.93564e+07
Total Investment [$] = 6.4458e+08

Land Capital Cost [$/year]       = 1.42082e+06
Plant Capital Cost [$/year]      = 4.08556e+07
Working Capital Cost [$/year]    = 1.48461e+06
Total Operating Cost [$/year]    = 2.6484e+07
Input Electricity Cost [$/year] = 3.06115e+07
                 Total [$/year] = 1.00857e+08
Specific Costs [$/kWh]: Land        = 0.00417421
                        Capital     = 0.120029
                        Working Cap = 0.00436162
                        Operating   = 0.077807        Plant costs = 0.206372
                        Input Elec = 0.0899331

 kWh-costs [$/kWh] = 0.296305
```

B.4 Winter Process of the MTH-System with Gas and Steam Turbines

```
Hydrogen Compressor

Streams: [kmol/s]
  IN = OUT: O2  = 0
            N2  = 0
            Ar  = 0
            H2  = 0.87
            CH4 = 0
            CO2 = 0

Massbalance: [kg/s]
  IN = OUT: O2  = 0
            N2  = 0
            Ar  = 0
            H2  = 1.75392
            CH4 = 0
            CO2 = 0
     total  = 1.75392

Inlet Temperature of Gas [K]    = 451.031
Inlet Pressure of Gas [Pa]      = 508792
Outlet Temperature of Gas [K]   = 462.926
Outlet Pressure of Gas [Pa]     = 550000

Energybalance: [J/s]=[W]
  Qin        = 3.88128e+06        (298.15K -> 451.031K)
  Qout       = 4.18357e+06        (298.15K -> 462.926K)
  Wcomp       = 302296        (451.031K -> 462.926K)
  elec        = 311646
  Qloss       = 9349.37
  balance   302296 = 302296

Investment [$] = 557112
Lifetime [year] = 19
Land Require [m^2] = 0.604593
Capital Cost [$/year]    = 50614.5
Operating Cost [$/year] = 16713.4


Heat Exchanger 1

numbank = 400    numtube = 50     dbank = 0.07m     dtube = 0.07m
din = 0.036m     dout = 0.0424m    length = 3m

HeatBalance [W]:
   Inside= 144799    Outside= 144801
   Heat Require [W] = 144801
   Heat Transfercoef. [W/m^2K] = 19.0814
Tempbegin [K] = 612.388     Tempend [K] = 611.385
Pressure (Out) [Pa] Begin= 100000    End= -16172    Diff=  116172
Pressure (Tube) [Pa] Begin= 550000    End= 549999    Diff=  0.951879
Temp. Product [K] = 611.719
Heat Exchange Area [m^2] = 72.4126

Investment [$] = 1.00968e+06
Lifetime [year] = 22
Land Require [m^2] = 14.4825
Capital Cost [$/year]    = 84323.8
Operating Cost [$/year] = 30290.3


Dehydrogenation Step 1

Number of Reactor = 20
din = 1.15m    length = 0.2m

Heat Balance per Reactor [W]: Reac= 144623    Inside= -144865
```

```
Mass Balance per Reactor [kg]: In= 1.14146    Out= 1.14146
 In  [kmol/s]: MCH= 0.0107221  TOL= 1.06266e-05  H2= 0.0435
 Out [kmol/s]: MCH= 0.0100535  TOL= 0.000679247  H2= 0.0455059
 Massvelocity [kg/sm^2] = 1.09894        LHSV [1/hr]  = 23.8389

Conversion = 0.0632872           (Equilibrium at 0.236847 )
Pressure (Tube) [Pa] Begin= 549999   End= 548510   Diff=  1489.3
Temp. Product [K] = 576.893

Investment [$] = 900037
Lifetime [year] = 22
Land Require [m^2] = 105.8
Capital Cost [$/year]   = 75167
Operating Cost [$/year] = 27001.1    + Catalyst [$/year] = 124643
```

Heat Exchanger 2

```
numbank = 400   numtube = 50    dbank = 0.07m    dtube = 0.07m
din = 0.036m    dout = 0.0424m   length = 3m

HeatBalance [W]:
   Inside= 3.77796e+06   Outside= 3.77888e+06
   Heat Require [W] = 3.77887e+06
   Heat Transfercoef. [W/m^2K] = 18.9151
Tempbegin [K] = 639.589    Tempend [K] = 613.5
Pressure (Out) [Pa] Begin= 100000   End= 98575.2   Diff=  1424.76
Pressure (Tube) [Pa] Begin= 548510   End= 548509   Diff=  0.983166
Temp. Product [K] = 622.121
Heat Exchange Area [m^2] = 72.4126

Investment [$] = 1.00968e+06
Lifetime [year] = 22
Land Require [m^2] = 14.4825
Capital Cost [$/year]   = 84323.8
Operating Cost [$/year] = 30290.3
```

Dehydrogenation Step 2

```
Number of Reactor = 20
din = 1.15m    length = 0.2m

Heat Balance per Reactor [W]: Reac= 160626   Inside= -160864

Mass Balance per Reactor [kg]: In= 1.14146    Out= 1.14146
 In  [kmol/s]: MCH= 0.0100535  TOL= 0.000679247  H2= 0.0455059
 Out [kmol/s]: MCH= 0.00931091  TOL= 0.00142185  H2= 0.0477337
 Massvelocity [kg/sm^2] = 1.09894        LHSV [1/hr]  = 23.5882

Conversion = 0.132478           (Equilibrium at 0.341278 )
Pressure (Tube) [Pa] Begin= 548509   End= 546929   Diff=  1579.39
Temp. Product [K] = 583.832

Investment [$] = 900037
Lifetime [year] = 22
Land Require [m^2] = 105.8
Capital Cost [$/year]   = 75167
Operating Cost [$/year] = 27001.1    + Catalyst [$/year] = 124643
```

Heat Exchanger 3

```
numbank = 250   numtube = 50    dbank = 0.07m    dtube = 0.07m
din = 0.036m    dout = 0.0424m   length = 3m

HeatBalance [W]:
   Inside= 5.89863e+06   Outside= 5.90064e+06
   Heat Require [W] = 5.90062e+06
   Heat Transfercoef. [W/m^2K] = 29.7095
Tempbegin [K] = 681.698    Tempend [K] = 641.298
Pressure (Out) [Pa] Begin= 100000   End= -316559   Diff=  416559
Pressure (Tube) [Pa] Begin= 546929   End= 546927   Diff=  2.43786
Temp. Product [K] = 653.151
Heat Exchange Area [m^2] = 45.2579

Investment [$] = 733468
```

```
Lifetime [year] = 22
Land Require [m^2] = 9.05158
Capital Cost [$/year]   = 61256
Operating Cost [$/year] = 22004
```

Dehydrogenation Step 3

```
Number of Reactors = 20
din = 1.15m    length = 0.25m

Heat Balance per Reactor [W]: Reac= 264847   Inside= -265086

Mass Balance per Reactor [kg]: In= 1.14146   Out= 1.14146
 In  [kmol/s]: MCH= 0.00931091  TOL= 0.00142185  H2= 0.0477337
 Out [kmol/s]: MCH= 0.00808647  TOL= 0.0026463  H2= 0.051407
 Massvelocity [kg/sm^2] = 1.09894       LHSV [1/hr]  = 18.6478

Conversion = 0.246562           (Equilibrium at 0.468842 )
Pressure (Tube) [Pa] Begin= 546927   End= 544771   Diff=  2156.08
Temp. Product [K] = 591.209

Investment [$] = 914434
Lifetime [year] = 22
Land Require [m^2] = 105.8
Capital Cost [$/year]   = 76369.4
Operating Cost [$/year] = 27433    + Catalyst [$/year] = 155804
```

Heat Exchanger 4

```
numbank = 80   numtube = 50    dbank = 0.07m    dtube = 0.07m
din = 0.036m    dout = 0.0424m    length = 3m

HeatBalance [W]:
   Inside= 8.24706e+06   Outside= 8.24951e+06
   Heat Require [W] = 8.24953e+06
   Heat Transfercoef. [W/m^2K] = 76.2959
Tempbegin [K] = 739.832    Tempend [K] = 684.022
Pressure (Out) [Pa] Begin= 100000   End= 77468.9   Diff=  22531.1
Pressure (Tube) [Pa] Begin= 544771   End= 544751   Diff=  19.8337
Temp. Product [K] = 686.313
Heat Exchange Area [m^2] = 14.4825

Investment [$] = 337974
Lifetime [year] = 22
Land Require [m^2] = 2.8965
Capital Cost [$/year]   = 28226.1
Operating Cost [$/year] = 10139.2
```

Dehydrogenation Step 4

```
Number of Reactors = 20
din = 1.15m
length = 0.25m

Heat Balance per Reactor [W]: Reac= 356486   Inside= -356518

Mass Balance per Reactor [kg]: In= 1.14146   Out= 1.14147
 In  [kmol/s]: MCH= 0.00808647  TOL= 0.0026463  H2= 0.051407
 Out [kmol/s]: MCH= 0.00643836  TOL= 0.00429441  H2= 0.0563513
 Massvelocity [kg/sm^2] = 1.09894       LHSV [1/hr]  = 18.2805

Conversion = 0.400121           (Equilibrium at 0.693695 )
Pressure (Tube) [Pa] Begin= 544751   End= 542328   Diff=  2422.99
Temp. Product [K] = 604.679

Investment [$] = 914434
Lifetime [year] = 22
Land Require [m^2] = 105.8
Capital Cost [$/year]   = 76369.4
Operating Cost [$/year] = 27433    + Catalyst [$/year] = 155804
```

```
Heat Exchanger 5

numbank = 20   numtube = 50    dbank = 0.07m    dtube = 0.07m
din = 0.036m    dout = 0.0424m    length = 3m

HeatBalance [W]:
   Inside= 8.18979e+06   Outside= 8.18975e+06
   Heat Require [W] = 8.1901e+06
   Heat Transfercoef. [W/m^2K] = 187.665
Tempbegin [K] = 796.779    Tempend [K] = 742.115
Pressure (Out) [Pa] Begin= 100000   End= 94604.7   Diff=  5395.33
Pressure (Tube) [Pa] Begin= 544771   End= 542081   Diff=  247.219
Temp. Product [K] = 697.961
Heat Exchange Area [m^2] = 3.62063

Investment [$] = 131669
Lifetime [year] = 22
Land Require [m^2] = 0.724126
Capital Cost [$/year]   = 10996.4
Operating Cost [$/year] = 3950.06


Dehydrogenation Step 5

Number of Reactors = 20
din = 1.15m
length = 0.25m

Heat Balance per Reactor [W]: Reac= 353798   Inside= -353677

Mass Balance per Reactor [kg]: In= 1.14147   Out= 1.14147
 In  [kmol/s]: MCH= 0.00643836  TOL= 0.00429441  H2= 0.0563513
 Out [kmol/s]: MCH= 0.00480268  TOL= 0.00593009  H2= 0.0612584
 Massvelocity [kg/sm^2] = 1.09895       LHSV [1/hr]  = 17.7862

Conversion = 0.552522           (Equilibrium at 0.84848 )
Pressure (Tube) [Pa] Begin= 542081   End= 539386   Diff=  2694.92
Temp. Product [K] = 617.87

Investment [$] = 914434
Lifetime [year] = 22
Land Require [m^2] = 105.8
Capital Cost [$/year]   = 76369.4
Operating Cost [$/year] = 27433    + Catalyst [$/year] = 155804


Heat Exchanger 6

numbank = 12   numtube = 50    dbank = 0.07m    dtube = 0.07m
din = 0.036m    dout = 0.0424m    length = 3m

HeatBalance [W]:
   Inside= 8.81496e+06   Outside= 8.8139e+06
   Heat Require [W] = 8.81461e+06
   Heat Transfercoef. [W/m^2K] = 247.275
Tempbegin [K] = 857.251    Tempend [K] = 799.198
Pressure (Out) [Pa] Begin= 100000   End= 96644.4   Diff=  3355.63
Pressure (Tube) [Pa] Begin= 544771   End= 538714   Diff=  671.787
Temp. Product [K] = 716.958
Heat Exchange Area [m^2] = 2.17238

Investment [$] = 93030.5
Lifetime [year] = 22
Land Require [m^2] = 0.434476
Capital Cost [$/year]   = 7769.49
Operating Cost [$/year] = 2790.92


Dehydrogenation Step 6

Number of Reactors = 20
din = 1.15m
length = 0.25m

Heat Balance per Reactor [W]: Reac= 358336   Inside= -357976

Mass Balance per Reactor [kg]: In= 1.14147   Out= 1.14147
 In  [kmol/s]: MCH= 0.00480268  TOL= 0.00593009  H2= 0.0612584
```

```
 Out [kmol/s]: MCH= 0.00314602  TOL= 0.00758675  H2= 0.0662284
 Massvelocity [kg/sm^2] = 1.09895       LHSV [1/hr]  = 17.2956

Conversion = 0.706878           (Equilibrium at 0.952057 )
Pressure (Tube) [Pa] Begin= 538714   End= 535691   Diff=  3022.71
Temp. Product [K] = 636.986

Investment [$] = 914434
Lifetime [year] = 22
Land Require [m^2] = 105.8
Capital Cost [$/year]    = 76369.4
Operating Cost [$/year] = 27433    + Catalyst [$/year] = 155804
```

Heat Exchanger 7

```
numbank = 8   numtube = 50     dbank = 0.07m    dtube = 0.07m
din = 0.036m    dout = 0.0424m    length = 3m

HeatBalance [W]:
   Inside= 9.00101e+06  Outside= 8.99919e+06
   Heat Require [W] = 9.00028e+06
   Heat Transfercoef. [W/m^2K] = 301.441
Tempbegin [K] = 918.187    Tempend [K] = 859.685
Pressure (Out) [Pa] Begin= 100000   End= 97701.3   Diff=  2298.7
Pressure (Tube) [Pa] Begin= 544771   End= 534168   Diff=  1523.9
Temp. Product [K] = 736.807
Heat Exchange Area [m^2] = 1.44825

Investment [$] = 70612.8
Lifetime [year] = 22
Land Require [m^2] = 0.28965
Capital Cost [$/year]    = 5897.26
Operating Cost [$/year] = 2118.38
```

Dehydrogenation Step 7

```
Number of Reactors = 20
din = 1.15m
length = 0.3m

Heat Balance per Reactor [W]: Reac= 347868   Inside= -347281

Mass Balance per Reactor [kg]: In= 1.14147   Out= 1.14147
 In  [kmol/s]: MCH= 0.00314602  TOL= 0.00758675  H2= 0.0662284
 Out [kmol/s]: MCH= 0.00153775  TOL= 0.00919502  H2= 0.0710532
 Massvelocity [kg/sm^2] = 1.09895       LHSV [1/hr]  = 13.9989

Conversion = 0.856724           (Equilibrium at 0.988495 )
Pressure (Tube) [Pa] Begin= 534168   End= 530093   Diff=  4074.15
Temp. Product [K] = 660.219

Investment [$] = 928831
Lifetime [year] = 22
Land Require [m^2] = 105.8
Capital Cost [$/year]    = 77571.8
Operating Cost [$/year] = 27864.9    + Catalyst [$/year] = 186964
```

Heat Exchanger 8

```
numbank = 8   numtube = 50     dbank = 0.07m    dtube = 0.07m
din = 0.036m    dout = 0.0424m    length = 3m

HeatBalance [W]:
   Inside= 9.14545e+06  Outside= 9.14314e+06
   Heat Require [W] = 9.14458e+06
   Heat Transfercoef. [W/m^2K] = 344.291
Tempbegin [K] = 979.242    Tempend [K] = 920.535
Pressure (Out) [Pa] Begin= 100000   End= 98237   Diff=  1762.96
Pressure (Tube) [Pa] Begin= 544771   End= 527268   Diff=  2825.17
Temp. Product [K] = 760.28
Heat Exchange Area [m^2] = 1.08619

Investment [$] = 58066.4
Lifetime [year] = 22
Land Require [m^2] = 0.217238
```

```
Capital Cost [$/year]   = 4849.44
Operating Cost [$/year] = 1741.99
```

Dehydrogenation Step 8

```
Number of Reactors = 20
din = 1.15m
length = 1.2m

Heat Balance per Reactor [W]: Reac= 320173   Inside= -319393

Mass Balance per Reactor [kg]: In= 1.14147   Out= 1.14147
 In  [kmol/s]: MCH= 0.00153775  TOL= 0.00919502  H2= 0.0710532
 Out [kmol/s]: MCH= 5.7523e-05  TOL= 0.0106752  H2= 0.0754939
 Massvelocity [kg/sm^2] = 1.09895      LHSV [1/hr]  = 3.39921

Conversion = 0.99464          (Equilibrium at 0.998199 )
Pressure (Tube) [Pa] Begin= 527268   End= 508792   Diff=  18476.2
Temp. Product [K] = 690.779

Investment [$] = 1.18798e+06
Lifetime [year] = 22
Land Require [m^2] = 105.8
Capital Cost [$/year]   = 99214.6
Operating Cost [$/year] = 35639.4    + Catalyst [$/year] = 747858
```

Summary Dehydrogenation

```
Investment [$] = 1.15759e+07
Land Require [m^2] = 889.583
Capital Cost [$/year]   = 970855
Operating Cost [$/year] = 347277    + Catalyst [$/year] = 1.80732e+06
```

Gas Turbine

```
Streams: [kmol/s]
  IN:  air      O2  = 1.1507
                N2  = 4.2883
                Ar  = 0.0518
                CO2 = 0
       fuel     H2  = 0.639877
                H2O = 0
                CH4 = 0
                CO2 = 0
  OUT: exhaust  O2  = 0.830761
                N2  = 4.2883
                Ar  = 0.0518
                H2  = 0
                H2O = 0.639877
                CH4 = 0
                CO2 = 0

Massbalance: [kg/s]
  IN:  air      O2  = 36.8212
                N2  = 120.128
                Ar  = 2.06931
                CO2 = 0
       fuel     H2  = 1.28999
                H2O = 0
                CH4 = 0
                CO2 = 0
  OUT: exhaust  O2  = 26.5835
                N2  = 120.128
                Ar  = 2.06931
                H2  = 0
                H2O = 11.5274
                CH4 = 0
                CO2 = 0
  IN total  = 160.309
  OUT total = 160.308

Inlet Temperature of Air [K]       = 360
Inlet Pressure of Air [Pa]         = 100000
Inlet Temperature of Fuel [K]      = 451.031
Inlet Pressure of Fuel [Pa]        = 508792
```

```
Temperature of compressed Air [K]    = 962.343
Pressure after Compression [Pa]      = 2.5e+06
Temperature after Combustion 1 [K]   = 1386.34
Pressure after first Turbine [Pa]    = 650000
Temperature after first Turbine [K]  = 1043.56
Temperature after Combustion 2 [K]   = 1417.32
Exhaust Temperature [K]              = 979.242
Exhaust Pressure [Pa]                = 100000

Energybalance: [J/s]=[W]
  heatvalue  = 1.54735e+08
  heat       = 1.58609e+08
  Qair       = 9.89137e+06      (298.15K -> 360K)
  Qfuel      = 2.85465e+06      (298.15K -> 451.031K)
  Qexhaust   = 1.24124e+08      (979.242K -> 298.15K)
  Wcomp      = 1.04265e+08
  Wcompfuel  = 6.12453e+06
  Wturb      = 1.53767e+08
  Wmech      = 4.33771e+07
  elec       = 4.25095e+07
  Qloss      = 848001
  efficiency = 0.274725
  balance  1.67481e+08 = 1.67501e+08

Investment [$] = 3.40501e+07
Lifetime [year] = 30
Land Require [m^2] = 2400
Capital Cost [$/year]    = 2.44201e+06
Operating Cost [$/year] = 1.0215e+06
```

<u>Steam Turbine</u>

```
T1 [K]       = 905.654
T2 [K]       = 320.557
T3 [K]       = 320.557
T4 [K]       = 319.099
T5 [K]       = 515.69
T6 [K]       = 515.69
T7 [K]       = 515.69
T8 [K]       = 515.69
H1 [J/kg]    = 3.75122e+06
H2 [J/kg]    = 2.58776e+06
H3 [J/kg]    = 191832
H4 [J/kg]    = 195356
H5 [J/kg]    = 1.04976e+06
H6 [J/kg]    = 2.80196e+06
H7 [J/kg]    = 1.0899e+06
H8 [J/kg]    = 1.0899e+06
S1 [J/kgK]   = 7516.77
S2 [J/kgK]   = 8160.42
S3 [J/kgK]   = 649.252
S4 [J/kgK]   = 649.252
S5 [J/kgK]   = 2725.27
S6 [J/kgK]   = 6122.85
S7 [J/kgK]   = 1.96182e+06
S8 [J/kgK]   = 1.96182e+06

Evaporation Pressure [Pa] = 3.5e+06
Condensing Pressure [Pa]  = 10000
Feedwater [kg/s] = 9.5

Energybalance: [J/s]=[W]
  Qliq     = 8.11681e+06       (319.099K -> 515.69K)
  Qvap     = 1.66459e+07       (515.69K -> 515.69K)
  Qgas1    = 0        (515.69K -> 515.69K)
  Qgas2    = 9.01797e+06       (515.69K -> 905.654K)
  Qreq     = 3.37807e+07       (319.099K -> 905.654K)
  Qcond    = 2.27613e+07       (320.557K -> 320.557K)
  Wturb1   = 0        (515.69K -> 515.69K)
  Wturb2   = 1.10529e+07       (905.654K -> 320.557K)
  Wpump    = 33470.3       (320.557K -> 319.099K)
  elec     = 1.07924e+07
  efficiency = 0.319485
  Qloss    = 226964
  balance  3.37807e+07 = 3.38142e+07

Investment [$] = 8.64473e+06
Lifetime [year] = 30
Land Require [m^2] = 2400
```

```
Capital Cost [$/year]   = 619983
Operating Cost [$/year] = 259342


Dehydrogenation Heat Exchange

Heat Require Heat Exchanger [W] = 5.54222e+07
  Heater1 [W] = 144801
  Heater2 [W] = 3.77887e+06
  Heater3 [W] = 5.90062e+06
  Heater4 [W] = 8.24953e+06
  Heater5 [W] = 8.1901e+06
  Heater6 [W] = 8.81461e+06
  Heater7 [W] = 9.00028e+06
  Heater8 [W] = 9.14458e+06     total = 5.32234e+07

Preheating of feed (liquid, vaporisation, gas)
  Qlfeed       [W] = 7.1847e+06        (298.15K -> 448.562K)
  condMCH      [W] = 5.61073e+06
  Qgfeed       [W] = 8.39698e+06        (448.562K -> 610K)
  Qhydfeed     [W] = 3.74493e+06        (462.926K -> 610K)
  total        [W] = 2.11924e+07        (298.15K -> 610K)

Cooling of Product (gas, condensation, liquid)
  Qhydproduct [W] = 1.06084e+07        (690.779K -> 451.031K)
  Qgproduct   [W] = 9.68082e+06        (690.779K -> 451.031K)
  condTOL     [W] = 6.2022e+06
  Qlproduct   [W] = 5.91965e+06        (451.031K -> 298.15K)
  total       [W] = 2.18027e+07        (690.779K -> 298.15K)

Heat Exchanger Network
  Request [W] = 2.11924e+07
                  Qgfeed      8.39698e+06
                  Qlfeed      7.1847e+06
                  condMCH     5.61073e+06
  Supply [W]  = 3.2411e+07
                  Qgproduct   9.68082e+06
                  Qhydproduct 1.06084e+07
                  Qlproduct   5.91965e+06
                  condTOL     6.2022e+06
  Rest    [W] =   1.12186e+07


  Gas Heater: transfercoef. [W/m^2K] = 50.0
              dT [K] = 80.7791
              area [m^2] = 2079
              cost [$] = 9.90034e+06
              capital costs [$/year]   = 963356
              operating costs [$/year] = 297010
              land [m^2] = 415.8
  Evaporator: transfercoef. [W/m^2K] = 70.0
              dT [K] = 62.0
              area [m^2] = 1292.79
              cost [$] = 7.16719e+06
              capital costs [$/year]   = 697406
              operating costs [$/year] = 215016
              land [m^2] = 277.83
  Liq Heater: transfercoef. [W/m^2K] = 150.0
              dT [K] = 90.0
              area [m^2] = 532.2
              cost [$] = 3.91959e+06
              capital costs [$/year]   = 381397
              operating costs [$/year] = 117588
              land [m^2] = 106.44


Streams

Air in:    Temperature = 360 [K]
      Ar= 0.0518 kmol/s
      N2= 4.2883 kmol/s
      O2= 1.1507 kmol/s
   Enthalpy = 9.89137e+06 [W]

Gas Turbine Feed    :    Temperature = 451.031 [K]
      H2 = 0.639877 kmol/s
      H2O= 0 kmol/s
   Enthalpy (heat) = 2.85465e+06 [W]
   Enthalpy (comb) = 1.54735e+08 [W]
```

```
Gas Turbine Exhaust :    Temperature = 979.242 [K]
      H2 = 0 kmol/s
      H2O= 0.639877 kmol/s
      Ar = 0.0518 kmol/s
      N2 = 4.2883 kmol/s
      O2 = 0.830761 kmol/s
   Enthalpy (heat) = 1.24124e+08 [W]
   Enthalpy (comb) = 0 [W]

Exhaust after Reactor:    Temperature = 611.3 [K]
      H2 = 0 kmol/s
      H2O= 0.639877 kmol/s
      Ar = 0.0518 kmol/s
      N2 = 4.2883 kmol/s
      O2 = 0.830761 kmol/s
   Enthalpy (heat) = 5.48458e+07 [W]

Exhaust after H2O Condenser:    Temperature = 374.883 [K]
      H2 = 0 kmol/s
      H2O= 0.639877 kmol/s
      Ar = 0.0518 kmol/s
      N2 = 4.2883 kmol/s
      O2 = 0.830761 kmol/s
   Enthalpy (heat) = 1.3213e+07 [W]

Dehydrogenation Feed:    Temperature = 610 [K]
      H2 = 0.87 kmol/s
      MCH= 0.214443 kmol/s
      TOL= 0.000212532 kmol/s
   Enthalpy = 2.18809e+07 [W]

Dehydrogenation Product:    Temperature = 690.779 [K]
      H2 = 1.50988 kmol/s
      MCH= 0.00115046 kmol/s
      TOL= 0.213505 kmol/s
   Enthalpy = 3.32271e+07 [W]

Dehydrogenation Reaction:
   Enthalpy = 4.36757e+07 [W]

Stream Balances:
   Qreac = 5.54222e+07 = 6.92777e+07
   Qevap = 4.16329e+07 = 4.16328e+07
   Gasturb 1.67481e+08 = 1.67501e+08
   total   1.45309e+08 = 1.46367e+08
```

<u>Economics</u>

```
Total Electricity Output [W] = 5.29903e+07
Winter Efficiency = 0.342487
Total Efficiency = 0.248392

Land Require [m^2] = 110397
Land Investment [$]  = 2.80628e+07
Plant Investment [$] = 5.27854e+08
Working Capital [$]  = 2.63927e+07
Total Investment [$] = 5.82309e+08

Land Capital Cost [$/year]       = 1.41919e+06
Plant Capital Cost [$/year]      = 3.55729e+07
Working Capital Cost [$/year]    = 1.33473e+06
Total Operating Cost [$/year]    = 2.29264e+07
Input Electricity Cost [$/year] = 3.06115e+07
                 Total [$/year] = 9.18647e+07
Specific Costs [$/kWh]: Land        = 0.00557961
                        Capital     = 0.139856
                        Working Cap = 0.00524754
                        Operating   = 0.0901359        Plant costs = 0.240819
                        Input Elec = 0.12035

 kWh-costs [$/kWh] = 0.361169
```

B.5 Best Case Study of the MTH-System

```
Initialisation Values

Electricity  = 3.2e+08 kW
Temp. Feed   = 660 K
Temp. Heat Medium    = 891.982 K
feedH2  = 1e-07 kmol/s
airoutAr= 0.0976185 kmol/s
airoutN2= 8.39616 kmol/s
airoutO2= 0.463956 kmol/s
pfeed   = 1.6e+06 Pa
pairout = 100000 Pa


Electrolyser

tempin [K]   = 300
tempreac [K] = 300
tempout [K]  = 300
Efficieny Power Conditioner = 0.97
          of Cells          = 0.75
Power Consumption [kWh/m^3] = 4

Streams: [kmol/s]
  IN:  H2O = 1.00431
  OUT: H2  = 1.00431       O2  = 0.502157

Investment [$] = 7.75146e+07
Lifetime [year] = 30
Land Require [m^2] = 16551.7
Capital Cost [$/year]    = 5.55919e+06
Operating Cost [$/year] = 4.65087e+06


Hydrogenation Reactor

tempin [K]   = 300
tempreac [K] = 550
tempout [K]  = 300
minimal Pressure [Pa] = 2.64511e+06

Streams: [kmol/s]
  IN:  H2  = 1.00431          TOL = 0.334738        MCH = 0.00334437
  OUT: H2  = 0.00110465          TOL = 0.000334738        MCH = 0.337748

Massbalance: [kg/s]
  IN:  H2  = 2.0247          TOL = 30.8431        MCH = 0.328377
     total = 33.1962
  OUT: H2  = 0.00222696          TOL = 0.0308431        MCH = 33.1628
     total = 33.1958

Energybalance: [J/s]=[W]
  Qfeed    = 152901
  Qinside = 2.73029e+07
  Qprod    = 2.5265e+07
  Qtank    = 115841
  Qreac    = 7.05504e+07
  Qext     = 4.32475e+07
   Balance Reactor = 0
   Balance Total    = -0.996222

Massflow [ton/hour] = 119.506
Electricity [kW] = 1.79259e+06
Catalyst Cost [$/hour] = 322.667
Investment [$] = 1.88171e+07
Lifetime [year] = 19
Land Require [m^2] = 128.042
Capital Cost [$/year]    = 1.70957e+06
Operating Cost [$/year] = 564514
    + Catalyst [$/year] = 1.03253e+06
```

<u>Tank</u>

```
Space [m^3]             = 540000 = 27 x 20000
minimal Space [m^3]     = 499187
Investment Costs [$] = 1.28136e+08
Land [m^2]              = 90000
Inventory [kmol]  MCH: 3.89085e+06  TOL: 3856.18
Out [kmol/s]  MCH: 0.225165  TOL: 0.000223159
Investment [$] = 1.28136e+08
Lifetime [year] = 65
Capital Cost [$/year]    = 7.42713e+06
Operating Cost [$/year] = 2.74576e+06
Land Require [m^2] = 90000
Toluene Investment  [$] = 9.33042e+07
Capital Cost Toluene [$/year]         = 4.71858e+06
Operating Cost (Byproducts) [$/year] = 0
```

<u>Heat Exchanger 1</u>

```
numbank = 17   numtube = 200     dbank = 0.07m    dtube = 0.07m
din = 0.036m    dout = 0.0424m    length = 3m

HeatBalance [W]:
   Inside= 7.69186e+06   Outside= 7.69376e+06
   Heat Require [W] = 7.69426e+06
   Heat Transfercoef. [W/m^2K] = 45.0245
Tempbegin [K] = 891.982     Tempend [K] = 811.501
Pressure (Out) [Pa] Begin= 100000    End= 99838.5    Diff=  161.465
Pressure (Tube) [Pa] Begin= 1.6e+06   End= 1.6e+06   Diff=  1.77936
Temp. Product [K] = 771.394
Heat Exchange Area [m^2] = 12.3101

Investment [$] = 302613
Lifetime [year] = 22
Land Require [m^2] = 2.46203
Capital Cost [$/year]    = 25272.9
Operating Cost [$/year] = 9078.4
```

<u>Dehydrogenation Step 1</u>

```
Number of Reactor = 4
din = 1.15m    length = 2m

Heat Balance per Reactor [W]: Reac= 3.00406e+06   Inside= -2.98206e+06

Mass Balance per Reactor [kg]: In= 5.53227   Out= 5.53228
 In  [kmol/s]: MCH= 0.0562913  TOL= 5.57896e-05  H2= 2.5e-08
 Out [kmol/s]: MCH= 0.0424029  TOL= 0.0139442  H2= 0.0416652
 Massvelocity [kg/sm^2] = 5.32619        LHSV [1/hr]  = 12.5154

Conversion = 0.24747           (Equilibrium at 0.247528 )
Pressure (Tube) [Pa] Begin= 1.6e+06   End= 1.56549e+06   Diff=  34511.1
Temp. Product [K] = 592.812

Investment [$] = 283667
Lifetime [year] = 22
Land Require [m^2] = 21.16
Capital Cost [$/year]    = 23690.5
Operating Cost [$/year] = 8510     + Catalyst [$/year] = 249286
```

<u>Heat Exchanger 2</u>

```
numbank = 50   numtube = 200     dbank = 0.07m    dtube = 0.07m
din = 0.036m    dout = 0.0424m    length = 3m

HeatBalance [W]:
   Inside= 1.2323e+07   Outside= 1.2337e+07
   Heat Require [W] = 1.23371e+07
   Heat Transfercoef. [W/m^2K] = 23.432
Tempbegin [K] = 891.982     Tempend [K] = 762.27
Pressure (Out) [Pa] Begin= 100000    End= 99522.9    Diff=  477.131
Pressure (Tube) [Pa] Begin= 1.56549e+06   End= 1.56549e+06   Diff=  0.468874
Temp. Product [K] = 776.42
Heat Exchange Area [m^2] = 36.2063
```

```
Investment [$] = 630206
Lifetime [year] = 22
Land Require [m^2] = 7.24126
Capital Cost [$/year]   = 52632
Operating Cost [$/year] = 18906.2
```

Dehydrogenation Step 2

```
Number of Reactor = 4
din = 1.15m    length = 2m

Heat Balance per Reactor [W]: Reac= 2.69221e+06   Inside= -2.67899e+06

Mass Balance per Reactor [kg]: In= 5.53228   Out= 5.53229
 In  [kmol/s]: MCH= 0.0424029  TOL= 0.0139442  H2= 0.0416652
 Out [kmol/s]: MCH= 0.0299562  TOL= 0.0263908  H2= 0.0790051
 Massvelocity [kg/sm^2] = 5.3262        LHSV [1/hr]  = 11.9947

Conversion = 0.468362          (Equilibrium at 0.468597 )
Pressure (Tube) [Pa] Begin= 1.56549e+06   End= 1.51404e+06   Diff=  51446.6
Temp. Product [K] = 618.713

Investment [$] = 283667
Lifetime [year] = 22
Land Require [m^2] = 21.16
Capital Cost [$/year]   = 23690.5
Operating Cost [$/year] = 8510    + Catalyst [$/year] = 249286
```

Heat Exchanger 3

```
numbank = 32   numtube = 200     dbank = 0.07m     dtube = 0.07m
din = 0.036m     dout = 0.0424m    length = 3m

HeatBalance [W]:
   Inside= 1.11812e+07   Outside= 1.11915e+07
   Heat Require [W] = 1.11917e+07
   Heat Transfercoef. [W/m^2K] = 35.6863
Tempbegin [K] = 891.982     Tempend [K] = 774.464
Pressure (Out) [Pa] Begin= 100000    End= 99695.4    Diff=  304.575
Pressure (Tube) [Pa] Begin= 1.51404e+06   End= 1.51404e+06   Diff=  1.50424
Temp. Product [K] = 782.463
Heat Exchange Area [m^2] = 23.172

Investment [$] = 465248
Lifetime [year] = 22
Land Require [m^2] = 4.63441
Capital Cost [$/year]   = 38855.4
Operating Cost [$/year] = 13957.5
```

Dehydrogenation Step 3

```
Number of Reactors = 4
din = 1.15m    length = 2m

Heat Balance per Reactor [W]: Reac= 2.52826e+06   Inside= -2.51828e+06

Mass Balance per Reactor [kg]: In= 5.53229   Out= 5.5323
 In  [kmol/s]: MCH= 0.0299562  TOL= 0.0263908  H2= 0.0790051
 Out [kmol/s]: MCH= 0.0182676  TOL= 0.0380795  H2= 0.114071
 Massvelocity [kg/sm^2] = 5.32621       LHSV [1/hr]  = 11.528

Conversion = 0.675803          (Equilibrium at 0.676422 )
Pressure (Tube) [Pa] Begin= 1.51404e+06   End= 1.44442e+06   Diff=  69622.3
Temp. Product [K] = 635.844

Investment [$] = 283667
Lifetime [year] = 22
Land Require [m^2] = 21.16
Capital Cost [$/year]   = 23690.5
Operating Cost [$/year] = 8510    + Catalyst [$/year] = 249286
```

```
Heat Exchanger 4

numbank = 27   numtube = 200    dbank = 0.07m    dtube = 0.07m
din = 0.036m    dout = 0.0424m    length = 3m

HeatBalance [W]:
   Inside= 1.04735e+07   Outside= 1.04816e+07
   Heat Require [W] = 1.04819e+07
   Heat Transfercoef. [W/m^2K] = 41.9462
Tempbegin [K] = 891.982    Tempend [K] = 782.004
Pressure (Out) [Pa] Begin= 100000   End= 99743.2   Diff=  256.843
Pressure (Tube) [Pa] Begin= 1.44442e+06   End= 1.44441e+06   Diff=  2.73062
Temp. Product [K] = 787.632
Heat Exchange Area [m^2] = 19.5514

Investment [$] = 414486
Lifetime [year] = 22
Land Require [m^2] = 3.91028
Capital Cost [$/year]   = 34616
Operating Cost [$/year] = 12434.6


Dehydrogenation Step 4

Number of Reactors = 4
din = 1.15m
length = 2m

Heat Balance per Reactor [W]: Reac= 2.31578e+06   Inside= -2.30763e+06

Mass Balance per Reactor [kg]: In= 5.5323   Out= 5.53231
 In  [kmol/s]: MCH= 0.0182676  TOL= 0.0380795  H2= 0.114071
 Out [kmol/s]: MCH= 0.00756122  TOL= 0.0487858  H2= 0.14619
 Massvelocity [kg/sm^2] = 5.32622        LHSV [1/hr]  = 11.0898

Conversion = 0.86581           (Equilibrium at 0.866791 )
Pressure (Tube) [Pa] Begin= 1.44441e+06   End= 1.3539e+06   Diff=  90513.2
Temp. Product [K] = 654.527

Investment [$] = 283667
Lifetime [year] = 22
Land Require [m^2] = 21.16
Capital Cost [$/year]   = 23690.5
Operating Cost [$/year] = 8510    + Catalyst [$/year] = 249286


Heat Exchanger 5

numbank = 25   numtube = 200    dbank = 0.07m    dtube = 0.07m
din = 0.036m    dout = 0.0424m    length = 3m

HeatBalance [W]:
   Inside= 9.76166e+06   Outside= 9.76816e+06
   Heat Require [W] = 9.76838e+06
   Heat Transfercoef. [W/m^2K] = 45.5076
Tempbegin [K] = 891.982    Tempend [K] = 789.571
Pressure (Out) [Pa] Begin= 100000   End= 99761.7   Diff=  238.287
Pressure (Tube) [Pa] Begin= 1.44442e+06   End= 1.3539e+06   Diff=  4.05631
Temp. Product [K] = 794.623
Heat Exchange Area [m^2] = 18.1032

Investment [$] = 393353
Lifetime [year] = 22
Land Require [m^2] = 3.62063
Capital Cost [$/year]   = 32851
Operating Cost [$/year] = 11800.6


Dehydrogenation Step 5

Number of Reactors = 4
din = 1.15m
length = 2m

Heat Balance per Reactor [W]: Reac= 1.55109e+06   Inside= -1.5448e+06

Mass Balance per Reactor [kg]: In= 5.53231   Out= 5.53232
```

```
 In  [kmol/s]: MCH= 0.00756122  TOL= 0.0487858  H2= 0.14619
 Out [kmol/s]: MCH= 0.000390182  TOL= 0.0559569  H2= 0.167703
 Massvelocity [kg/sm^2] = 5.32623        LHSV [1/hr]  = 10.6883

Conversion = 0.993075            (Equilibrium at 0.993256 )
Pressure (Tube) [Pa] Begin= 1.3539e+06   End= 1.23621e+06   Diff=  117691
Temp. Product [K] = 707.108

Investment [$] = 283667
Lifetime [year] = 22
Land Require [m^2] = 21.16
Capital Cost [$/year]   = 23690.5
Operating Cost [$/year] = 8510     + Catalyst [$/year] = 249286


Summary Dehydrogenation

Investment [$] = 3.62424e+06
Land Require [m^2] = 127.669
Capital Cost [$/year]   = 302680
Operating Cost [$/year] = 108727     + Catalyst [$/year] = 1.24643e+06


Fuel Cells

Inlet Temperature of Air [K]       = 1096.24
Outlet Temperature of Air [K]      = 1096.24
Inlet Temperature of Fuel [K]      = 1175
Exhaust Temperature [K]            = 1175
Inlet Temperature of Steam [K]     = 0
Outlet Temperature of Steam [K]    = 0
Temperature of Streams to Cell [K] = 1096.24
Temperature Inside Cell [K]        = 1250

Streams: [kmol/s]
  IN:  air      O2  = 0.89439
                N2  = 10.1159
                Ar  = 0.117613
                CO2 = 0
       fuel     H2  = 0.745348
                H2O = 0
                CH4 = 0
                CO2 = 0
  OUT: air      O2  = 0.558983
                N2  = 10.1159
                Ar  = 0.117613
                CO2 = 0
       exhaust H2  = 0.0745348
                H2O = 0.670813
                CH4 = 0
                CO2 = 0
  STEAM:        H2O = 0

Massbalance: [kg/s]
  IN:  air      O2  = 28.6196
                N2  = 283.376
                Ar  = 4.69839
                CO2 = 0
       fuel     H2  = 1.50262
                H2O = 0
                CH4 = 0
                CO2 = 0
  OUT: air      O2  = 17.8869
                N2  = 283.376
                Ar  = 4.69839
                CO2 = 0
       exhaust H2  = 0.150262
                H2O = 12.0847
                CH4 = 0
                CO2 = 0
  IN total  = 318.196
  OUT total = 318.196

Energybalance: [J/s]=[W]
  effcell   = 0.88
  effsyst   = 0.650773
  heatvalue =  1.62203e+08
  hr        =  -4.9924e+06
  T*sr      =  -1.01814e+07
```

```
  wrev      =  1.19951e+08
  elec      =  1.05557e+08

  heat      =  6.1638e+07
  Qcell     = 6.10226e+07        (1096.24K -> 1250K)
  Qair      = 0          (1096.24K -> 1096.24K)
  Qfuel     = -1.79966e+06        (1175K -> 1096.24K)
  Qexhaust  = 2.37715e+06        (1250K -> 1175K)
  Qoutair   = 5.56567e+07        (1250K -> 1096.24K)
  Qreflux   = 0          (1250K -> 1096.24K)
  Qsteam    = 0          (0K -> 0K)

  Qrest     = heat-Qcell-Qreflux-Qsteam = 615336

Investment [$] = 1.04512e+08
Lifetime [year] = 25
Land Require [m^2] = 7125.09
Capital Cost [$/year]    = 8.16118e+06
Operating Cost [$/year] = 5.22561e+06



Dehydrogenation Heat Exchange

Heat Require Heat Exchanger [W] = 5.14733e+07
  Heater1 [W] = 7.69426e+06
  Heater2 [W] = 1.23371e+07
  Heater3 [W] = 1.11917e+07
  Heater4 [W] = 1.04819e+07
  Heater5 [W] = 9.76838e+06
Heat Supply Fuel Cell        [W] = 5.19923e+07
Heat Loss                    [W] = 518997
Rest for Heat Ex. Network    [W] = 2.41499e+06

Preheating of feed (liquid, vaporisation, gas)
  Qlfeed     [W] = 1.17324e+07         (298.15K -> 512.871K)
  condMCH    [W] = 4.34301e+06
  Qgfeed     [W] = 8.76237e+06         (512.871K -> 660K)
  total      [W] = 2.48377e+07         (298.15K -> 660K)

Cooling of Product (gas, condensation, liquid)
  Qgproduct [W] = 1.31083e+07         (707.108K -> 502.09K)
  condTOL    [W] = 5.4791e+06
  Qlproduct [W] = 1.26016e+07         (502.09K -> 298.15K)
  total      [W] = 3.1189e+07        (707.108K -> 298.15K)

Heat Exchanger Network
  Request [W] = 1.03873e+08
          Qair    5.96369e+07
          Qfuel   1.93985e+07
          Qgfeed  8.76237e+06
          Qlfeed  1.17324e+07
          condMCH 4.34301e+06
  Supply [W]   = 1.16446e+08
        Qexhaust  2.37715e+06
        Qoutair   5.56567e+07
        Qgproduct 1.31083e+07
        Qlproduct 1.26016e+07
        condTOL   5.4791e+06
        condH20   2.72236e+07
  Rest     [W] = 1.25732e+07

  Gas Heater: transfercoef. [W/m^2K] = 50.0
              dT [K] = 47.1076
              area [m^2] = 3720.15
              cost [$] = 1.47059e+07
              capital costs [$/year]   = 1.43096e+06
              operating costs [$/year] = 441176
              land [m^2] = 744.03
  Evaporator: transfercoef. [W/m^2K] = 70.0
              dT [K] = 50.0
              area [m^2] = 1240.86
              cost [$] = 6.97013e+06
              capital costs [$/year]   = 678231
              operating costs [$/year] = 209104
              land [m^2] = 248.172
  Liq Heater: transfercoef. [W/m^2K] = 150.0
              dT [K] = 50.0
              area [m^2] = 1564.32
              cost [$] = 8.15924e+06
              capital costs [$/year]   = 793938
```

```
            operating costs [$/year] = 244777
            land [m^2] = 312.863
```

Streams

```
Netout    :    Temperature = 1175 [K]
      Ar= 0.02 kmol/s
      N2= 1.72 kmol/s
      O2= 0.43 kmol/s
   Enthalpy = 5.96369e+07 [W]

Cellin    :    Temperature = 1096.24 [K]
      Ar= 0.117618 kmol/s
      N2= 10.1162 kmol/s
      O2= 0.893956 kmol/s
   Enthalpy = 2.74279e+08 [W]

Cellout   :    Temperature = 1250 [K]
      Ar= 0.117613 kmol/s
      N2= 10.1159 kmol/s
      O2= 0.558983 kmol/s
   Enthalpy = 3.21199e+08 [W]

Netin     :    Temperature = 1250 [K]
      Ar= 0.0199941 kmol/s
      N2= 1.7197 kmol/s
      O2= 0.0950271 kmol/s
   Enthalpy = 5.46039e+07 [W]

Reflux    :    Temperature = 1076.7 [K]
      Ar= 0.0976185 kmol/s
      N2= 8.39616 kmol/s
      O2= 0.463956 kmol/s
   Enthalpy = 2.14603e+08 [W]

Reac begin:    Temperature = 891.982 [K]
      Ar= 0.163999 kmol/s
      N2= 14.1056 kmol/s
      O2= 0.779446 kmol/s
   Enthalpy = 2.70013e+08 [W]

Reac end  :    Temperature = 782.882 [K]
      Ar= 0.163999 kmol/s
      N2= 14.1056 kmol/s
      O2= 0.779446 kmol/s
   Enthalpy = 2.1802e+08 [W]

Fuel Cell feed    :    Temperature = 1175 [K]
      H2 = 0.745348 kmol/s
      H2O= 0 kmol/s
   Enthalpy (heat) = 1.93985e+07 [W]
   Enthalpy (comb) = 1.8024e+08 [W]

Fuel Cell Exhaust :    Temperature = 1250 [K]
      H2 = 0.0745348 kmol/s
      H2O= 0.670813 kmol/s
   Enthalpy (heat) = 2.49006e+07 [W]
   Enthalpy (comb) = 1.8024e+07 [W]

Stream Balances:
   2.7424e+08 = 2.74279e+08
   5.19937e+07 = 5.19923e+07
```

Economics

```
Total Electricity Output [W] = 1.01335e+08
Winter Efficiency = 0.624742
Total Efficiency = 0.475006

Land Require [m^2] = 115238
Land Investment [$]  = 2.92934e+07
Plant Investment [$] = 4.55743e+08
Working Capital [$]  = 2.27872e+07
Total Investment [$] = 5.07824e+08

Land Capital Cost [$/year]      = 1.48142e+06
Plant Capital Cost [$/year]     = 3.07815e+07
```

```
Working Capital Cost [$/year]    = 1.15239e+06
Total Operating Cost [$/year]    = 1.64695e+07
Input Electricity Cost [$/year] = 3.06178e+07
                 Total [$/year] = 8.05026e+07
Specific Costs [$/kWh]: Land        = 0.00304565
                        Capital     = 0.0632834
                        Working Cap = 0.00236919
                        Operating   = 0.0338596        Plant costs = 0.102558
                        Input Elec = 0.0629469

 kWh-costs [$/kWh] = 0.165505
```

Leer - Vide - Empty

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Curriculum Vitae

of Gregor Wolfgang Hugo Scherer
born in Schaffhausen the 22nd of August 1967

Education

1993-1997	PhD studies in chemical engineering at ETH Zürich
1987-1993	Studies in physics and nuclear physics at ETH Zürich
1982-1987	Kantonsschule Schaffhausen
1974-1982	Primary and secondary school in Schaffhausen

Professional Experience

1995-1997	Research assistant in General Energy Research at Paul Scherrer Institute
1993-1995	Research assistant in the Systems Engineering Group at ETH Zürich
1989-1993	Part-time software developer in the Financial Systems Division at NCR (Switzerland)