Advanced Process Integration Aspects of Tubular Reactors

Master's Thesis within the Innovative and Sustainable Chemical Engineering programme

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Division of Heat and Power Technology
CHALMERS UNIVERSITY OF TECHNOLOGY
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MASTER’S THESIS

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ABSTRACT

The chemical industry had the third largest energy demand of Swedish industry in 2011. One way to lower the energy requirement is to increase the energy efficiency of a process through energy integration and therefore lower the demand of primary energy. Chemical reactors are often the part of a chemical process where most of the primary energy is consumed such as in form of combustion heat, or where large amount of heat is available which can for instance used for steam production for power generation, heating or even for cogeneration. The choice of the reactor design is a crucial aspect that can influence significantly the share of energy cost in the overall process costs.

This master's thesis was partially motivated by the 2011 years course project in the Preliminary Plant Design within the master program in Innovative and Sustainable Chemical Engineering at Chalmers University of Technology. The outline of the project was to design a plant for production of methyl-ethyl-ketone, MEK, where the suggested reactor design for the plant had a very high primary energy demand due to reactor specifications.

This master's thesis has investigated important aspects for energy integration of tubular reactors and how Pinch Analysis can be used to find the optimal reactor design. Two case studies have been performed to achieve this, one for an endothermic reaction and one for an exothermic reaction. The endothermic case study was based on the production of MEK and one intermediate target was to find a better reactor design than the design in the course Preliminary Plant Design. The exothermic case study was based on the methanation process in production of synthetic natural gas.

The results from the case studies showed that pinch analysis is not a sufficient tool to evaluate the best choice in utility temperatures for heated or cooled reactors because of the intrinsic relation between heat transfer and kinetics cannot be taken into account rigorously when selecting different type of utility streams. This makes it impossible to define an energy target for the utility consumption of a tubular reactor system independent of the specific design. Nonetheless pinch analysis can be used to evaluate energy consequences of different reactor design thus allowing to identify the most suitable configuration based on the trade-off between investment and energy targets.

Key words: process integration, pinch analysis, tubular reactors

Avancerade processintegrationsaspekter av tubreaktorer

Examensarbete inom masterprogrammet Innovativ and Sustainable Chemical Engineering.

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SAMMANFATTNING

Den kemiska industrin hade det tredje största energibehovet av Sveriges industri 2011. Ett sätt att minska energibehovet är att öka energieffektiviteten för en process genom energiintegration och därmed minska behovet av primär energi. I kemiska processer är det ofta reaktorerna som antingen kräver värme eller avger värme vid hög temperatur. Designen av en reaktor påverkar i hög grad energibehovet samt kostnad för denna för hela processen.

Det här masterabetet har delvis motiverats av ett projekt i masterkursen Preliminary Plan Design på Chalmers tekniska högskola. Projekted går ut på att designa en process för tillverkning av kemikalien metyl-etyl-keton, MEK och pga. specifikationer för reaktorn så kräver den föreslagna reaktordesignen väldigt mycket primär energi i form av förbränning av naturgas.

Det här masterabetet har gått ut på att undersöka viktiga aspekter för energiintegrering av tubreaktorer och hur pinchanalys kan användas för att hitta en optimal reaktordesign. För att göra detta har det gjorts två fallstudier, en för en endoterm reaktion och en för en exoterm reaktion. Den endoterma fallstudien handlar om produktionen av MEK och ett delmål var att hitta en bättre design av reaktorn till projektet i kursen Preliminary Plant Design. Den exoterma fallstudien handlar om metaniseringsprocessen vid produktion av syntetisk naturgas.

Resultat från fallstudierna visar på att pinchanalys inte går att använda för att bestämma ett optimum for värme och kylbehov för en reaktor oberoende av reaktordesign på grund av det inneboende sambandet mellan värmeöverföring och kinetik. Däremot kan pinchanalys användas för att utvärdera energikonsekvenserna för olika reaktorkonstruktioner och därmed vara till hjälp för att identifiera den optimala konfigurationen baserad på en avvägning mellan investering och energimål.

Nyckelord: process integrering, pinchanalys, tubreaktor

Contents

Preface

In this master thesis, process integration aspects of tubular reactors are investigated through two case studies. The thesis has investigated the usefulness of pinch analysis for process integration of tubular reactors and what parameters that are important form an energy efficiency point of view. The project has been carried out at the Division of Heat and Power Technology, Chalmers University of Technology, Sweden.

I would like to thank my supervisor Matteo Morandin and examiner Simon Harvey at the Division of Heat and Power Technology, Chalmers University of Technology for all their help and time spent on this project.

Göteborg June 2013

Helena Olsson

Notations

Abbreviations

GCC	Grand composite curve
MEK	Methyl ethyl ketone
SNG	Synthetic natural gas

Chemical notations

H_2	Hydrogen
H_2O	Water

Symbols

A	Area
A	Pre-exponential factor for Arrhenius equation
C_p	Specific heat capacity
d_p	Catalyst particle diameter
d_t	Tube diameter
E_a	Activation energy
F	Mass flow
G	Mass flux
$\Delta H_{j,a}$	Enthalpy change of adsorption for species j
k	Reaction rate constant
K	Dimensionless equilibrium constant
K_p	Pressure equilibrium constants
L	Reactor length
Δp	Pressure drop
p_i	Partial pressure for species i
P	Total pressure
PPD	Preliminary plant design
R	Molar gas constant
Re_p	Reynolds number for a packed bed
ΔT_{min}	Minimum temperature difference
U	Overall heat transfer coefficient
u_0	Fluid superficial velocity
Q	Heat load

Greek letters

ε_B	Porosity of the catalyst bed
μ	Viscosity for the reactor fluid

1 Introduction

According to the Swedish Energy Agency the chemical industry accounted for 8% of the energy used by Swedish industry in 2011. This makes the chemical industry the third largest energy demanding industrial sector in Sweden (Energimyndigheten, 2011). One way of decreasing the energy need of chemical plants involving thermal processes is to increase energy recovery through a better heat integration of the process units thus saving on heating and cooling utilities (Kemp, 2007).

Chemical reactors are often the part of a chemical process where most of the primary energy is consumed such as in form of combustion heat, or where large amount of heat is available which can for instance used for steam production for power generation, heating or even for cogeneration. The choice of the reactor design is a crucial aspect that can influence significantly the share of energy cost in the overall process costs.

The present study was partially motivated by the large disproportion between the primary energy requirement and the feedstock / product balance appearing when dealing with the design of a methyl-ethyl-ketone process via vapour phase dehydrogenation of 2-butanol in the course project of Preliminary Plant Design within the master program in Innovative and Sustainable Chemical Engineering.

In the MEK project the one through reactor is designed for high conversion and needs heating at moderate temperatures that are higher than the temperature of conventional steam or oil utility and lower than typical furnace temperatures. The temperature level is primarily limited by the catalyst deactivation.

If a furnace is used to supply flue gases for heating the reactor large amount of air shall be used for decreasing the flue gases temperature prior the reactor and thus wasting the fuel high quality energy into heat at moderate and low temperatures. As an example, Figure 1.1 illustrates the disproportion between fuel combustion and process heating by means of the background foreground grand composite curve representation, a graphical tool that will be used in this work to study the energy consequences of alternative reactor designs.

The reason for the large amount of excess energy is related to the fact that the reactor needs heat at a specific temperature and the furnace is a lot hotter than that. Steam is produced with the high temperature furnace heat which is partly used for process heating and mainly sold for a profit. However the large amount of excess energy is not justified from an economic point of view for a plant which aim is to primarily produce chemicals and not steam.

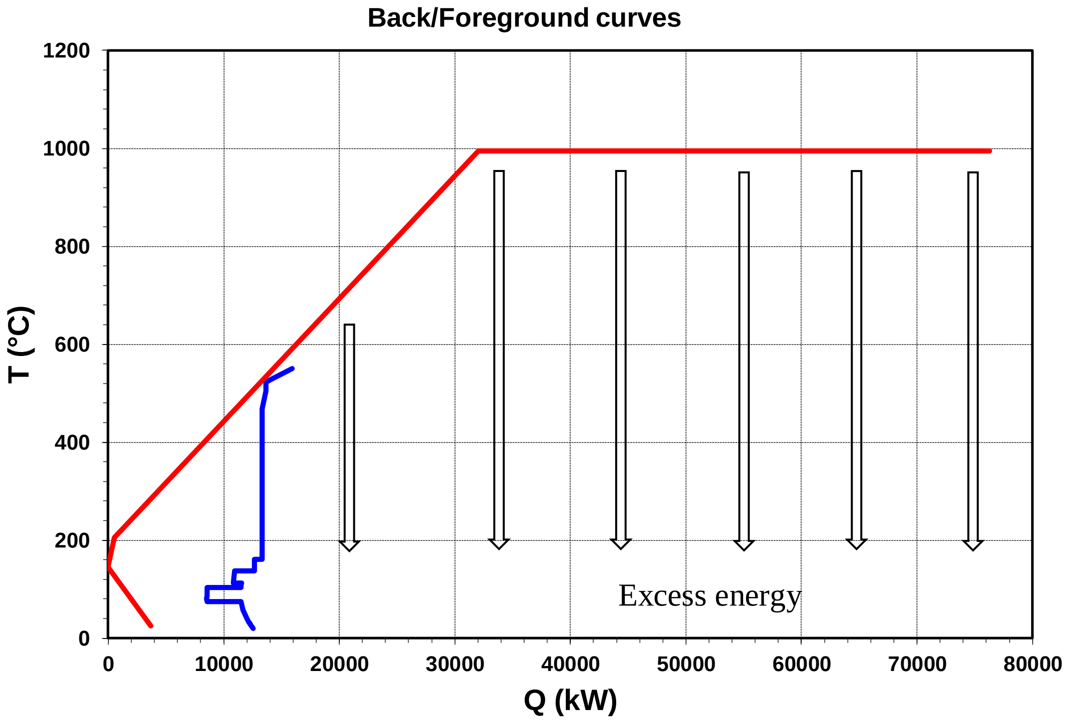


Figure 1.1 The red line represents the energy supplied by the furnace and the blue line represents the plant.

Even if the project in Preliminary Plant Design not necessary represent a regular plant of today do the production of basic chemicals and intermediates use or release large quantities of energy from chemical reactions. Depending on how the reactor(s) operates, the need for heating or cooling can differ. In the case of adiabatic reactors no external heating or cooling is needed in principle and the best reactor operating conditions can be established regardless of process heat integration aspects (intercooling or reheating between multiple reactor stages can however impact the process heat recovery potential). Not all reactions can be technically carried out in adiabatic reactors and external heating or cooling is often necessary to ensure process safety, increase the conversion of the feed or to increase the selectivity of the desired product (Fogler, 2006; Smith, 2007).

Although there are many reaction technologies, reactors are commonly categorized into three major sets corresponding to ideal models and specific behaviours. These are batch reactors, continuous-stirred tank reactors (CSTR) and tubular reactors. Batch reactors are time-dependent and are suited for small scale production. CSTRs and tubular reactors are operated continuously and are usually selected for large scale production (Sinnott & Towler, 2009). In a stirred tank reactor operated at steady state, the temperature in the reactor will be the same as the product temperature. The heat integration of a CSTR can therefore be studied by idealizing its thermal behaviour to that of a thermal stream at constant temperature. Unlike CSTR, in a tubular reactor the temperature changes as the reaction progresses along the tubes. For this reason, the study of heat integration of a tubular reactor becomes more challenging as it cannot be idealized to a constant temperature thermal stream. A different approach is in fact required to take into account the intrinsic relation between temperature and heat load.

1.1 Overview of synthesis and design of chemical processes

As reactors often involve a thermal process at medium high temperatures, studying process integration aspects of reactive systems and identifying possible design guidelines is of high interest. This is particular true for non autothermal (non-adiabatic) reactors which requires cooling or heating.

As the reactor is the core of the chemical process, the process conceptual design often starts with the design of the reactor and its integration with the rest of the process is often not investigated until the final process design stage. This principle is illustrated by Figure 1.2. As a consequence the reactor design affects the design and performance of all other plant units. Thus, if an appropriate reactor design is considered that favours process heat integration large primary energy saving can be achieved. Thus a properly conducted conceptual design procedure is necessarily an iterative process.

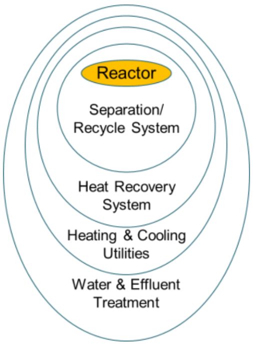


Figure 1.2 An onion diagram over the process systems found in a chemical plant.

For this reason, it is of interest to take into account the reactor heat integration aspects directly during the first phase of reactor design in order to minimize the effort of further changes. Often substantial heat recovery can be achieved in the direct proximity of reactor (feed preheating and product cooling).

In addition, an accurate characterization of the reactor thermal profile can help identifying the best integration of utility streams such as hot gases from combustion for endothermic reactions or steam production and steam superheating for exothermic ones. This task is of difficult application for the tubular reactors since the temperature of the utility stream directly influences the temperature profile inside the reactor and therefore the reaction kinetics and product yields.

1.2 Relevance of tubular reactors in chemical production

Tubular reactors are often used in the industry at high temperatures. A selection of chemicals produced in tubular reactors can be seen in Table 1.1 together with temperature range for the production and operation type. The majority of the selected chemicals are exothermic but other endothermic reactions in tubular reactors are present in the chemical industry, e.g. cracking in fired tubular reactors to produce ethylene and propylene (Zimmermann & Walzl, 2009).

Table 1.1 A selection of chemical products that are produced in tubular reactors in the chemical industry

Product	**Feedstock**	**Type of reaction**	**Operation type**	**Temperature (°C)**	**Reference**
Acrylic acid	Propylene	Exotherm	Cooled	200-300	(Ohara, et al., 2011)
Carbon tetrachloride	Methane	Exotherm	Adiabatic or isothermal	500-700	(Rossberg, et al., 2011)
Chloroform	Methane	Exotherm	Adiabatic	350-450	(Rossberg, et al., 2011)
Ethylene oxide	Ethylene	Exotherm	Cooled	200-300	(Rebsdat & Mayer, 2001)
Formaldehyde	Methanol	Exotherm	Cooled	680-720	(Reuss, et al., 2000)
Maleic anhydride	Benzene	Exotherm	Cooled	340-500	(Lohbeck, et al., 2000)
Methanol	CO/(H2)	Exotherm	Cooled	200-300	(Fiedler, et al., 2011)
Methyl ethyl ketone	2-Butanol	Endotherm	Heated	400	(Hoell, et al., 2009)
Methylene chloride	Methane	Exotherm	Adiabatic	350-450	(Rossberg, et al., 2011)
Phthalic anhydride	Naphtalene	Exotherm	Cooled	360-390	(Lorz, et al., 2007)

1.3 Tubular reactors

Tubular reactors are used in the industry since they are relatively easy to maintain due to no moving parts and usually have the highest conversion per reactor volume of other types of reactor (Fogler, 2006, p. 23). Tubular reactors can be used either for homogenous or heterogeneous reaction chemistry. Homogenous reactors have only one phase in the reaction environment and heterogeneous have more than one. One common type of heterogeneous reactor is the packed bed reactor which ‘is essentially a tubular reactor that is packed with solid catalyst particles’ (Fogler, 2006, p. 23).

Typical temperature profiles in adiabatic tubular reactors can be seen in Figure 1.3. The temperature changes quickly in the beginning of the reactor due to high reaction rate. The reaction rate is generally affected by concentration of reactants and temperature which means that the reaction rate is high in the beginning and then lowers trough the reactor and the change in temperature follows accordingly.

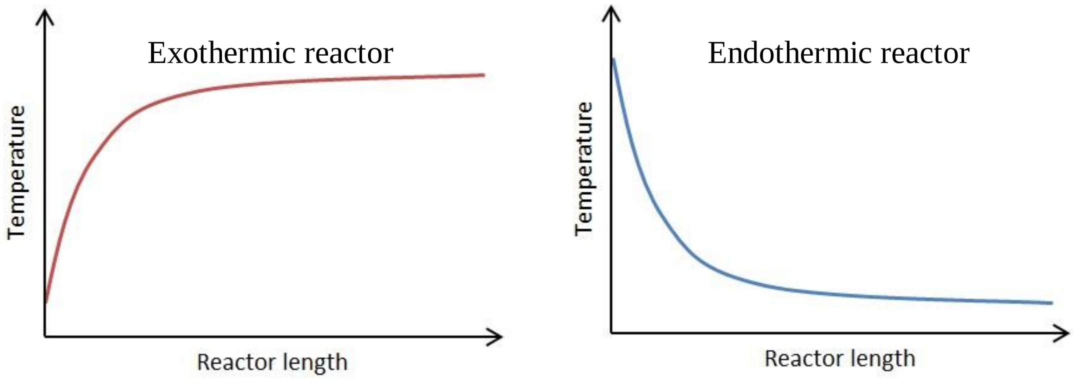


Figure 1.3 *Generic temperature profiles in an exothermic and endothermic tubular reactor.*

To keep the reaction rate high and therefore increase the reaction conversion of with a given reactor cooling of exothermic reactors and heating of endothermic reactors is employed, the typical shapes of the temperature profiles looking as in Figure 1.4.

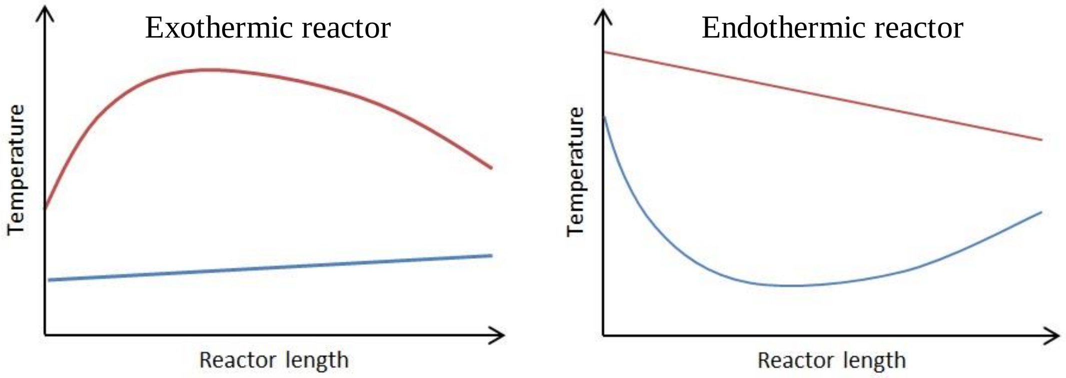


Figure 1.4 *Generic temperature profiles in a cooled exothermic reactor and a heated endothermic reactor.*

As a consequence the heat transfer between the reactive stream and utility is strictly connected with the reaction kinetics which therefore cannot be ignored when designing the utility system. In particular this makes the study of the heat integration of tubular reactors an iterative process where changes in the utility streams (either type or temperature level), affects the kinetics and therefore the conversion. Nonetheless the energy consequences of a tubular reactor should not be ignored.

1.4 Heat integration of reactors

Pinch analysis is a methodology that allows estimating the energy targets of a given thermal system, i.e. maximization of heat recovery. Pinch Analysis offers also a set of graphical tools for interpreting the so-called process thermal cascade in order to investigate heat integration opportunities between different process units or between multiple processes. Guidelines for design and retrofitting of heat exchanger network are also provided.

Given the process thermal cascade and its graphical representation, the grand composite curve (GCC), the integration of process units can be studied with respect to the process pinch point, the point that separates the process behaviour as a heat sink (above pinch) and as a heat source (below pinch). Process internal heat recovery can be studied by representing different thermal cascade of different process units and by studying the possible graphical integration of different unit cascades in a subsequent step. This is done in practice by identifying in a foreground grand composite curve a specific process unit and in a background grand composite curve the remaining process unit thermal streams. The integration is achieved by selecting an appropriate placement of the foreground cascade with respect to the background pinch point.

Any exothermic process unit should therefore be placed above the pinch and any endothermic process unit should be placed below the pinch. This applies for reactors as well, whereby the appropriate placement of exothermic reactors is above the process pinch and endothermic below the process pinch (Glavič, et al., 1988).

Different solutions can be suggested in order to improve the integration of reactors. To match the reactor profile with the profile of the remaining process, the process structure and the design parameters can be changed.

Kravanja and Glavič (1989) proposed a double step procedure to achieve total energy integration through total system synthesis, see Figure 1.5. The first step of the procedure was a new approach to energy integration and the second step was an improvement of the earlier standard simultaneous approach.

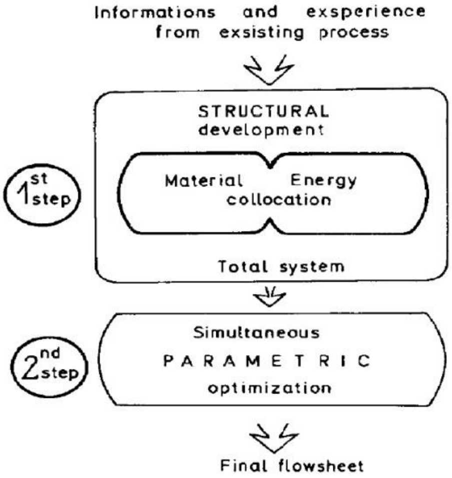


Figure 1.5 Double-step-like synthesis of the total system (Kravanja & Glavič, 1989).

The energy system and the impact of choices on the process structure are studied in the first step and in the second step modifications are performed by parametric optimization. To achieve the first step the second-law analysis is applied to the total energy balance. In so doing the minimum possible utility requirement can be determined for a selected ΔT_{min} independently of the Heat Exchanger Network (HEN) design.

1.5 Reactor design

It is not always possible or suitable to place the reactor appropriately with respect to the process pinch temperature since the reaction temperature is chosen based on thermodynamic and kinetic aspects, the latter being also determined by the possible presence of a catalyst. Pinch violations associated with reactors are justified by a thermodynamic principle whereby exothermic reactions are favoured by low temperature and endothermic ones by high temperatures thus contradicting in principle the appropriate placement with respect to a typical process thermal cascade. This often results in synthesis processes having large excess of heat and dissociation/reforming processes having a heat demand at high temperatures.

Endothermic reactors can especially have a much higher temperature than the remaining process pinch. To minimize the primary energy requirement the reactor itself needs therefore to be appropriately designed to minimize its energy demand. One way of saving energy is to optimize the design to improve the heat integration of the streams around the reactor, considering possible preheating/cooling of the feed and product streams. Several different design options are used in the industrial practise, some of them are briefly described below.

Intermediate feed injection

Part of the feed is used as a fresh feed injection into the reactor at an intermediate point. In case of exothermic reaction this is called a “cold shot” and in case of an endothermic reaction “hot shot”. For the hot shot to work the feed needs to be heated up to considerably high temperature in order to shift the overall reactive medium to favourable thermodynamic conditions away from the equilibrium. The injection of fresh feed into the reactor will work as temperature control by both heat transfer and concentration control (Smith, 2007)

Reactor staging and intermediate heat exchange

One common use of heat exchange is to preheat the feed with the product stream. To increase the conversion by crossing the equilibrium a reactor can be divided into two or more reactors and then the intermediate streams between reactor can used for heat exchange. As an example M.E.E Abashar (2000) has suggested two designs with intermediate heat exchange to enhance the performance of ammonia production in adiabatic reactors. The schematic reactor design and equilibrium curve for the design with three reactors can be seen in Figure 1.6.

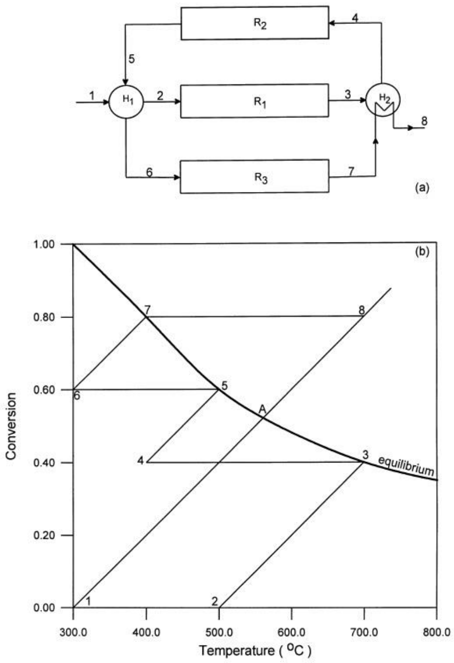


Figure 1.6 *(a) Reactor scheme for ammonia production with internal heat exchange, (b) crossing equilibrium in a three reactor system. Adapted from (Abashar, 2000).*

Reverse flow reactor

A reverse flow reactor (RFR) can be used for weakly exothermic reactions and is based on thermal coupling between exothermic and endothermic reactions. One setup of a RFR is a packed bed reactor with switching valves at the inlet and outlet of the reactor to manage the flow direction, Figure 1.7. In a weakly exothermic reaction the packed bed is heated by the reaction heat and then the hot bed heats up the cold feed for the reversed flow. For a coupled reactor the exothermic reaction heats up the bed and then the endothermic reaction uses the heat from the bed. Usually it is the endothermic reaction that produces the desired product and the exothermic reaction are used as a heater (Kolios, et al., 2000).

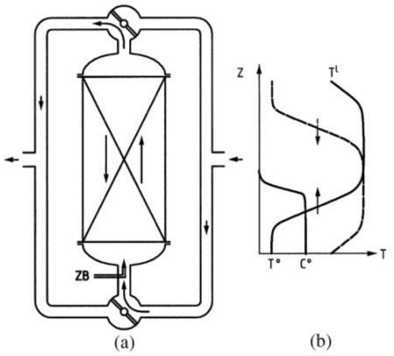


Figure 1.7 *Adiabatic reverse flow reactor: (a) reactor scheme with switching valves; (b) temperature and concentration profiles in the periodic steady state with feed values T0, c0. Adapted from (Kolios, et al., 2000)*

Countercurrent fixed-bed reactor

A countercurrent fixed-bed reactor works for exothermic reactors where the hot effluent heats up the feed of the reaction through countercurrent heat exchange. One way of doing this is to divide the feed into two parts and let them flow through the reactor from opposite directions in separate channels. Since the temperature profile for one side of the reactor of this type will be the mirror image of the other side another set-up can be used with only one inlet and one outlet, Figure 1.8. In the middle the stream is reversed in order for it to release its heat to the incoming streams as it goes out. The counter-current configuration usually results in a simpler reactor design than the RFR since it is continuous and does not need switches but it demands a higher quality for the separating walls to achieve good heat transfer (Kolios, et al., 2007).

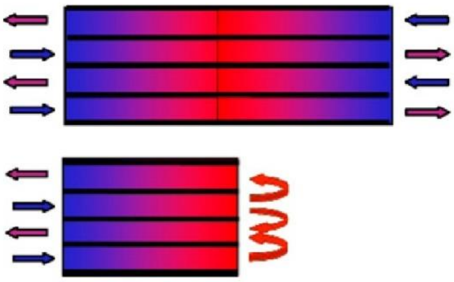


Figure 1.8 *Heat profile in two countercurrent fixed-bed reactors where the lower configuration exploits the temperature profile symmetry. Adapted from (Kolios, et al., 2007).*

1.6 Purpose and objective

The objective of this master thesis is to investigate the crucial aspects of heat integration of tubular reactors. As previously highlighted this type of reactor should be treated by taking into account the intrinsic relation between temperature, heat load and reaction conversion, since the heat transfer depends locally on the temperature difference between the reactive medium and the utility medium, and the temperature of the reactive medium is related to the reaction kinetics.

The temperature that should be achieved on the reaction side (typically within the tubes) also determines the temperatures of the heating or cooling media. Accordingly, different designs can be suggested to achieve the best arrangement of the tube(s) and of the utility medium passes in order to minimize the total costs.

A specific research question is formulated for the MEK production plant:

- Is it possible to design the reactor process in a different way that the energy requirement is reduced?

The general research questions behind this thesis are:

- Is it possible to apply pinch analysis tools to the choice of the appropriate temperatures of the utility stream for heating or cooling a tubular reactor?
- Is it possible to define an energy target for utility consumption of a tubular reactor system independently of the specific design?
- To what extent can pinch analysis targets be used to subsequently identify a suitable reactor design?
- Which are the fixed and operating cost components leading to the final design?

2 Methodology

In this work, a methodology based on successive iterations on reactor arrangements and operating parameters is employed.

A general description of the methodology is firstly introduced. The application to two case studies is subsequently discussed.

Two case studies were investigated to examine the crucial design aspects of tubular reactors with respect to their size, complexity and overall heat integration with the utility system. In the first case an endothermic reaction process was studied while in the second case an exothermic reaction process was studied.

For the both case studies data about temperature and heat loads of various heat sinks and sources were studied by means of pinch analysis tools in order to estimate the overall impact on hot utility consumption or excess heat export of different reactor designs.

For this purpose, the focus of the investigations was restricted to the reactor and remaining parts of a process such as product upgrading through separation were neglected. The general system investigated, as shown in Figure 2.1, primarily consisted of the reactor, the feed and the product streams.

Figure 2.1 A simplified model of the reactor system.

2.1 Synthesis and design approach

To examine crucial design aspect for tubular reactors a variety of reactor layouts shall be considered.

The approach for defining the different layouts is related to the following aspects:

- Type of reactor
- Number of reactor stages
- Stream connections around and between reactors.

First the type of reactor has to be defined. It can be continuous or batch. It can be a stirred tank or a tubular reactor. It can be un-packed, a packed bed or a fluidized bed. It can be adiabatic, isothermal, heated or cooled.

This work focuses on tubular reactors with a specific attention on packed bed reactors the type of reactor. Isothermal tubular reactors are possible, but were discarded for this thesis. The final choice was between adiabatic or heated or cooled. For both case studies both types of reactors were used.

After deciding on what type of reactor the number of reactor stages should be investigated. While the aim of staging can be of reducing the total volume in tank reactors systems, using several tubular reactors is primarily related to increase the degrees of freedom of last step of the layout design which is the stream connections between stages and of possible different heat exchange that can occur in between. Generally several reactors are used for adiabatic reactors to be able to heat or cool the reactor stream between reactors.

The different connections choices between two stages are:

- Series
- Parallel feed

For each reactor unit there is also the possibility of recycling the product into the main feed to increase the passages of reactants.

The different connections can be combined in different ways to create different designs and the number of reactors greatly affects how complex a design could be. In this thesis some simple configurations are investigated in order to discuss the main consequences of different layouts while simplifying process modelling and simulation.

Design

After deciding on the different layouts operating and geometric parameters should be chosen.

The geometric design involves decisions upon the reactor length, diameter and number of tubes.

The operating parameters are the reactor temperature and pressure. If the design is completely defined a given conversion and pressure drop is obtained

This means that a specific conversion and pressure drop can be achieved for a set of temperatures and pressures by adjusting the reactor geometry.

2.2 Reactor performance and size criteria

To evaluate which of the proposed reactor layouts is the best a set of criteria was defined.

In principle, the design of a reactor should be adjusted according to the overall process economics thus accounting for instance the effect that a given conversion and selectivity has on the separation part of the process.

As the discussion is here limited to the reaction part of the process only, the criteria were chose in order to measure the trade-off between capital investment in reactor size and the primary energy consequences.

The chosen criteria for the case studies were:

- Volume of reactor
- Fuel consumption (for endothermic)
- Steam generation (for exothermic)

The reactor volume was chosen as an indicator for keeping track of the investment cost. The amounts of fuel consumed for reactor heating or the steam generated through reactor cooling are different quantities used for keeping track of the energy consequences of different reactor layouts. For the endothermic study is a low fuel consumption desirable and for the exothermic is a high steam generation desirable.

2.3 Modelling

Modelling and simulation were done in Aspen HYSYS, a modelling program by Aspen Technology, in order to take rigorously into account the effect of different operating and geometric parameters on the reaction kinetics. Specific settings for the different study cases are found in chapter 3 and 4.

2.3.1 Reactor modelling

Tubular reactors were modelled as plug flow reactors with heterogeneous catalytic reactions. Heterogeneous reactions are reactions that involve more than one phase (Fogler, 2006), in this case the gaseous fluid and the solid catalyst. The catalyst is needed in both case studies for the reactants to react. The reactors were actually packed bed tubular reactors since solid catalyst were needed for both cases, the difference from regular tubular reactors being that packed bed reactors have a fixed bed of some sort of packing material, in these cases, catalyst.

For heated or cooled reactors a tube and shell arrangement is usually considered where multiple tubes are used to ensure room for the heating or cooling media at the shell side. If the reactor is adiabatic, the reactor can be idealized as a single large tube.

2.3.1.1 Dimensions

As the product yield (conversion) depends on the reactants residence time, given the molar flow rate of reactants, the conversion is therefore dependent on the size of reactor.

According to a sequential solution of a simulation, the size of the reactor shall be specified to estimate the conversion. The parameters needed are in this case the length, diameter, number of the tubes and thickness of the tube walls so that the total reactor volume is also determined.

It is apparent that the set of model equations can be in principle rearranged so that any model variable can be calculated as a function of the others.

As opposed to Aspen Plus, where the simulation is solved with a sequential approach and where the reaction conversion is estimated based on reactor geometric parameters (unless a design specification is used which requires a nested sequence of iterations), Aspen HYSYS uses a simultaneous approach whereby the set of model equations can be closed in several ways. This makes possible for instance to calculate the reactor length to achieve a desired conversion. In this work, the simulations were primarily conducted in this way (when possible), and the conversion was treated as a sensitivity parameter in order to compare different design alternatives.

While the reactor length is substantially decided upon the desired conversion, the values of the remaining geometrical parameters where set based on engineering heuristics.

The tube diameter, d_t for heated or cooled reactors was assumed from the catalyst particle diameter, d_p according to equation (2.1), to minimize wall effects on the flow. A high d_t/d_p ratio minimizes the wall effect on the flow but also lowers the heat transfer efficiency. A scaling factor of 10 was used here.

$$d_t = 10\, d_p \tag{2.1}$$

The number of tubes was calculated from the total cross sectional area and the tubular cross sectional area:

$$n = \frac{A_{tot}}{A_t} = \frac{4 * A_{tot}}{\pi * d_t^2} \tag{2.2}$$

The total cross sectional area was calculated with equations *(2.3)* and *(2.4)*:

$$A_{tot} = \frac{F}{G} \tag{2.3}$$

$$Re_p = \frac{d_p * G}{\mu * (1 - \varepsilon_B)} \tag{2.4}$$

where F is the mass flow rate in the reactor, μ is the dynamic viscosity of the fluid, ε_B is the porosity of the bed and G is a suitable mass flux for a plug flow reactor with Reynolds number Re_p set to 1000.

The amount of catalyst used in the reactor is specified with the porosity of the bed or void fraction which is the volume of space around the catalyst particles in the reaction divided by the volume of catalyst particles in the reaction. If the void fraction is set to one no catalyst is present in the reactor.

2.3.1.2 Reactions

The heterogeneous catalytic reaction model was used since the simulated reactors are of the tubular type packed with solid catalyst and therefore heterogeneous reactors .

For a given reaction, the reaction stoichiometry and the rate law have to be specified.

In particular the rate law is specified according to the rate law model appropriate for each case study. The rate laws for the reactions are specified in HYSYS on the form:

$$r = \frac{\overset{forward}{k_f \prod_{i=1}^{F} p_i^{\alpha_i}} - \overset{reverse}{k_r \prod_{j=1}^{R} p_j^{\beta_j}}}{\left(1 + \sum_{k=1}^{M} \left\{K_k \prod_{g=1}^{M} p_g^{\gamma_{k,g}}\right\}\right)^n} \tag{2.5}$$

where:

> k_f and k_r is the reaction rate constants of the forward and reverse kinetic rate expressions
> K is the absorption rate constant
> F and R is the number of species present in the forward and reverse kinetic rate expressions

M is the number of absorbed reactants and products plus absorbed inert species
$p_{i,j\ or\ g}$ is the partial pressure for species i, j or g with exponents α, β or γ.

The reaction rate constants and adsorption rate constants are expressed in Arrhenius form, equation (2.6), where A is the pre-exponent factor and E_a is the activation energy.

$$k = Ae^{-E_a/(RT)} \tag{2.6}$$

The reaction rate constant is the specific rate of reaction and quantifies the speed of reaction. Similarly the adsorption rate constant quantifies the speed of adsorption on the catalyst surface.

In HYSYS, if several reaction rate constants are present for the forward and backward reaction they have to be grouped together to form a single term. The stoichiometry and rate law for each reaction that takes place in the reactor are added to the reaction set. The catalyst data is also required, where particle diameter, particle sphericity, solid density and solid heat capacity needs to be specified. Particle sphericity is how close to a sphere the particle is and affects the pressure drop.

2.3.1.3 Heat transfer

The heat transfer is in HYSYS either specified as a direct Q value, which is the total amount of heat transferred to or from the reactor, or calculated based on the physical properties of the reactive medium and utility stream and of the tube heat transfer characteristics. To evaluate the impact of different temperatures and flow rates of the utility stream on the reactor performance, the second approach was used. The parameters needed are in this case the wall heat transfer coefficient, the mole flow, the heat capacity and the inlet temperature of the utility stream.

If the wall heat transfer coefficient is not available from literature or other sources it can be estimated from the overall heat transfer coefficient by equation (2.7) if the overall heat transfer coefficient is assumed. If the fluids on both the tube side and shell side are similar, e.g. both are gases; h_{tube} and h_{shell} can be approximated to be the same and therefore the wall heat transfer coefficient is twice the overall heat transfer coefficient.

$$\frac{1}{U} = \frac{1}{h_{tube}} + \frac{1}{h_{shell}} \tag{2.7}$$

2.3.1.4 Pressure drop

The pressure drop inside the reactor is calculated in HYSYS with the Ergun equation (Fogler, 2006):

$$\frac{\Delta p}{L} = \frac{150\mu(1-\varepsilon_B)^3 u_0}{\varepsilon_B^3 d_p^3} + \frac{1.75(1-\varepsilon_B)\rho u_0^2}{\varepsilon_B^3 d_p} \tag{2.8}$$

Where Δp is the pressure drop, L is the length of the reactor, μ is the dynamic viscosity of the fluid, u_0 is the superficial fluid velocity, ε_B is the catalyst porosity, d_p is the catalyst partible diameter and ρ is the fluid density.

2.4 Equilibrium curve

The highest conversion that can be achieved in reversible reactions is the equilibrium conversion. Therefore estimating the dependency of the equilibrium conversion against the temperature of the reactive media (here called equilibrium curve) is a useful tool for deciding temperature settings. The equilibrium curve is the relationship between the equilibrium conversion and temperature and can be constructed from the equilibrium constant for the reaction. If the equilibrium constant is unknown for the reaction the equilibrium curve can be constructed from the reaction rate by setting it to zero, as shown in equation (2.9).

$$-r_A = 0 \tag{2.9}$$

The equilibrium curve was constructed for each case study and the method of construction is described in the Appendix.

2.5 Sensitivity analysis

Different reactor designs were considered in this study as it has been discussed in section 2.1.

As the ultimate objective of this study is to investigate how different reactor arrangements and different values of the design parameters can affect the reactor volume and the overall primary energy consumption or the potential for excess heat export, different values of some parameters were investigated by means of a sensitivity analysis.

After the design structures were set sensitivity analysis was performed for each design to evaluate the significance of some design parameters. The parameters to vary and the ranges of their values were chosen differently for each design. Generally two parameters were chosen for each design and three different values were used.

The reactor design parameters that in general should be taken into account are:

- Reactor conversion
- Reactor geometry
- Feed temperature
- Utility inlet temperature
- Utility outlet temperature
- Utility flow
- Recycle ratio
- Feed splitting ratio
- Number of reactor vessels

The number of vessels is actually a synthesis parameter as it is related to the layout.

The different parameters are not all independent from each other, which mean that if some parameters are set as design parameters others become decided too. For example, if the utility inlet and outlet temperatures are set the flow of the utility stream results consequently as well if also the other reactor geometrical and operating parameters are given. .

2.6 Pinch Analysis tools

To estimate the impact of the different choices in reactor design (both structure and geometrical and operating parameters) on the primary energy required by a system or on the excess heat export potential, the heating and cooling processes occurring within the investigated systems where considered on their own that is as half heat exchangers (here called thermal streams). In this way the energy demand or availability of the system is decoupled from a specific arrangement of the heat exchangers and the theoretical performance can be estimated using a thermodynamic targeting procedure.

For this purpose Pinch Analysis tools were used using the Excel add-in Pro-pi developed at the division of Heat and Power Technology.

First data about temperatures and heat loads of the thermal streams were collected as a result of HYSYS energy and mass balances. It is apparent that the heat transfer of a tubular reactor is intrinsically coupled with the reaction kinetics and therefore the possible heat integration of the reactive medium cannot be analysed in similar way as the other process streams but should be rigorously determined through process simulation. In practise this means that given the thermal profile of the reactive medium, it is not possible to investigate alternative profiles of the heating medium without affecting the local heat transfer and therefore the reaction rate.

Still, it appears useful from a purely theoretical investigation to represent the reactor as a heat exchanger in order to have a picture of how the actual reactor design constraints the utility medium to follow particular profiles and of how much energy and exergy losses result.

For this purpose, a detailed representation of the temperature profile of the reactive medium is obtained by plotting the heat load of small part of the reactor according to the discretization of the plug flow model.

Care should be taken to ensure that exothermic reactor streams are represented as hot streams and endothermic reactor streams as cold streams. This is done by switching the inlet and outlet streams when necessary so that the inlet stream temperature is higher than the outlet temperature for exothermic reactions and the other way round for endothermic reactors, so that the pinch analysis representation is consistent with the direction of the heat

Grand composite curves (GCCs) are created to evaluate minimum hot and cold utility demand. Back/Foreground analysis is used to see how to best fit the utility system according to the heating and cooling demands of the reactor system.

2.7 Case studies

Two case studies have been performed to examine heat integration aspects for both an endothermic and an exothermic reactor. For the endothermic case study the production of methyl ethyl ketone (MEK) was chosen and for the exothermic case study methanation of syngas for the production of synthetic natural gas (SNG) was chosen.

The production of MEK was set as a case study inspired by the course project on Preliminary Plant Design held at Chalmers University of Technology. In the course project the total process for MEK production is design and the reactor is designed regardless energy efficiency consideration.

The methanation process was set as a case study inspired by the increasing interest in producing SNG from biomass. Biomass based SNG is carbon neutral which is a positive way to reduce the dependence on fossil fuels.

The description of the processes is found in chapter 3 and 4.

2.8 Procedure

The final procedure to carry out this master thesis can be summarized in four steps:

1. Select case studies
2. Define 3-4 different reactor designs for each case study
3. Perform sensitivity analysis for all layouts
4. Evaluate the effect on the criteria for all layouts

3 MEK process case study

In this chapter the study of the structural and design parameter of an endothermic reactor is discussed.

To this end a case study of the dehydrogenation of 2-butanol for the production of methyl ethyl ketone (MEK) is considered. Such choice is based on the relevance of the present study for the possible development of course project on Preliminary Plant Design held at Chalmers University of Technology within the master program in Innovative and Sustainable Chemical Engineering.

The objective of the investigations in the present work is to study the effects on utility consumptions of different alternative reactor designs and to highlight possible approaches for reactor design that take into account heat integration of process streams right before and after the reactor and thermal utilities.

3.1 Background

The reactor investigated here is the heart of a process that produces a desired amount of MEK at given purity as shown in Table 3.1. For this purpose dehydrogenation of 2-butanol and subsequent separation are needed to be designed. From the given specifications the needed feed into the reactor is calculated and corresponds to 12.08 tons 2-butanol per hour.

Table 3.1 MEK plant specifications.

MEK production	90000 tons/year
Raw material	2-butanol
Conversion in the reactor	96 %
Purity of produced MEK	99 wt% MEK
Loss of MEK from the plant	1 wt% based on the feed
Operation time	8000 h/year
Flue gas stack temperature	150 °C

In the design of the process as developed during the course project, the reactor is designed first and the required separation process and the heat exchanger network for heat recovery are found by solving subsequent synthesis and design sub-problems without looking at the process as a whole. The process design can be seen in Figure 3.1.

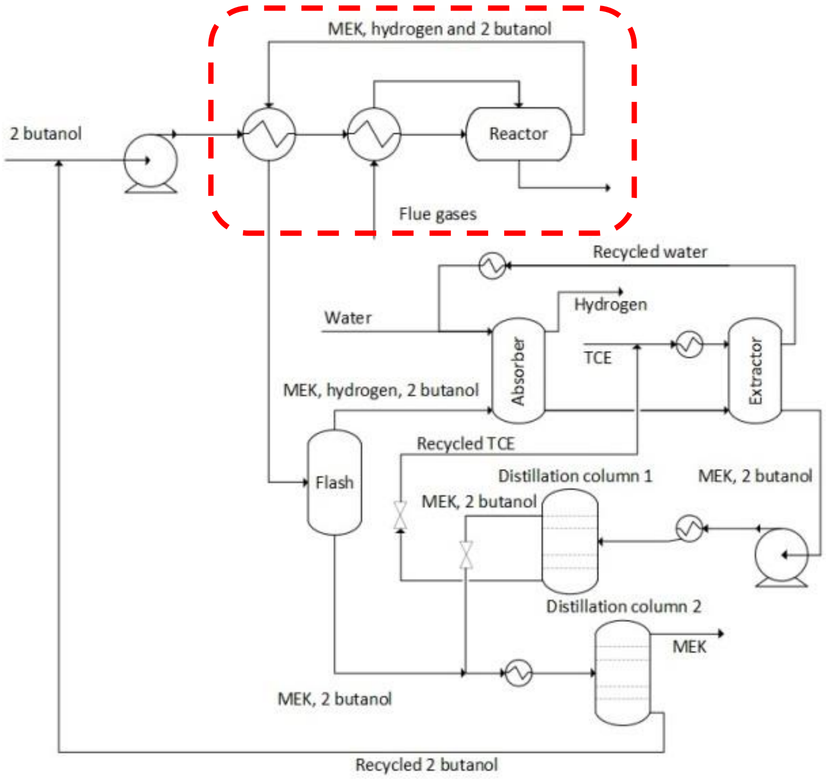


Figure 3.1 The flow scheme for the MEK production plant constructed in the course project in Preliminary Plant Design with the reactor system of interest marked with red.

In particular fixed design specification was imposed to the reactor to obtain the desired conversion regardless the type and amount of utility stream required for reactor heating.

Although in this study the focus is on the reactor design, the idea is to extend the system boundaries to include part of the heat recovery and utility system directly in order to be able to estimate since the first reactor design stages the impact of some critical assumptions on the process primary energy requirement.

The system considered here consists therefore of the reactant as it is delivered to the process (liquid 2-butanol), the reactor and the product stream. As the system required a certain amount of heat for the endothermic reaction to occur heating is required. To supply the needed external heat a furnace burning natural gas is used.

Note that, in this first conceptual design stage, heating or cooling are represented as half heat exchangers as the matching of the various heat sources and sinks is done through Pinch Analysis in a subsequent conceptual design phase. Reactor heating should be however considered as intrinsically connected in this case to the reactor performance as highlighted in chapter 1, and therefore the match between utility stream and reactor should be considered fixed.

A process flow sheet of the system is shown in Figure 3.2.

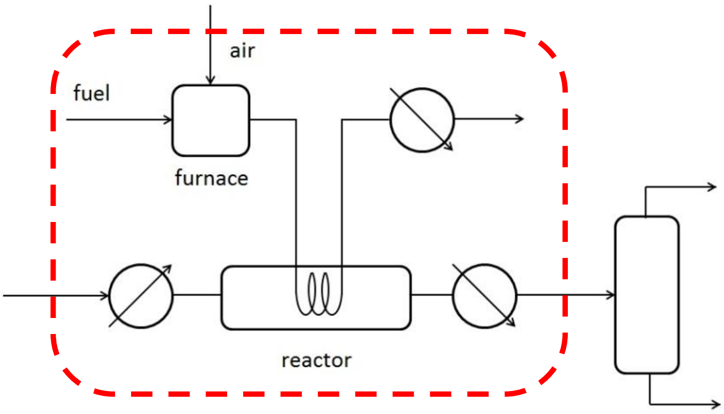


Figure 3.2 The reactor system for MEK production.

3.1.1 Reactor modelling

Aspen HYSYS is used to model and simulate the reactor system.

The fluid package was chosen to be the same as in the course project. Therefore was UNIQUAC (Universal QuasiChemical) used with the binary coefficients estimated by UNIFAC VLE (UNIQUAC Functional-group Activity Coefficients Vapour-Liquid Equilibrium). The equation of state was set to be ideal.

The reactor is modelled accordingly to chapter 2.

3.1.2 Catalyst

The catalyst bed consists of cylindrical brass particles with properties given in Table 3.2. The catalyst activity decays quickly at too high temperatures which limits the maximum temperature of the heating utility. In this study has the maximum temperature for the catalyst been assumed to be around 580-600 °C.

Table 3.2 Properties of the catalyst bed.

Length	d_p	0.0032 m
Particle density	ρ_p	8500 kg/m^3
Thermal conductivity	λ_s	125.4 W/(m K)
Heat capacity	c_p	0.38 kJ/(kg K)
Porosity of the bed	ε_B	0.39

3.1.3 Reactor

MEK is produced by dehydrogenating 2-butanol in a catalytic reactor. The reaction is endothermic and reversible, and follows the stoichiometry shown in equation *(3.1)*.

$$C_4H_{10}O \leftrightarrow C_4H_8O + H_2 \quad \Delta H_R^0 = 54\ \mathrm{kJ/mol} \qquad (3.1)$$

The reaction rate is dependent on partial pressures and temperatures according to the relation in equation (3.2) where A stands for 2-butanol, K for MEK and H for hydrogen.

$$r_A = \frac{k_1 p_A p_K^{-1} - k_2 p_H}{1 + K_A p_A + K_{AK} p_A p_K^{-1}} \qquad (3.2)$$

The reaction rate constants k_1 and k_2 and adsorption constants K_A and K_{AK} are dependent on the temperature as shown in Table 3.3 and p_A, p_K and p_H are the partial pressures expressed in bar.

Table 3.3 Rate law parameters where R is the molar gas constant and T is the temperature given in K.

k_1	$92.47 \times 10^9 \times e^{-\frac{114170}{RT}}$	mole/(s m^3 bed)
k_2	$64.05 \times 10^3 \times e^{-\frac{60762}{RT}}$	mole/(s bar m^3 bed)
K_A	$17.02 \times 10^4 \times e^{-\frac{65567}{RT}}$	bar^{-1}
K_{AK}	$0.6356 \times e^{\frac{9304}{RT}}$	

The pressure was set to 300 kPa according to given settings for the course project. The inlet temperature was set to 500 °C to ensure a good starting reaction rate. As can be seen from the equilibrium curve in Figure 3.3 is a high reaction temperature preferable to acquire a high conversion. The construction of the equilibrium curve is presented in the Appendix A.

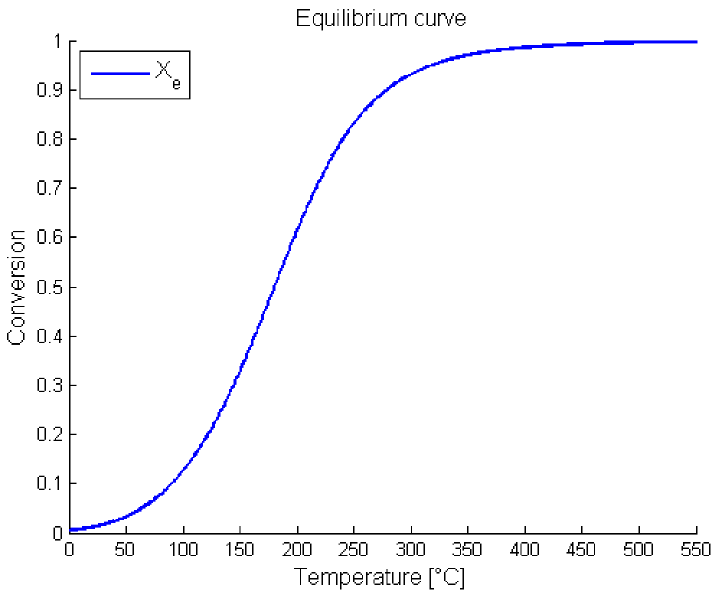


Figure 3.3 Equilibrium curve for MEK production.

The reactor specifications can be seen in Table 3.4 where the given values from the course project were used to calculate reactor dimensions as well as the wall heat transfer coefficient described in section 2.3.1. To calculate the number of tubes the mass flow rate of 12.08 tons / hour at the inlet flow of the reactor was used.

Table 3.4 Reactor specifications.

Given values from the course project	
Fluid viscosity	$1.89 * 10^{-5}$ Pa s
Wall thickness	4.0 mm
Thermal conductivity	15 W/(m K)
Overall heat transfer coefficient	50 W/(m^2 K)
Minimum temperature difference for heating the reactor	50 ºC
Calculated values	
Tube diameter	32 mm
Number of tubes	1156
Wall heat transfer coefficient	100 W/(m^2 K)

3.1.4 Heating utility

To simplify the evaluation of the reactor all external heating is provided from a natural gas fuelled furnace. When temperature limitations apply, i.e. when heating the catalytic reactor, only the flue gases from the furnace is used and they are cooled to the appropriate temperature by mixing with air.

The furnace it modelled in HYSYS with a conversion reactor where the conversion of the combustion reaction is set to 100 %.

The natural gas is simplified to consist of pure methane and is assumed to be available at 25°C and at a sufficient pressure to burn in an atmospheric burner. Air is needed for the combustion according the combustion stoichiometry shown in equation *(3.3)*.

The air is preheated from 25 °C to 200°C and the flow is set to 20 % air-excess (this corresponds to 20 % of the oxygen supply to be unused and still present in the combustion flue gases).

$$CH_4 + 2O_2 \rightarrow 2H_2O + CO_2 \qquad (3.3)$$

Two different configurations were used for the furnace depending on if there was a limitation on the temperature of the heating utility or not.

If the reactor is heated then the catalysts temperature limitations means that only flue gases at a limited temperature can be used. Therefore is no convection heat from the furnace used, i.e. the furnace is adiabatic, Figure 3.4, and the flue gas temperature from the furnace gets over 2000 ºC. The flue gases are mixed with air at 25 °C to lower the temperature to the desired one. By doing this the flow of the flue gases increases which means that less natural gas may be burned to achieve the desired flue gas flow at a desired temperature as would have been burned if the flue gas temperature was decreased by other measures.

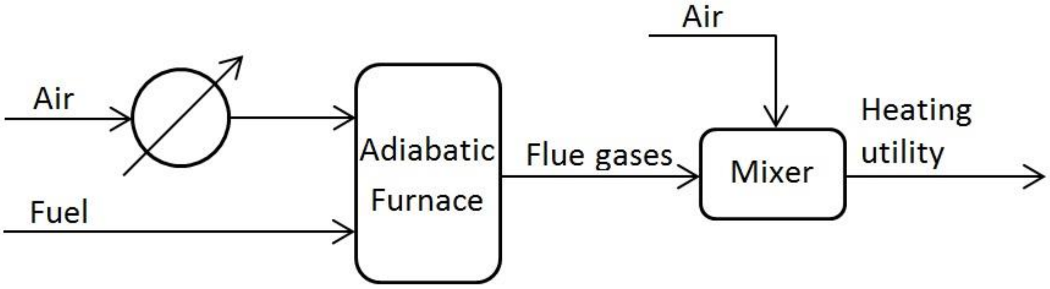


Figure 3.4 Flow sheet for the adiabatic furnace.

If no limitations on the temperature are present then the convection heat from the furnace can be used, Figure 3.5. This means that the furnace radiative heat at high temperature can be used. For this purpose the furnace is modelled as reactor with an outlet temperature at 1000 °C to represent the radiative portion of the combustion heat and with a subsequent heat exchanger cooling the exhaust gases to the stack temperature of 150 °C. The heat from the flue gases can also be used at higher temperatures which mean that no mixing with air is necessary prior the reactor to decrease the utility stream temperature.

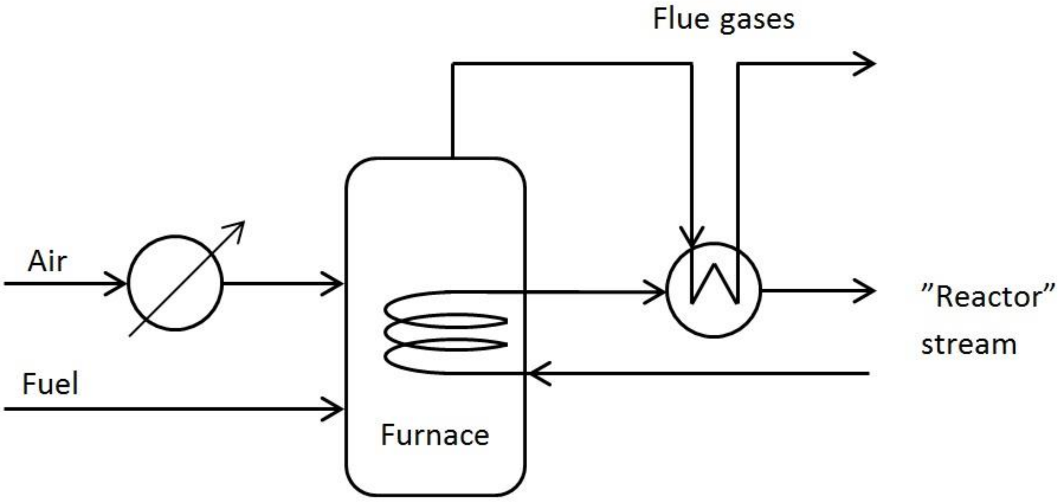


Figure 3.5 Flow sheet of the furnace with convective heating.

After each reactor design was modelled in HYSYS data for all thermal streams were extracted and used to build grand composite curves in Excel by means of the Pro Pi add-in.

When heated reactors re considered the total heating from a furnace was extrapolated from the heat capacity of the utility stream appropriate for the specific reactor setup. From HYSYS inlet and outlet temperatures for the heating medium were extracted together with the duty of the reactor. This was used to calculate the heat capacity (FC_p) by equation *(3.4)* which was then used to calculate the total utility heat content for the utility exit temperature from the system.

$$F * C_P = \frac{Q}{T_{in} - T_{out}} \tag{3.4}$$

A Background/Foreground curve was constructed to confirm that the heating needed by the reactor system was met by the available utility. After the final temperatures were determined together with the total heat content of the heating utility the actual fuel need for the furnace was estimated by simulations in HYSYS. This was done by connecting a cooler to the heating utility stream with the outlet temperature of 150 ºC and then adjusting the amount of fuel until the heat flow in the cooler was the same as the total utility heat content that was needed in the system. The air supplied to the furnace needed pre heating so the air also needed to be incorporated into the back/foreground curve. The heat needed for pre heating the air should be readily available in the system without increasing the fuel demand. A final back/foreground curve was constructed to ensure that the heat supplied from the utility system was enough to cover both the reactor system and the furnace air supply.

If adiabatic reactors were considered the needed hot utility was extracted from the constructed GCC for the process. To determine the fuel demand for the furnace the second type of furnace (radiative) was simulated in HYSYS. For this furnace two types of heat was available, the convective heat in the furnace and the heat from the flue gases. The amount of fuel was adjusted until the total available heat corresponded to the total hot utility demand. Some iteration were needed to supply enough heat to also supply the pre heater of the air to the furnace since more fuel means more air and thus a larger heat demand. After the simulations in HYSYS were done a back/foreground curve was constructed to confirm that no pinch violations were present.

3.2 Reactor concepts

Three different reactor layouts were investigated for the MEK case:

1. a single reaction vessel heated by an external utility stream
2. a staged reactor with a split feed
3. a sequence of adiabatic reactors with intermediate heating

The first concept is merely an adaption of the design in the PPD course project and the second and third are described in section 1.5.

3.3 Parametric study

The effect of design parameters on reactor utility requirement and reactor length (criteria) was investigated through a sensitivity analysis. Due to the time constraints of this thesis work only two design parameters were considered for each of three concepts above:

1. Single reaction vessel:
    a. Reactor conversion
    b. Utility inlet temperature
2. Staged reactor with a split feed:
    a. Reactor conversion
    b. Feed splitting ratio
3. Sequence of adiabatic reaction vessels:
    a. Reactor conversion
    b. Number of reaction vessels

These design parameters were selected from the list of general possible design parameters in section 2.4 and were chosen based on their significance to represent each reactor concept. For all concepts reactor conversion was used as one of the design parameters since the conversion should have a large impact on the length of reactor. A lower conversion gives a lower length but on the other hand less product. The conversion settings were chosen to 85, 90 and 95 %.

For the single heated reactor the second variable was the inlet temperature of the utility stream. This was chosen since a rise in temperature difference between the reactor material stream and the heating utility should give a better energy transfer and therefore benefit the reaction rate and thus lower the length. A higher inlet temperature should also mean that the flow of utility should be able to be lowered and therefore decrease the fuel demand. The chosen temperatures were 560 ºC, 590 ºC and 620 ºC. They were chosen to be larger than the minimum temperature difference between the reactor and heating utility but not so large that the temperature of reactive stream gets too high and therefore damages the catalyst.

For the staged reactor configuration with split feed injection the feed splitting ratio was considered as the second parameter. This was chosen because it appeared more relevant to examine the effect of the feed injection than continue to investigate the effect from the utility inlet temperature for this concept too. The utility inlet temperature was instead fixed as the middle value used for the single heated reactor. The feed ratio to the beginning of the reactor was set to 50%, 65% or 80% of the total feed.

For the adiabatic case the temperature of the utility is not limited by the catalyst since heating of the reactor is not required. Therefore was the number of reaction vessels (stages) set as a parameter. The vessel number was chosen since it affects reaction rate, and therefore reactor length and the number of heat exchangers needed to reheat the reactor material fluid. The number of vessels was set to 2, 3 and 4 vessels.

The outlet temperature for the reactor could be decided by some different methods since it is coupled with the utility flow. It could be calculated by HYSYS for a set utility flow, it could be set at a fixed temperature or it could be coupled with the outlet temperature for the utility. The first alternative was discarded since one of the purposes was to investigate the effects on the utility requirement for different settings and concepts. The second alternative seemed like a simple solution but proved to be difficult to simulate in HYSYS. For the two highest inlet utility temperatures an outlet reactor temperature of 450 °C could not be achieved without violating the minimum temperature difference between the utility and reactor temperatures. On the other hand a reactor outlet temperature of 500 °C could not be achieved by the lowest utility inlet temperature.

Therefore the third option for the utility outlet temperature was chosen. The outlet temperature for the reactor was set to ΔTmin °C below the utility outlet temperature for the heated reactors. This temperature was chosen to avoid unreasonably high utility flows while maintaining the outlet as a pinch point. The outlet temperature is regulated by the utility flow.

Three settings for each design variable give nine simulations for each reactor concept. This gives an indication of how each parameter affect the length of reactor and fuel consumption without consuming too much iteration time and still possibly getting a curve representation with local minima or maxima.

3.3.1 Single endothermic reaction vessel

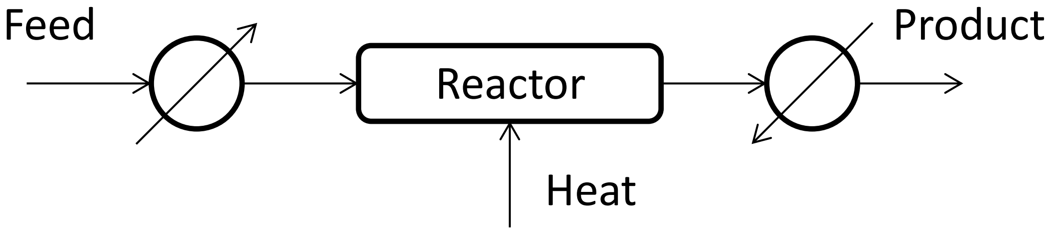


Figure 3.6 Flow scheme for a single heated endothermic reaction vessel

The single heated reactor is the basic case investigated in the project during Preliminary Plant Design course. The temperature of the utility stream is limited by the catalyst that deactivates at too high temperatures, here assumed at 600 ºC. The second design variable is the utility inlet temperature which has minimum temperature limited by the minimum temperature difference between the reactor stream and the utility stream and a maximum temperature limited by the catalyst. The three values of the utility stream inlet temperatures are chosen to be 560 °C, 590 °C and 620 °C.

Due to temperature limitations for the catalyst the first furnace model in section 3.1.4 was used. It was simulated in HYSYS and sized to supply the required heat demand.

3.3.1.1 Results

For the first reactor concept the impact of the utility inlet temperature and of the reactor conversions on reactor volume and furnace fuel consumption were investigated. Since the conversion affects the amount of MEK in the product stream, and since the system was modelled with fixed amount of raw material (in this case 2-butanol) the results (value of reactor length and fuel requirement) were scaled with the mass flow of MEK in the product stream so the best design per unit of produced product can be evaluated.

The temperature profiles inside the reactor are similar between the different utility inlet temperatures as can be seen in Figure 3.7.

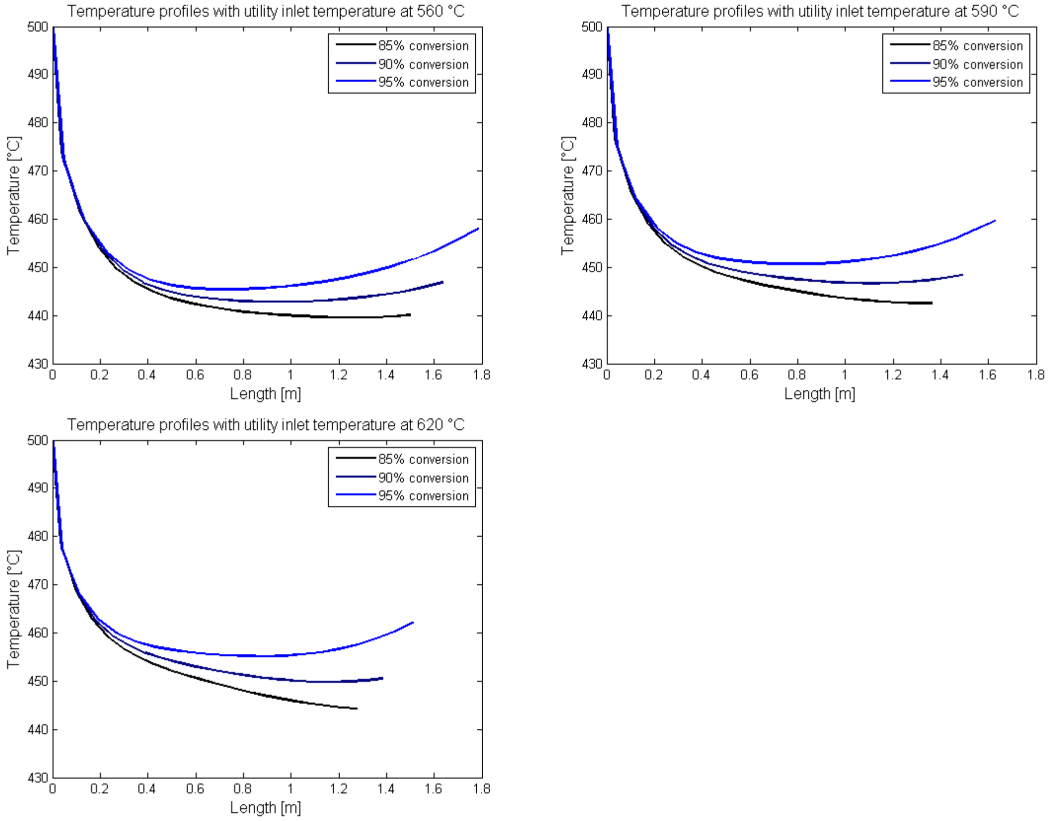


Figure 3.7 Temperature profiles for a single heated reactor for different utility inlet temperatures and conversions.

The grand composite curves for the reactor do not change drastically between conversions and temperature due to the similarities of the temperature profiles of the reactor. In Figure 3.8 is the GCC plotted for different conversions for the reactor with utility inlet temperature at 590 °C. The main change is for the reactor part which is the part above 500 °C. The temperature axis is in interval temperatures which make the highest temperature in the GCC 550 ºC for the reactor. The GCCs for 560 and 620 ºC utility inlet temperature is similar to the ones for 590 °C in Figure 3.8.

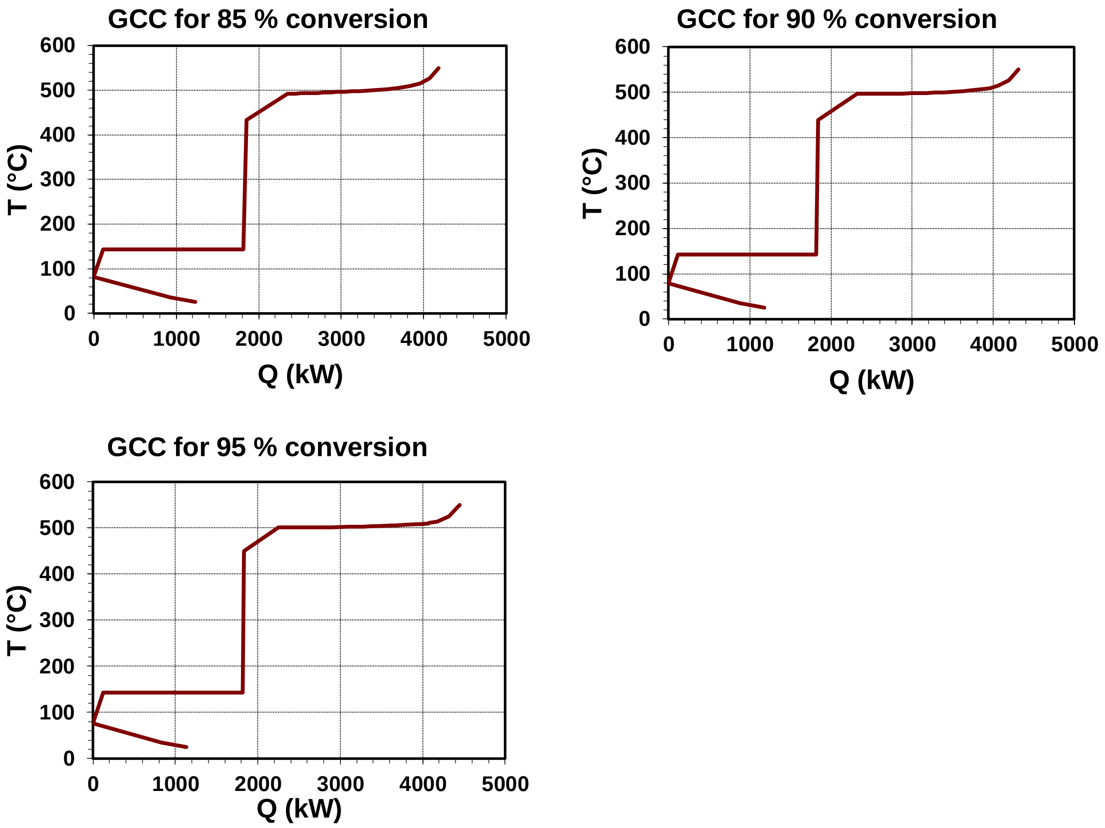


Figure 3.8 Grand composite curves for different conversions for a single heated reactor with utility inlet temperature at 590 ºC.

A back/foreground analysis is done for each scenario with the utility stream with pre heating of air as the foreground, the back/foreground curve for 90 % conversion and utility inlet temperature at 590 ºC is shown in Figure 3.9. The pinch point is located at the lowest temperature of the reactor contribution to the background curve since the utility outlet temperature is set to be ΔT_{min} above the reactor outlet temperature and the temperature profiles in Figure 3.7 gives that the temperature difference will never be lower than for the outlet. Due to the high temperature of the reactor there is lot of excess energy in the utility. According to pinch analysis the excess can be lowered by changing the slope of the utility stream. This is done by lowering the flow and rising the temperature and leads to a lower fuel consumption, and as can be seen in Figure 3.10 is this accurate for this situation.

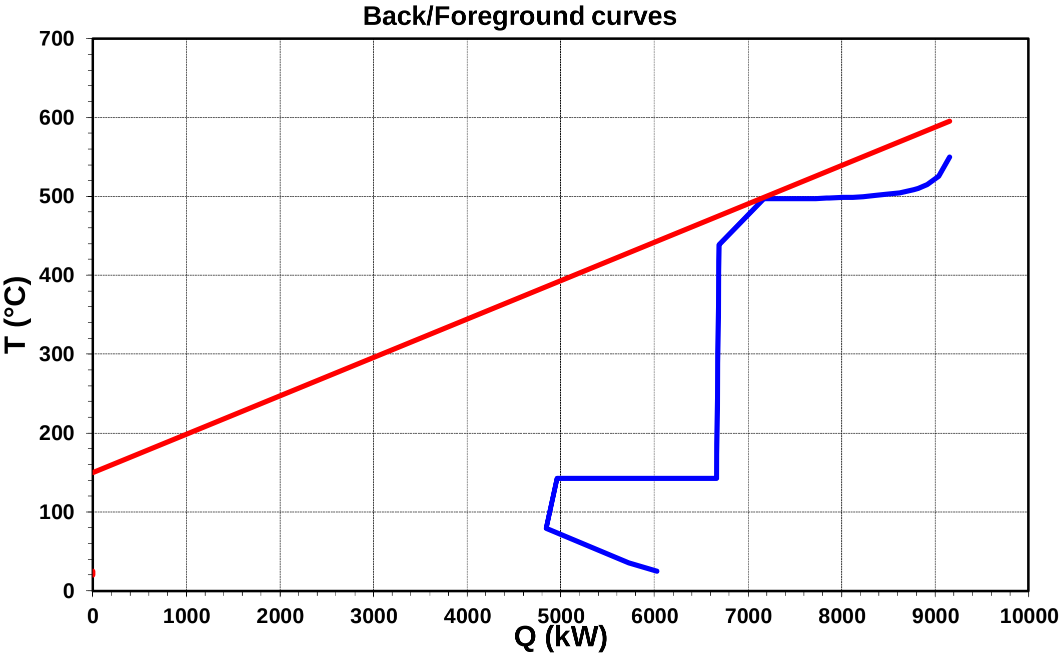


Figure 3.9 Back/Foreground curve for 90 % conversion and 590 °C utility inlet temperature.

The fuel consumption increases with increasing conversion and decreases with increasing utility inlet temperature as can be seen in the left figure in Figure 3.10. The same trends are observed for the scaled fuel consumption, Figure 3.10 right, but the conversion dependence decrease in importance with increasing utility inlet temperatures.

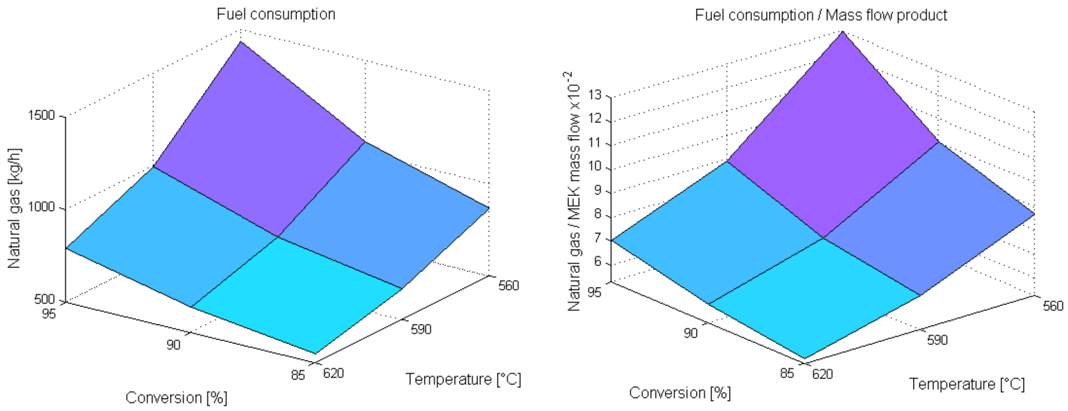


Figure 3.10 Left: Conversion and temperature dependence for the fuel consumption of a single heated reactor. Right: Conversion and temperature dependence for the scaled fuel consumption of a single heated reactor

The reactor volumes dependence on the conversion was expected. Lower conversion gives a shorter reactor, and therefore a smaller volume, as shown in Figure 3.11 left, and the same applies for higher utility inlet temperatures. The conversion relation is similar when scaling the volume against the produced MEK, Figure 3.11 right and it is also preferable with a high utility inlet temperature.

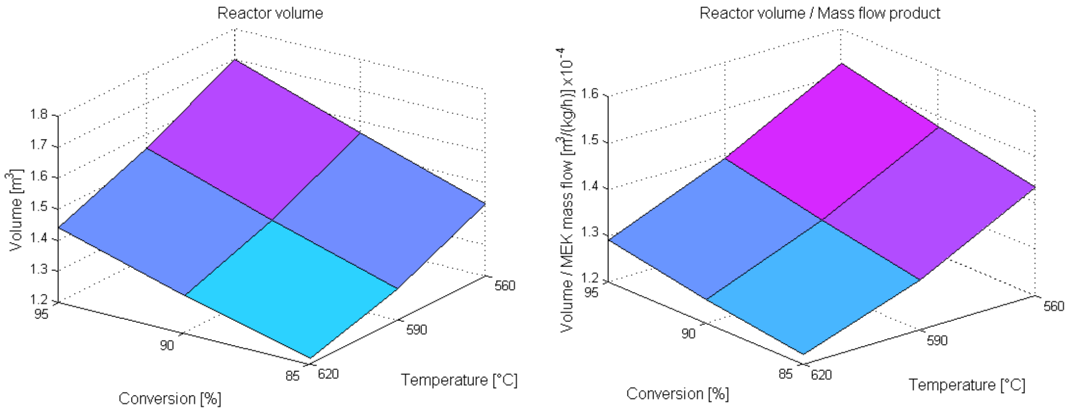


Figure 3.11 Conversion and temperature dependence for the length of a single heated reactor.

3.3.2 Staged heated reactors with intermediate feed injection

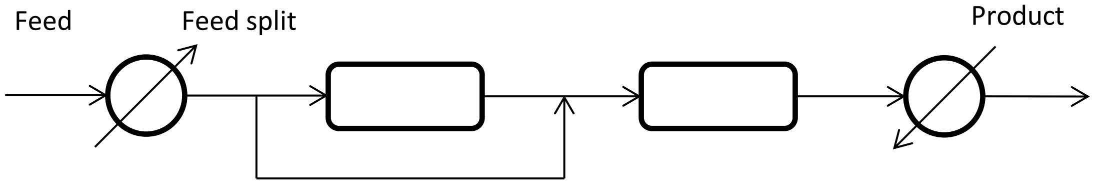


Figure 3.12 Flow scheme for a staged heated reactor with intermediate feed injection.

A staged reactor with an injection of fresh feed into the second reactor affects the reaction rate in two different ways, the temperature rises and the concentration of 2-butanol increases. From equation ***(3.2)*** and Table 3.5 it can be seen that the two terms, $k_1p_Ap_K^{-1}$ and k_2p_H in the numerator are positively affected by a rise in temperature from the temperature dependence on k_1 and k_2. For the denominator is the term K_Ap_A affected positively by a rise in temperature and $K_{AK}p_Ap_K^{-1}$ affected negatively which means that K_Ap_A affects the reaction rate negatively and $K_{AK}p_Ap_K^{-1}$ affects it positively. As can be seen in Table 3.5 is k_1 highly dominant for temperatures lower than 500 °C which means that the total effect from a rise in temperature is a higher reaction rate.

Table 3.5 The values for the reaction rate and adsorption constants for the production of MEK

T [°C]	k_1	k_2	K_A	K_{AK}
300	3.61	0.00	0.179	4.481
325	9.84	0.00	0.319	4.130
350	24.73	0.00	0.541	3.831
375	57.88	0.00	0.882	3.574
400	127.18	0.00	1.386	3.352
425	264.13	0.00	2.109	3.158
450	521.50	0.0525	3.117	2.988
475	983.89	38.0677	4.488	2.837
500	1781.59	1059.1730	6.312	2.703

The concentration also affects the different terms since a higher concentration of a species increases the partial pressure of that species. An injection of pure 2-butanol will therefore increase the partial pressure p_A but decrease p_K and p_H. This means that the forward term in the numerator will benefit from the injection and the reverse term will decrease. Both adsorption terms in the denominator will benefit which may decrease the positive effect.

Although different number of reactor stages only two heated reactor stages were investigated here where the length of the first reactor was set to 25 % of the reactor length for the corresponding single reactor case. The different lengths for the three different conversions can be seen in Table 3.6. The length of the second reactor was adjusted to achieve the desired conversions.

Table 3.6 Reactor length for the first reactor for different conversions.

Conversion	Length [m]
0.85	0.35
0.90	0.38
0.95	0.42

The feed was split in three different ways, 50/50, 65/35 and 80/20 where the larger flow is the main feed and the smaller is the feed injection.

The reactor was modelled by using two plug flow reactors. The feed is split and the main part goes into the first reactor then is the outgoing reactor stream combined with the remaining feed injection and goes thereafter into the second reactor. The utility stream is set to have the same flow rate for both reactors and the outlet temperature for the first reactor is set as the inlet temperature for the second reactor. The flow rate is adjusted to get ΔT_{min} as the temperature difference at the outlet for the second reactor according to the principle described in section 3.2. Another configuration of the utility stream is to split the utility and have two streams with the same high utility inlet temperature and ΔT_{min} as the temperature difference at the outlet for both reactors. This has not been done in this study due to time constraints.

The first furnace model in section 3.1.4 was used for this design due to temperature limitations from the catalyst.

3.3.2.1 Results

For the second reactor concept the feed injection ratio and reactor conversion impact on reactor volume and furnace fuel consumption were investigated through a parametric study.

The combined temperature profiles for both reactors changes noticeably while changing the feed ratio, Figure 3.13. There is a temperature peek for the feed injection for all ratios and the peek increases with decreasing ratio. This effect is expected since a lower feed ratio into the beginning of the reactor gives a bigger fresh feed injection at the second stage.

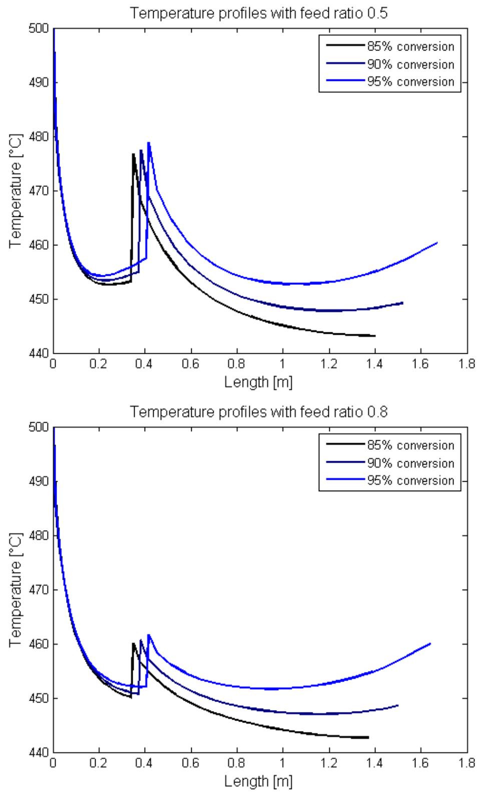


Figure 3.13 Temperature profiles for a staged reactor with feed injection for different feed ratios and reactor conversions.

Grand composite curves and back/foreground curves are similar to curves for the single heated reactor except that the reactor part appears almost at the same temperature with a sharper bend at one end, Figure 3.14. This is explained by the two sharp peeks of high temperature at the beginning of each reactor stage.

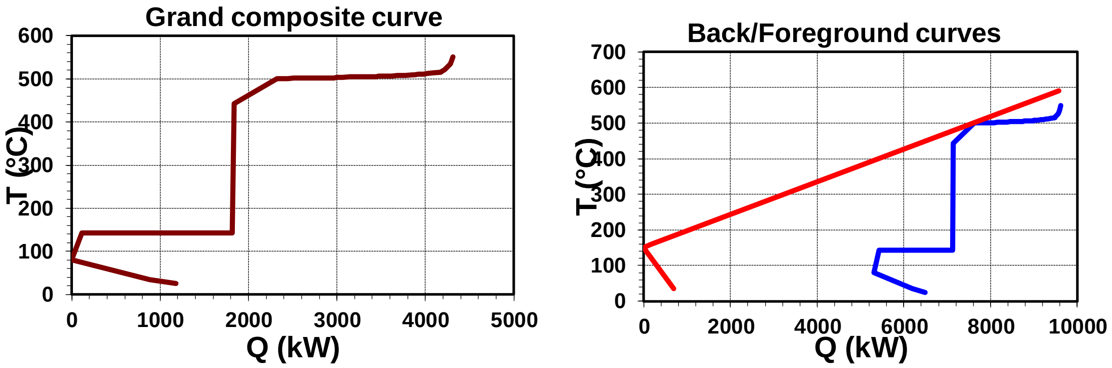


Figure 3.14 Grand composite curve and back/foreground curves for 90 % conversion and feed ratio 0.65 into the beginning of the reactor.

The fuel consumption is Figure 3.15 left, with the scaled fuel consumption to the right. Data for the single heated reactor at the same utility temperature has been included and the results clearly show that the feed ratio has no real significance. The reactor conversion highly influences the fuel consumption where a low conversion is favourable.

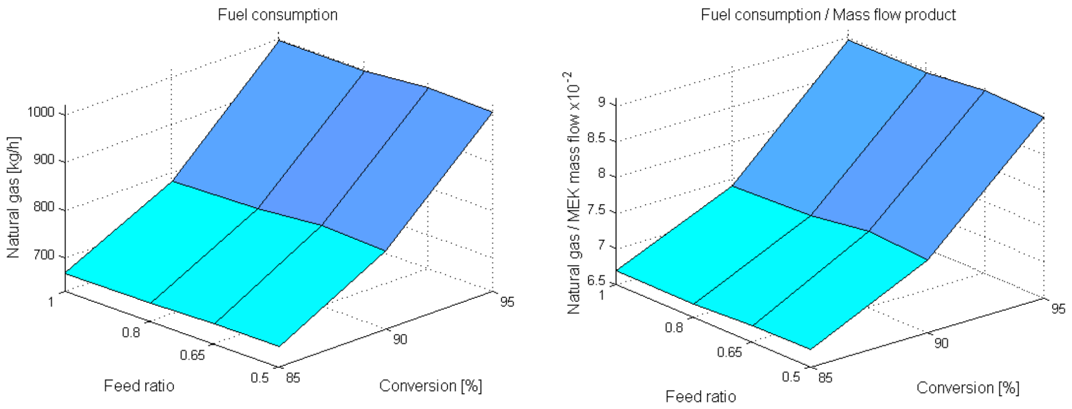


Figure 3.15 Conversion and fuel ratio dependence for the fuel consumption of a heated reactor with feed injection where the left figure is for the ratios used for this concept and the right figure include data for a reactor with no feed injection at the same utility temperature.

The reactor length decreases with increasing feed ratio into the beginning of the reactor but when compared to the single heated reactor the trend breaks, Figure 3.16. Higher conversion gives a longer reactor and also increases the difference between feed ratios. The importance of the conversion diminishes when scaling the results to the product mass flow but it is still favourable to have a lower conversion.

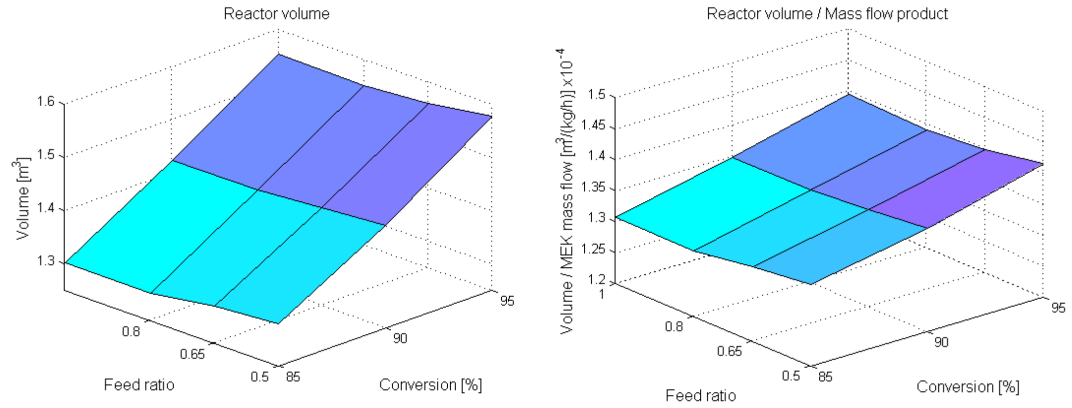


Figure 3.16 Conversion and fuel ratio dependence for the reactor length of a heated reactor with feed injection where the left figure is for the ratios used for this concept and the right figure include data for a reactor with no feed injection at the same utility temperature.

The results indicate that feed injection is not effective to lower the energy use but it seems reasonable that the point of injection is important and another configuration may change these results. The reactor length does not seem to be positively affected by feed injection and one reason for this can be that the feed injected has a lower residence time than the feed going in to the first reactor and therefore less time to react. The reaction rate is also very dependent on the total pressure of the system so it decreases with the pressure drop inside the reactors.

3.3.3 Adiabatic reactors with intermediate heating

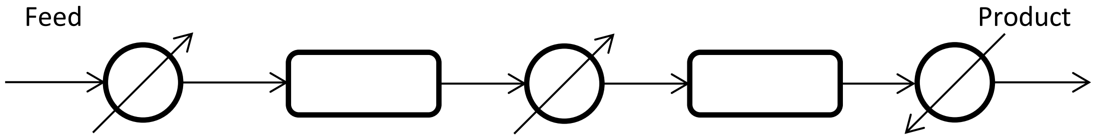


Figure 3.17 Flow scheme for two adiabatic reactors with intermediate heating

When the reaction is performed in an adiabatic reactor the reaction will either proceeds until it reaches equilibrium or until the temperature is too low for the reaction to occur since it is not possible to affect the kinetics through external media. The reaction rate for the production of MEK approaches zero when the temperature drops below 300 °C as can be seen in Figure 3.18. This means that the reaction can continue at lower temperatures only with unreasonably long reactor which turns to be unpractical due the dramatic increase in investment costs and operating costs due to sever pressure drop. The construction of the temperature-conversion curve is described in Appendix A.

Figure 3.18 shows which conversion is theoretically possibly if the limits of the reaction rate are not taken into account. Note that the line with negative slope represents the enthalpy balance of the reactive medium against the temperature and it is slightly curved due to the dependency of the specific heats on the temperature.

To reach higher conversion while still benefitting from the intrinsic simplicity of adiabatic vessels it is necessary to use several reactors with intermediate heating.

As shown in Figure 3.19, intermediate heating allows to re-establish the temperature of the reactive fluid, which composition is temporarily frozen as the reaction does not proceed in the heat exchanger without catalyst bed, far away from the equilibrium thus letting the reaction proceed in a second stage towards much higher value of the conversion.

The reactor stream will be heated to the first feed temperature of 500 ºC between all reactors. A deviation of a few degrees is noted between the results from the calculated temperature-conversion trajectory and results from the model in HYSYS. Some of the difference can be explained by that the calculations do not include the pressure drop in the reactor. Since the difference is only a few degrees for a desired conversion the calculations still gives a good hint on at which temperature to stop the reactors.

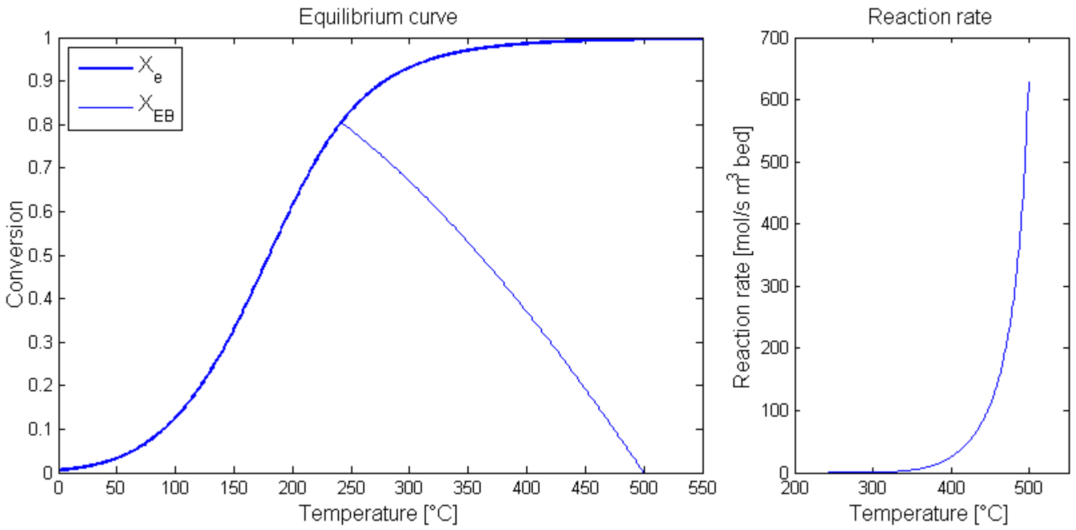


Figure 3.18 Left: Equilibrium curve and temperature-conversion trajectory for one MEK reactor. Right: The reaction rate temperature dependence in the reactor.

The number of reactors affects which temperature each reactor stops at and therefore the total reactor length. Since the reaction rate rapidly decreases with temperature will the reactor length for one reactor be longer than the total reactor length for two reactors with intermediate heating since the overall temperature is higher in two reactors. The chosen numbers of reactors are two, three and four reactors.

The equilibrium curve and temperature-conversion curve together with the reaction rate is used to decide when to stop the reaction in each reactor stage.

As previously mentioned the reaction rate closes to zero after 300 °C but according to simulations in HYSYS the reaction stops already at 350 °C due to too large pressure drops related to the length of the reactor. If the first reactor is set to an outlet temperature of 350 °C and then the stream is reheated to 500 °C this corresponds to a different temperature-conversion trajectory which can be seen in Figure 3.19. Theoretically the highest chosen conversion of 95 % is reachable with only two reactors but the low reaction rate in the second reactor makes the reactor length and therefore the pressure drop too high.

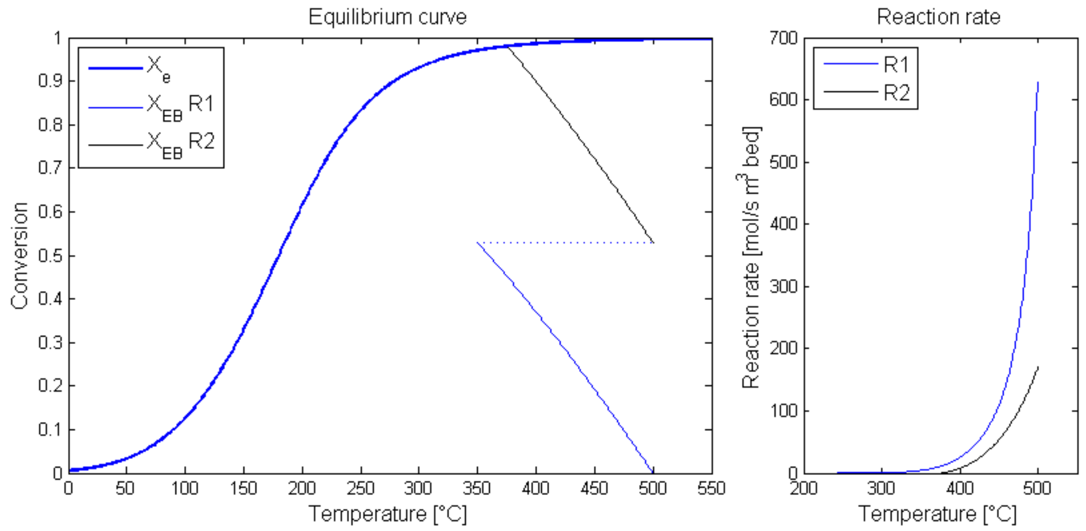


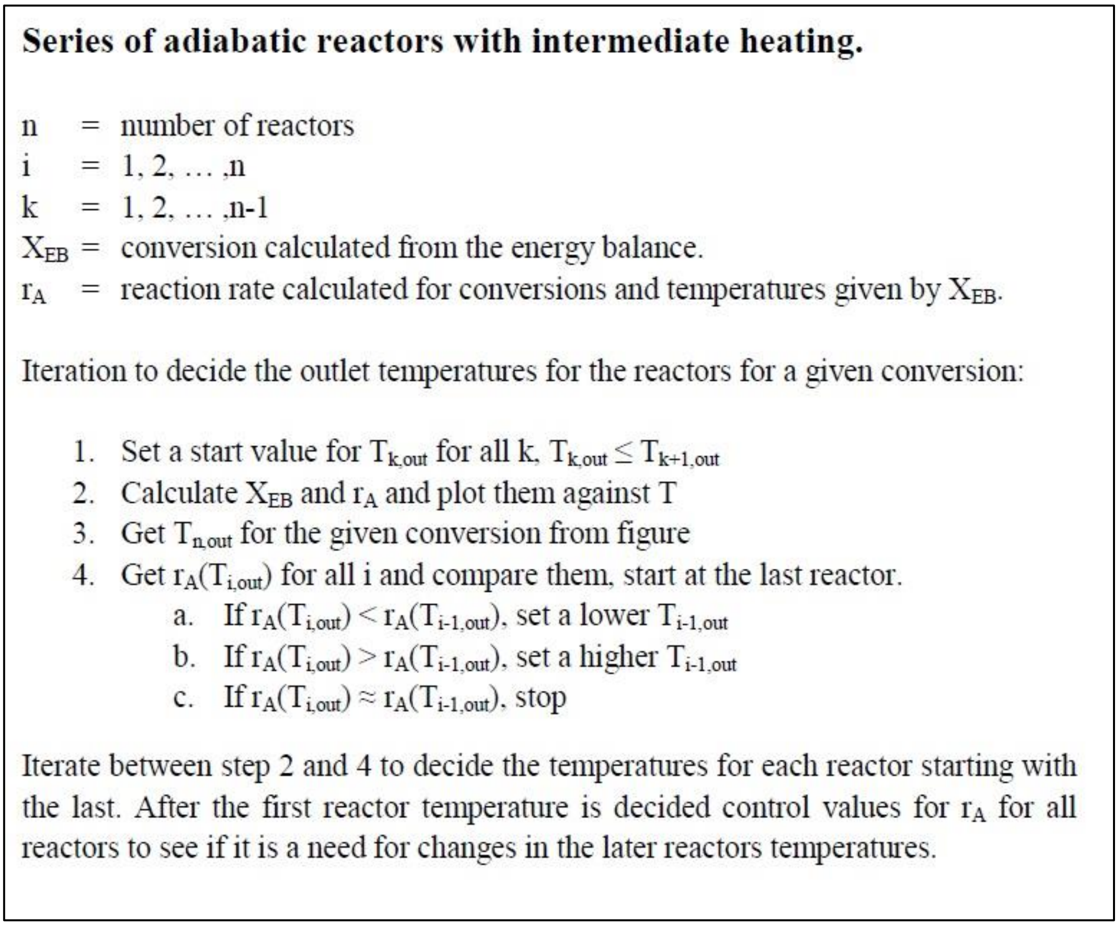
Figure 3.19 Left: Equilibrium curve and temperature-conversion trajectory for two reactors with intermediate heating. Right: The reaction rate temperature dependence in the reactors.

For the two other conversions two reactors are sufficient and the first reactor is stopped at 365 °C for 90 % conversion and at 375 °C for 85 % conversion.

To minimize the reactor length the outlet temperatures is chosen by starting at one out temperature for the first reactor and read the corresponding out temperature for the second reactor at the desired conversion. After the two out temperatures are known the final reaction rate for each reactor is read. If the final reaction rate for the second reactor is higher than for the first reactor the first reactor can be stopped at a higher temperature. A higher outlet temperature for the first reactor is chosen and the same procedure is done again. After some iteration a valid temperature can be tried in HYSYS where some adjustment is done to compensate for the difference between the prediction based on the equilibrium curve and the accurate HYSYS model. An algorithm for this procedure is shown in Figure 3.20.

When optimizing the temperature values in HYSYS to reach the lowest length the step for each change was limited to 5 ºC to simplify the HYSYS convergence to the right conversion.

The same procedure was used to decide the outlet temperatures for three and four reactors. Since more reactors are added the method gets more time consuming but as a guideline should the outlet temperature rise with reactor number. The final outlet temperatures for three reactors can be seen in Table 3.7 and for four reactors in Table 3.8.



Series of adiabatic reactors with intermediate heating.

n = number of reactors
i = 1, 2, … ,n
k = 1, 2, … ,n-1
X_{EB} = conversion calculated from the energy balance.
r_A = reaction rate calculated for conversions and temperatures given by X_{EB}.

Iteration to decide the outlet temperatures for the reactors for a given conversion:

1. Set a start value for $T_{k,out}$ for all k, $T_{k,out} \leq T_{k+1,out}$
2. Calculate X_{EB} and r_A and plot them against T
3. Get $T_{n,out}$ for the given conversion from figure
4. Get $r_A(T_{i,out})$ for all i and compare them, start at the last reactor.
    a. If $r_A(T_{i,out}) < r_A(T_{i-1,out})$, set a lower $T_{i-1,out}$
    b. If $r_A(T_{i,out}) > r_A(T_{i-1,out})$, set a higher $T_{i-1,out}$
    c. If $r_A(T_{i,out}) \approx r_A(T_{i-1,out})$, stop

Iterate between step 2 and 4 to decide the temperatures for each reactor starting with the last. After the first reactor temperature is decided control values for r_A for all reactors to see if it is a need for changes in the later reactors temperatures.

Figure 3.20 Algorithm to decide the outlet temperatures for a series of endothermic adiabatic reactors with intermediate heating

Table 3.7 The out temperatures for three reactors with intermediate heating.

Conversion [%]	T_{out} Reactor 1 [°C]	T_{out} Reactor 2 [°C]
85	415	420
90	410	415
95	395	405

Table 3.8 The out temperatures for four reactors with intermediate heating.

Conversion [%]	T_{out} Reactor 1 [°C]	T_{out} Reactor 2 [°C]	T_{out} Reactor 3 [°C]
85	430	440	445
90	430	435	440
95	425	430	435

The fuel demand was determined by simulations in HYSYS of the second type of furnace from section 3.1.4 since there were no temperature limitations on the utility for designs with adiabatic reactors.

3.3.3.1 Results

For the third reactor concept the impact of the number of reaction vessels and reactor conversion on reactor length and furnace fuel consumption were investigated.

Adiabatic reactors with intermediate heating are simpler to design from an energy effective view point. This is due to the fact that the reaction is taken away from the energy analysis and therefore the changes in the utility temperature and flow do not affect either length of the reactors, the conversion or the reaction rate for set feed temperatures. This facilitates the minimization of the primary energy need. Since there should be no excess heat for the system is it important to include the energy need to pre heat the air that goes into the furnace. This stream is set as a cold stream for the foreground and the back/foreground curves can be seen in Figure 3.21.

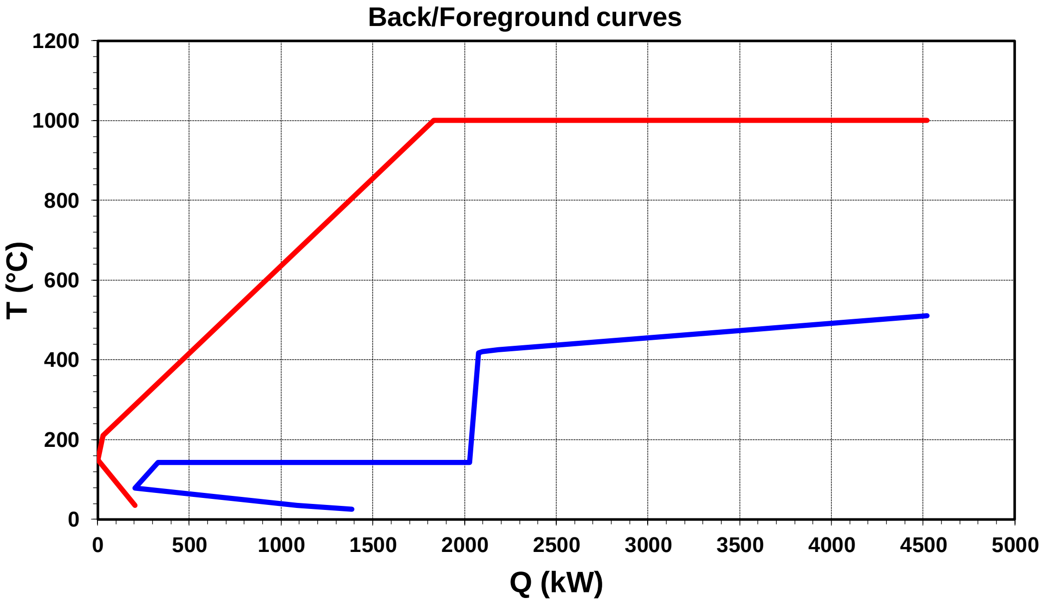


Figure 3.21 Back/Foreground curve for 90 % conversion and three reactors.

The fuel consumption increases with increasing conversion, Figure 3.22, which is quite expected since increased conversion gives lower reactor outlet temperatures, as shown in section 3.3.3, and the more heating is required between the reactors. Increasing number of reactors lowers the fuel consumption of the same reason as for decreasing conversion but the difference between three and four reactors is marginal. It should also be noted that the difference between the lowest and highest fuel consumption for three reactors is around 20 kg/h. The relationship between conversion and fuel consumption reverses when scaling the results to the mass flow of product. This can be explained by that the difference between the conversions is so small and each conversion level changes the amount of product that is produced.

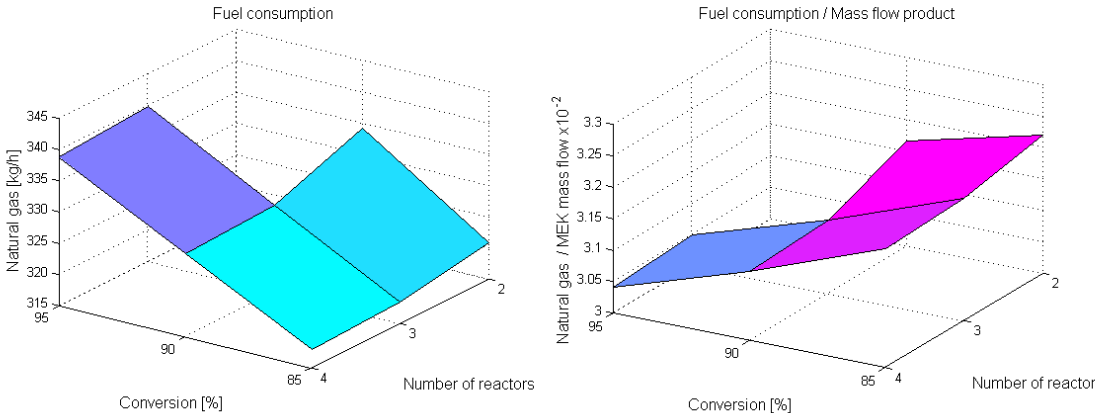


Figure 3.22 Conversion and number of reactor dependence for fuel consumption of adiabatic reactors with intermediate heating.

The total reactor volume follows similar patterns as the fuel consumption, Figure 3.23, but with a more severe difference between two and three reactors. The reason the volume increases so much for two reactors is due to the fact that each reactor needs to go on to a low temperature and low reaction rate and a slow reaction means a longer reactor which gives a higher volume. The importance of the conversion lowers with increasing number of reactors but for two reactors is the conversion crucial, for example is 95 % conversion not possible for the circumstances of this case study. The results does not significantly change when scaling the volume with the mass flow of product.

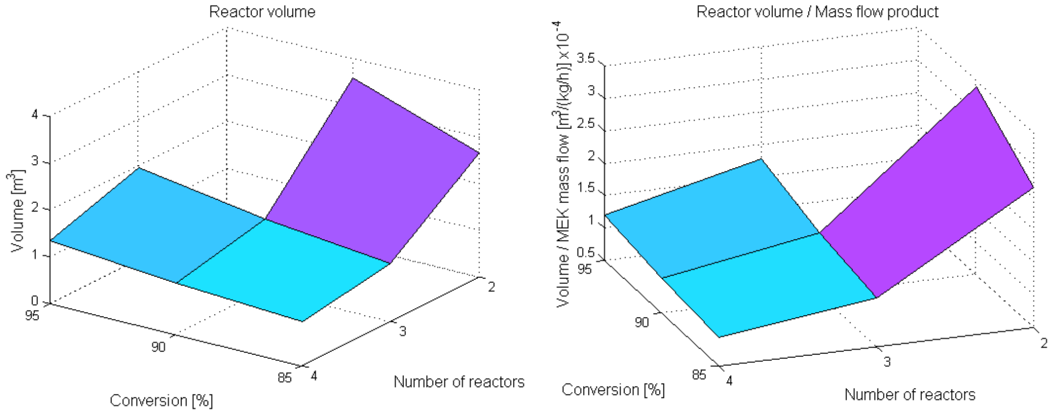


Figure 3.23 Conversion and number of reactor dependence for the total length of adiabatic reactors with intermediate heating.

3.3.4 Comparison between reactor designs

The grand composite curves do not change significantly for either shape nor heat load for different parameter settings for the different reactor layouts. It can also be seen in ***Figure 3.24*** that the first two layouts has similar GCCs, and the last layout differs since the reactor is not included because it is adiabatic. This means that energy targeting is not a sufficient tool to investigate the different reactor designs if not accompanied by a discussion of the reactor design and an investigation of how kinetics affect the utility requirement.

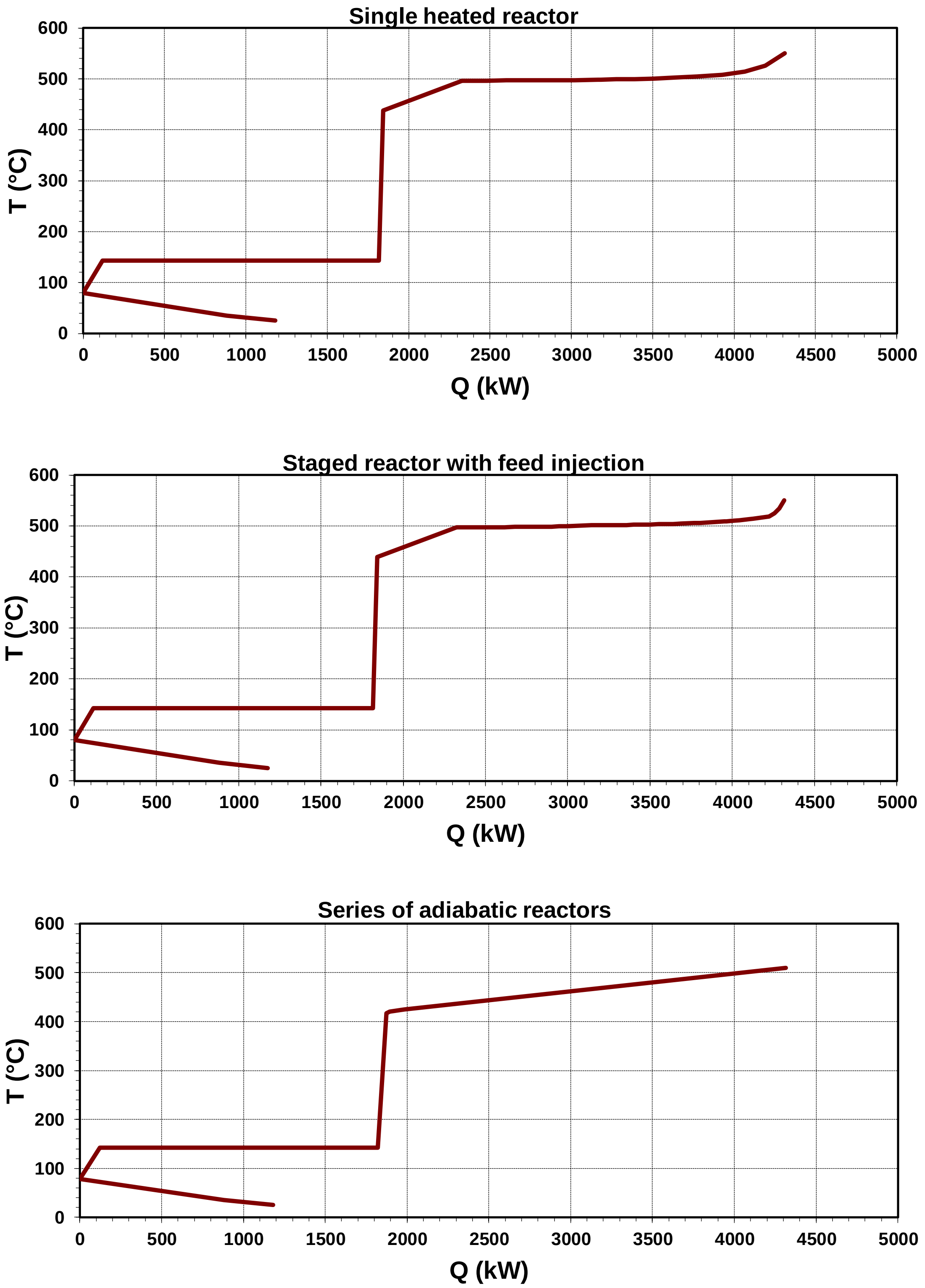


Figure 3.24 *One example of a GCC for each reactor design. The conversion is 90 % for all cases, and for the single heated reactor is the inlet utility temperature 590 ºC, for the staged reactor with feed injection is the feed ratio 65 % and for the series of adiabatic reactors is the vessel number 3.*

To determine a favourable reactor design a volume against natural gas consumption plot has been constructed in Figure 3.25. It can be seen that the adiabatic reactor design has the smallest fuel consumption but can get a really large reactor volume for few reactors.

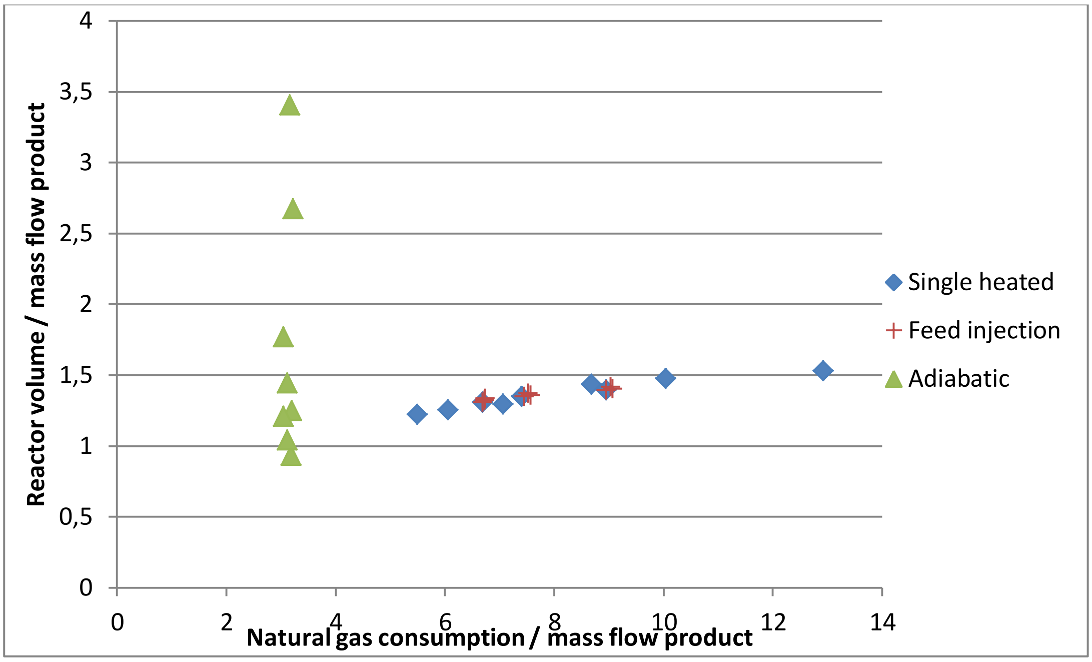


Figure 3.25 Scaled reactor volume against the scaled natural gas consumption for all different designs and parameters.

The results for the single heated reactor are a bit hard to interpret, so a different diagram has been constructed for only that design in Figure 3.26. Here it is easier to see that high utility inlet temperatures are favourable. The arrows indicate increasing conversion.

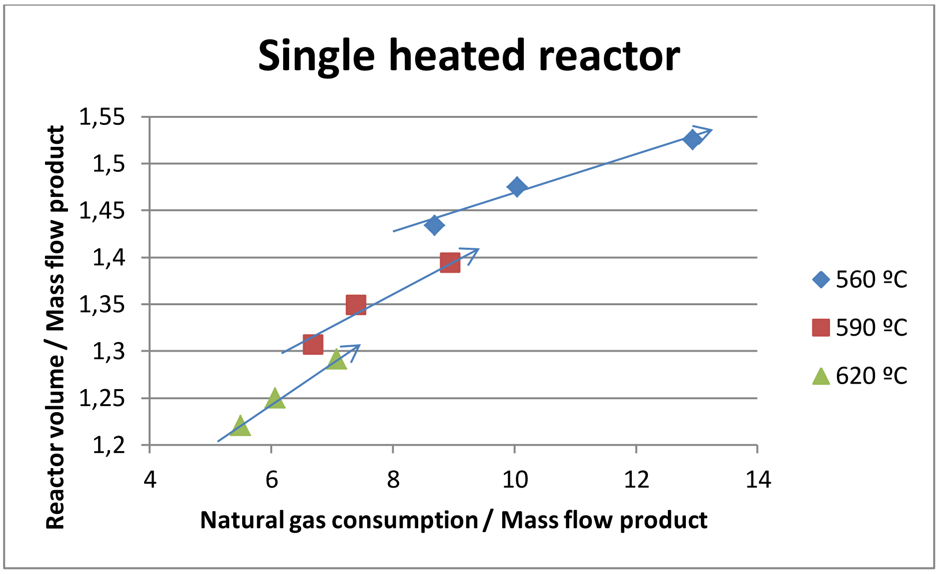


Figure 3.26 *Scaled reactor volume against the scaled natural gas consumption for the single heated reactor. The reactor volume increases with increasing conversion and the trends for the different utility inlet temperatures are indicated by the arrows.*

Finally is it interesting to see how the new designs stand against the reactor design from the course project in Preliminary Plant Design and Figure 3.27 clearly shows that all new design regardless of parameter settings is much more energy efficient. It can therefore be concluded that if nothing else is done at least should the flue gases be mixed with air to reach the desired temperature which decreases the fuel demand to less than a third. It is also important to use the right furnace for the different layouts. Since the heated reactors cannot use very high temperature utility is the radiation heat from the furnace wasted on those layouts. Therefore is an adiabatic furnace a way to increase the flue gas exit temperature from the furnace which increases the amount of air that can be mixed to reach the right temperature and heat content. This leads to a lower fuel demand than had been possible for a lower exit temperature.

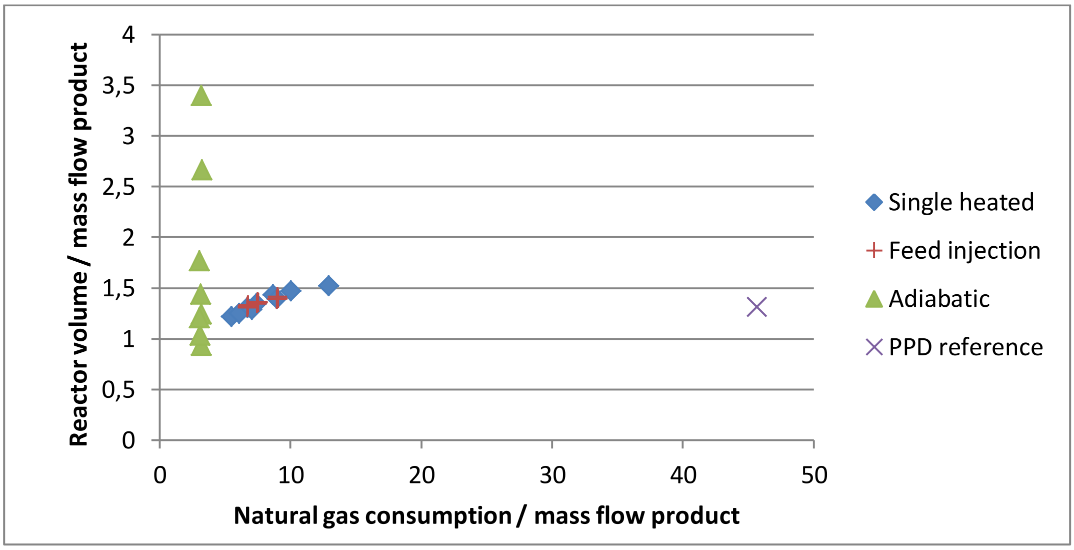


Figure 3.27 *Scaled reactor volume against the scaled natural gas consumption for the single heated reactor with the reactor design from Preliminary Plant Design.*

4 Methanation process case study

In this chapter the study of the structural and design parameter of an exothermic reactor is discussed.

The case study was chosen to be the fixed-bed methanation of syngas from coal biomass. This type of SNG production has become interesting as an option to natural gas.

4.1 Background

The one complete process to produce SNG from coal can be seen in Figure 4.1. There are several reactors in the plant but this study is focused on the methanation process at the final stages of the SNG production process.

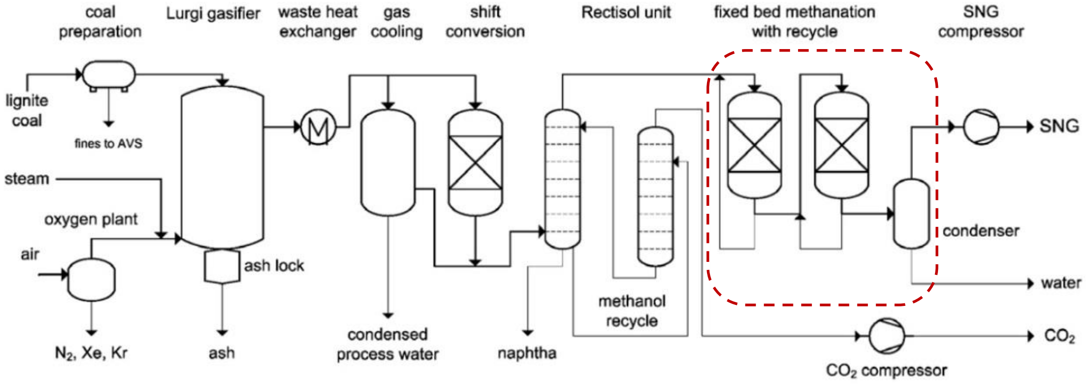


Figure 4.1 *Flow scheme for a SNG production plant with coal as base. The selected area shows the methanation unit which is the focus in this case study (Kopyscinski, et al., 2010).*

Synthetic natural gas can also be produced from biomass which is very interesting from an environmental view point. SNG produced from biomass should be carbon neutral, and if CO_2 is captured when it is separated it can also be carbon negative. One big difference between SNG produced from coal or biomass is the scale. Biomass sources are often smaller than the possible coal sources which mean that the SNG plant also becomes smaller. This mainly affects the processes before the final methanation so it has not been affecting the work on this case study (Kopyscinski, et al., 2010).

4.1.1 Reactor modelling

Aspen HYSYS is used to model and simulate the reactor system.

The fluid package was chosen to be Peng-Robinson which works well for gaseous systems.

4.1.2 Kinetics

There are three main reactions that take place in a methanation unit and they are the methanation of carbon monoxide, equation ***(4.1)***, the reverse or forward water gas shift reaction, equation ***(4.2)*** and methanation of carbon dioxide, equation ***(4.3)*** (Pearce, et al., 1989).

$$3\mathrm{H_2} + \mathrm{CO} \leftrightarrow \mathrm{CH_4} + \mathrm{H_2O} \ \ \Delta \mathrm{H_R^0} = -206\ \mathrm{kJ/mol} \tag{4.1}$$

$$\mathrm{CO} + \mathrm{H_2O} \ \leftrightarrow \mathrm{CO_2} + \mathrm{H_2} \ \ \Delta \mathrm{H_R^0} = -41\mathrm{kJ/mol} \tag{4.2}$$

$$4\mathrm{H_2} + \mathrm{CO_2} \leftrightarrow \mathrm{CH_4} + 2\mathrm{H_2O} \ \ \Delta \mathrm{H_R^0} = -165\ \mathrm{kJ/mol} \tag{4.3}$$

Another important reaction that takes place in the methanation process is the Boudouard reaction, see equation ***(4.4)***, where carbon monoxide forms carbon and carbon dioxide. The carbon formation can lead to catalyst deactivation but steam can be added to the feed as a way to avoid it (Kopyscinski, et al., 2010).

$$2\mathrm{CO} \ \leftrightarrow \mathrm{C} + \mathrm{CO_2} \ \ \Delta \mathrm{H_R^0} = -173\ \mathrm{kJ/mol} \tag{4.4}$$

The Boudouard reaction has been neglected in this work but the water content in the feed is discussed in the results.

To find a suitable kinetics models was a particularly difficult task due to lacking of literature in the field. The main problem was to find models that covered both methanation of carbon monoxide and carbon dioxide. The final study used for the kinetics was a study on the reverse process, methane steam reforming (Hou & Hughes, 2001). The kinetics for this process should work satisfactory since the considered reactions are reversible and similar catalysts are used. Equations ***(4.5)***, ***(4.6)*** and ***(4.7)*** are the rate law expressions for CO production from methane, the water gas shift reaction and CO_2 production from methane.

$$r_1 = \frac{k_1\left(P_{CH_4}P_{H_2O}^{0.5}/P_{H_2}^{1.25}\right)\left(1-\left(P_{CO}P_{H_2}^{3}/K_{p_1}P_{CH_4}P_{H_2O}\right)\right)}{\left(1+K_{CO}P_{CO}+K_HP_H^{0.5}+K_{H_2O}\left(P_{H_2O}/P_{H_2}\right)\right)^2} \tag{4.5}$$

$$r_2 = \frac{k_2\left(P_{CO}P_{H_2O}^{0.5}/P_{H_2}^{0.5}\right)\left(1-\left(P_{CO_2}P_{H_2}/K_{p_2}P_{CO}P_{H_2O}\right)\right)}{\left(1+K_{CO}P_{CO}+K_HP_H^{0.5}+K_{H_2O}\left(P_{H_2O}/P_{H_2}\right)\right)^2} \tag{4.6}$$

$$r_3 = \frac{k_3\left(P_{CH_4}P_{H_2O}/P_{H_2}^{1.75}\right)\left(1-\left(P_{CO_2}P_{H_2}^{4}/K_{p_3}P_{CH_4}P_{H_2O}^{2}\right)\right)}{\left(1+K_{CO}P_{CO}+K_HP_H^{0.5}+K_{H_2O}\left(P_{H_2O}/P_{H_2}\right)\right)^2} \tag{4.7}$$

Table 4.1 Activation energies, adsorption enthalpies and pre-exponential factors.

E_1 (kJ/mole)	E_2 (kJ/mole)	E_3 (kJ/mole)	$\Delta H_{CO,a}$ (kJ/mole)	$\Delta H_{H,a}$ (kJ/mole)	$\Delta H_{H2O,a}$ (kJ/mole)
209.2	15.4	109.4	−140.0	−93.4	15.9

A_1	A_2	A_3	$A(K_{CO})$	$A(K_H)$	$A(K_{H2O})$
5.922×10^{8}	6.028×10^{-4}	1.093×10^{3}	5.127×10^{-13}	5.68×10^{-10}	9.251

Table 4.2 Equilibrium constants

K_{p1}	$1.198 \times 10^{17} \exp(-26830/T)$
K_{p2}	$1.767 \times 10^{-2} \exp(4400/T)$
K_{p3}	$2.117 \times 10^{15} \exp(-22430/T)$

4.1.3 Catalyst

The catalyst used for methanation is assumed to be a nickel/alumina catalyst as it was used in the study which the kinetic model used for the simulations was adapted from (Hou & Hughes, 2001). In the steam reforming study the catalyst is crushed into particles of with a diameter of around 0.15 mm but in this work the catalyst is assumed to be solid spheres with a diameter of 5 mm. It was assumed to be solid spheres since that is the simplest form to simulate and the diameter was chosen to the outer diameter of a ring-formed methanation catalyst, PK-7R from Haldor Topsøe A/S (Haldor Topsoe A/S). The heat capacity of the catalyst is estimated to be the same as for nickel oxide and was found in the Methanation chapter in the Catalyst Handbook (Pearce, et al., 1989).

Table 4.3 Properties for the catalyst

Length	d_p	0.005 m
Particle density	ρ_p	3200 kg/m^3
Heat capacity	c_p	0.743 kJ/(kg K)
Porosity of the bed	ε_B	0.44

The maximum temperature for the catalyst is 825 ºC (Katalco, 2007).

4.1.4 Model verification

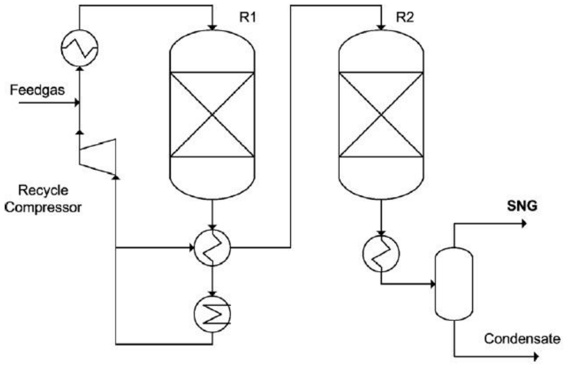


Figure 4.2 Flow scheme for the methanation process in the Lurgi pilot plant. (Kopyscinski, et al., 2010)

To verify the kinetics for the reactor model a simulation of a pilot plant of the Lurgi process was conducted, Figure 4.2. The properties for the inlet stream to the first reactor, R1, were set to match the properties for the pilot plant and the recycle ratio was also the same for both the pilot plant and the simulation. Details assumptions for the pilot plant and the simulation can be found in Table 4.4. For the second reactor was only temperature and water content adjusted to fit the pilot plant.

Table 4.4 Properties for the inlet flow to the first and second reactor in the Lurgi pilot plant (Moeller, et al., 1974).

	R1 in	R2 in
Temperature °C	300	260
Gas flow rate Nm3/h	96	8,2
H2	21,3	7,7
CO	4,3	0,4
CO2	19,3	21,5
CH4	53,3	68,4
N2+C2	1,8	2,05
H2O (vol/vol dry gas)	0,37	0,04

The reactor diameter of the two simulated reactors, given in Table 4.5 has been decided according to section 2.3.1 on reactor dimensions. The length was set to 0.4 m to achieve a temperature profile in the first reactor similar to temperature profiles for the pilot plant.

Table 4.5 Reactor dimensions for the two simulated reactors

R1		R2	
Diameter	Length	Diameter	Length
0.127 m	0.4 m	0.0334 m	0.4 m

From Figure 4.3 it can be seen that the reaction is very fast and occurs in the beginning for the reactor. For a reactor length of 0.4 m the reaction will occur at the first 20 % of the reactor which can be translated into 20 % of the catalyst bed. The temperature axis for the figure from HYSYS starts at the temperature for the first step of the simulation of the reactor. The first temperature is much higher than 300 °C since the reaction is fast.

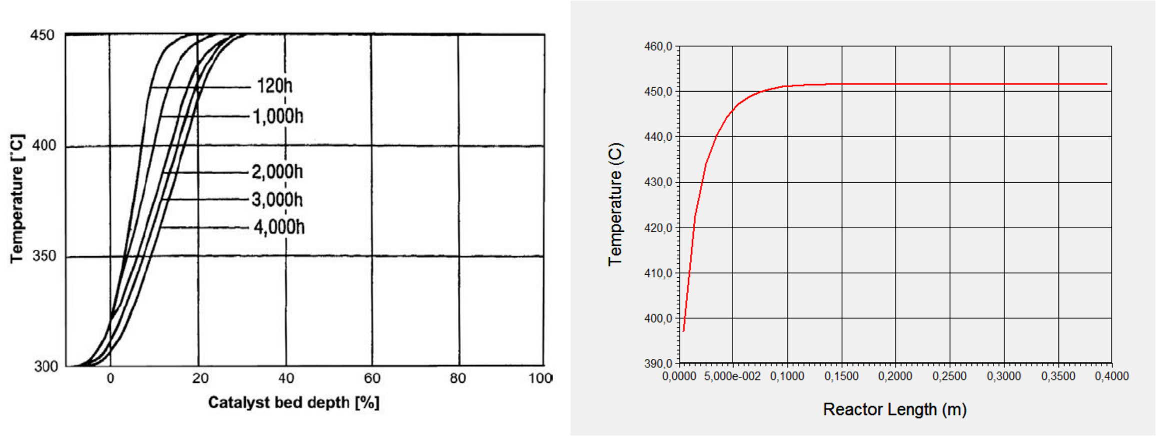


Figure 4.3 Left: Temperature profiles for the first reactor for the Lurgi pilot plant (Kopyscinski, et al., 2010). Right: Temperature profile for the first reactor simulated in HYSYS.

From Table 4.6 it can be seen that the simulation of the first reactor is quite accurate, both in temperature and composition. The second reactor gets on the other hand a noticeably higher temperature for the simulation and the reaction of CO is too low. The percentage difference for literature and the simulation shows that the temperature difference is below 5 % which can be considered good. The difference in composition is below 15 % for the outlet of the first reactor, this is not outstanding but it is regarded adequate. The difference in CO composition for the outlet of the second reactor is not reasonable; the simulation gets over 500 % larger mole fraction of CO. This together with the large difference in hydrogen and water content implies that the model does not work satisfactory for a very low CO content coupled with a high CO_2 content in the feed. The CO_2 content has been kept low to avoid this situation.

Table 4.6 Properties for the different streams for the Lurgi pilot plant (Moeller, et al., 1974) and the simulation in HYSYS.

	From literature				*HYSYS*				*Percentage difference*			
	R1 in	R1 out	R2 in	R2 out	R1 in	R1 out	R2 in	R2 out	R1 in	R1 out	R2 in	R2 out
Temperature °C	300	450	260	315	300	451,7	260	329,4	0,0	0,4	0,0	4,6
Gas flow rate Nm3/h	96	89,6	8,2	7,9	96,04	82,75	7,58	6,98	0,0	-7,6	-7,6	-11,6
H2	21,3	7,7	7,7	0,7	21,3	8,71	8,72	0,46	0,0	13,1	13,2	-34,3
CO	4,3	0,4	0,4	0,05	4,3	0,44	0,44	0,31	0,0	10,0	10,0	520,0
CO2	19,3	21,5	21,5	21,3	19,3	21,8	21,8	21,74	0,0	1,4	1,4	2,1
CH4	53,3	68,4	68,4	75,9	53,3	66,97	66,96	76	0,0	-2,1	-2,1	0,1
N2+C2	1,8	2,05	2,05	2,05	1,8	2,09	2,09	1,49	0,0	2,0	2,0	-27,3
H2O (vol/vol dry gas)	0,37	0,5	0,04	0,08	0,37	0,54	0,04	0,15	0,0	8,0	0,0	87,5

4.1.5 Reactor

The reactions is very exothermic for methanation which means that the temperature in the reactor will rise very fast if it's not controlled by something. The primary method used in this work was temperature control by product recycling. When introducing part of the product to the feed stream of the reactor the concentration of the reactants is decreased which leads to a lower reaction rate.

The properties for the fresh feed were provided from a PhD student at the institution, Maria Arvidsson. The stream has been scrubbed from impurities and carbon dioxide before entering the system in this thesis. The composition of the feed can be seen in Table 4.7 and the temperature was 39.9 °C and the pressure 26.6 bar.

Table 4.7 Fresh feed composition.

Species	Mole fraction
CO	0.218
CO_2	0.001
CH_4	0.124
H_2	0.657

The desired temperature range for the reactors was estimated by constructing an equilibrium curve, Figure 4.4. The curve has been constructed from the equilibrium constant for the methanation of carbon monoxide. The given equilibrium constant in section 4.1.2 was for the reverse process, steam reforming of methane, so first the constant had to be converted. This is done by inverting it:

$$K_{forward} = \frac{1}{K_{reverse}}$$

How to construct the equilibrium curve for this specific reaction can be found in Appendix B.

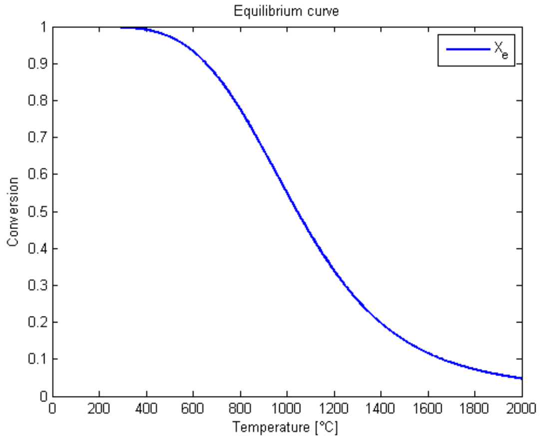


Figure 4.4 Equilibrium curve for methanation of carbon monoxide.

From the equilibrium curve for methanation of carbon dioxide it can be seen that the reaction is favoured at relatively low temperatures. Literature suggests a starting temperature of 300 ºC which corresponds well to the curve (Kopyscinski, et al., 2010). The curve was only used as a guide line since it only represents one of the reactions in the process. Very high temperatures should be avoided both according to the indications from the equilibrium curve and for catalyst limitations.

4.1.6 Cooling utility

If a cooled methanation reactor is used the cooling is done by water evaporation thus producing steam.

HYSYS does not allow modelling cooling by evaporation that is with a medium undergoing a phase change and only convective heating or cooling can be modelled for a plug flow reactor.

Rigorously, the heat transfer between the reactive medium and another heating or cooling medium could be modelled as heat exchanger whereby an enthalpy change can correspond to any kind of change in utility temperature or phase.

In this work it was assumed that the methanation reactors, when cooled, are used to produce steam as commonly done in the technical practice due to high heat transfer capacity of evaporating water and indirect advantages in process control.

For the above reasons, it was necessary to model a latent heat as a particular case of convective heat in which the heat capacity of the utility medium is sufficiently large to limit the its temperature increase to a few degrees, in this thesis less than 1 ºC.

To simulate the utility as boiling water is the heat capacity set to an arbitrary high number of 100 000 kJ/kmoleºC to minimize the rise of the utility temperature. The heat transfer coefficient for the heating medium is set to 16200 kJ/h m^2 C. This value corresponds to 4.5 kW/m^2 K which is a typical value of the heat transfer coefficient used for steam condensation.

The temperature of the cooling water is set to the temperature of the desired quality of the produced steam that is its pressure level. In this work it was assumed low pressure steam at 150 °C, medium pressure steam at 200 °C and high pressure steam at 250 °C (this is not commonly refer as high pressure but corresponds to the highest quality of the steam in this study).

The quality of the steam is a parameter of great interest when looking at process integration aspects as a low pressure generally allows to recover larger quantities of heat but might be used only where heating is required at relatively lower temperatures and vice versa for high pressure steam. In addition, reactor cooling at low temperatures corresponds to larger temperature differences which allow using smaller heat transfer area.

Equation ***(4.8)*** was used to calculate the amount of steam produced by cooling the reactor. Q is the total heat load of the reactor, F is the steam flow and $\Delta\mathrm{H}_{\mathrm{vap}}$ is the enthalpy of vaporization. $\Delta\mathrm{H}_{\mathrm{vap}}$ is calculated from steam tables by extracting the enthalpy for saturated liquid and saturated vapour.

$$\mathrm{Q} = \mathrm{F} * \Delta\mathrm{H}_{\mathrm{vap}} \tag{4.8}$$

Two levels of steam were used in this thesis, low pressure, LP and high pressure, HP. The properties for each level are given in Table 4.8 and were taken from a MatLab program, XSteam created by Magnus Holmgren.

Table 4.8 Properties for the steam used in this study.

	Temperature [°C]	Pressure [bar]	ΔH_{vap} [kJ/kg]
HP	200	39.8	1715
LP	150	4.8	2114

Since the heat transfer properties of the utility steam are excellent compared to the reactive medium, the tube side heat transfer settings do become important. When the utility heat transfer is really high the main resistance for the total heat transfer is on the inside. For a less efficient utility heat transfer the main resistance is on the outside and therefore the inside becomes less important. The standard settings for HYSYS, which calculate the tube side heat transfer coefficient from the Nusselt number, can be used for a low utility side heat transfer coefficient but work unsatisfactory for steam.

The tube side heat transfer coefficient was instead estimated by equation (4.9), (Katan, 1957).

$$h_t = \frac{c_p\mu}{d_t} * 0.813 * exp\left(-6\frac{d_p}{d_t}\right)\left(\frac{d_p}{d_t}\right)^{0.9} Re^{0.9}Pr^{-1} \tag{4.9}$$

With the Prandtl number set to 0.74 (according do (Katan, 1957)), Reynolds number to 1000 and $d_p/d_t = 0.1$ equation (4.9) becomes:

$$h_t = \frac{c_p\mu}{d_t} * 0.0759 * Re^{0.9} \tag{4.10}$$

As mentioned in section 2.3.1 is the Reynolds number set to 1000 to get a suitable flux in the reactor and the scaling factor for the tube diameter from the catalyst particle diameter was set to 10 in section 2.3.1.1. The heat capacity and viscosity is taken from the feed stream.

4.1.6.1 Steam generation

Steam can be generated not only from the reactor but also by cooling the process streams. Pinch analysis was used to determine the heat available for steam generation and then the steam flow could be calculated by equation ***(4.8)***. A more detailed description for each reactor design can be found at their respective sections. Reactor concepts

4.2 Reactor concepts

Four different reactor layouts for methanation were investigated:

1. A single adiabatic reactor.
2. A sequence of two adiabatic reactors with intermediate cooling.
3. A sequence of two adiabatic reactors with intermediate cooling and feed splitting.
4. A single reactor cooled by steam generation.

As a general basic design option in the industrial practise for this type of reactors, all layouts had a product recycle stream to the feed to decrease the reaction rate and temperature. A sensitivity analysis was conducted for each layout to investigate the impact of the following design parameters on reactor volume, possible generation of saturated steam and quality of product:

1. A single adiabatic reactor
    a. Recycling ratio
    b. Water content
2. A sequence of two adiabatic reactors with intermediate cooling
    a. Recycling ratio
    b. Water content
    c. Recycling stream configuration
3. A sequence of two adiabatic reactors with intermediate cooling and feed splitting
    a. Recycling ratio
    b. Feed splitting ratio
4. A single reactor cooled by steam generation
    a. Recycling ratio
    b. Steam pressure level for the reactor cooling

Due to the complex kinetic model for the system the simulation in HYSYS were quite time consuming which led to some limitations in the sensitivity analysis. For this reasons the number of values of the different parameters varies from two to four for different layouts.

The recycling ratio was investigated for all layouts since the recycling stream had a potential to have a big impact on reactor volume. The recycling ratio was set to 50, 70 and 90 % of the product stream for all layouts and for the second and third layout was also a recycling ratio of 80 % investigated.

Water content was briefly investigated for the first and second layout where two settings were used, 30% water in the reactor feed and no added water. Water is a by-product of the reaction which means that the water content will vary depending on recycle rate if no steam is added.

The configuration for the recycle stream was investigated for the second layout, a sequence of two adiabatic reactors with intermediate cooling, by changing the location where the gas is recycled from. The recycling stream was connected either from the first reactor or from the second reactor. The water contents impact was only investigated for the recycling from the first reactor, for the other case the water content was held at 30 % by adjusting the steam injection depending on the portion of recycled water.

The feed splitting ratio was chosen since it affects both the total volume (by reducing the flow to the first reactor) and reaction rate in the second reactor. The feed was split so 60, 70 and 80% of the feed went to the first reactor.

The last layout was cooled by steam generation and therefore was the pressure level for the generated steam set as a design parameter. The pressure level for the generated steam affects the temperature at which the cooling appear and this affects the heat transfer for the reactor and therefore the reaction rate. The two levels for the steam were at 150 °C, LP and 250 °C, HP.

4.2.1 Single adiabatic reactor

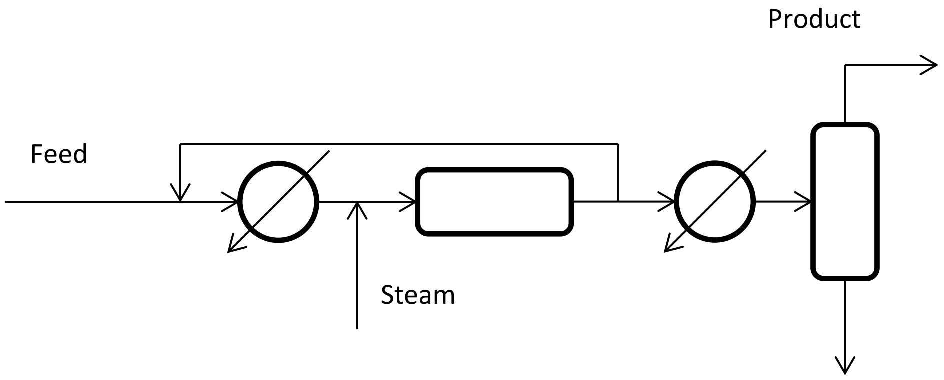


Figure 4.5 Flow scheme for the single adiabatic reactor layout.

The first layout was used as a basic design from which for all the other reactor layouts were derived. It consisted of an adiabatic reactor with recycling and possible steam injection before the reactor, see Figure 4.5. After the fresh feed and recycling stream was mixed the gas is cooled to 300 °C. Steam was injected between the cooler and the reactor for the cases where the water content was set to 30 % of the reactor feed. After the reactor the recycling stream was split of before the rest of the product was cooled to 25 °C. The cooled product stream entered a flash where the majority of the water was separated from the SNG product stream.

Steam was generated from the separated water if steam was injected to the reactor feed. The evaporation and heating of the steam to 300 ºC was also taken into account for the energy analysis when present.

4.2.1.1 Results

The methane mole fraction in the product is affected by the reactor conversion and the methane selectivity. A high methane mole fraction means that there is less by-products and remaining reactants that have to be separated. It is clearly shown in Figure 4.6 that the water content does not significantly affect the methane mole fraction but the recycle ratio is highly important. It is only with the highest recycle ratio that a single adiabatic reactor gives good methane content in the product.

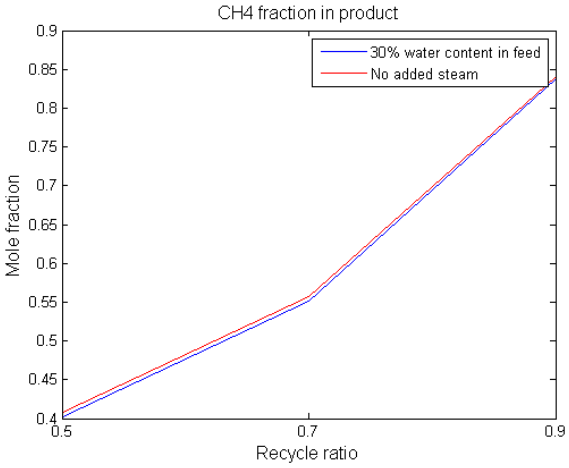


Figure 4.6 The mole fraction dependence on the recycle ratio for the two levels of water content in the feed.

The water content has larger effect on the reactor volume than the product composition as can be seen in Figure 4.7. No addition of steam leads to a smaller volume but this effect decreases with increasing recycle ratio. The reason for that is that the recycling stream contains a fair amount of water which means that a high recycle ratio leads to a smaller steam injection to reach 30 % water content. The reactor volume increases fast with increased recycling.

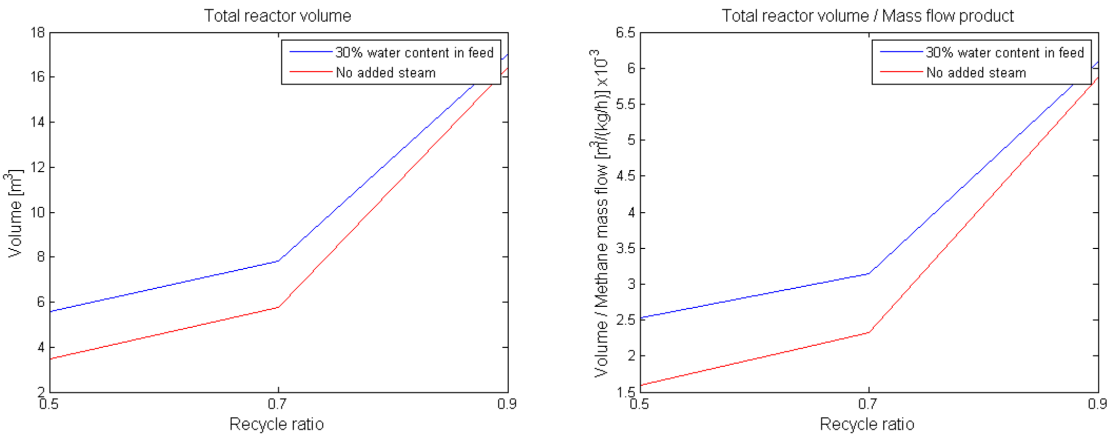


Figure 4.7 The reactor volume dependence on the recycle ratio for the two levels of water content in the feed.

Grand composite curves were constructed for all parameter variations and can be seen in Figure 4.8. The shape of the GCCs changes quite a lot when changing the water content. When keeping the water content at 30 % in the feed, steam has to be added and the generation of that steam imposes a heat demand, the water vaporization appearing as a straight line in the GCCs at roughly 230 °C. It can be seen that the amount of vaporized water decreases with increasing recycle rate and also that the difference between adding water and not diminishes. Another noticeable thing is that the maximum temperature decreases with increased recycling and the total heat load for the system increases.

Steam generation was used to quantify the available heat. To evaluate the possible steam generation the background/foreground curves were constructed where the steam generation is set as the foreground. This was done for both HP steam at 250 °C and LP steam at 150 °C. By fitting the steam curve closely to the background the maximum available heat for each level could be determined; an example for 30 % water content and 70% recycling can be seen in Figure 4.9. The heat load was then converted to mass flow for the steam by the method described in section 4.1.6. The heat loads for different parameters can be found in Table 4.9.

Table 4.9 Heat content in the maximum amount of generated steam for high pressure and low pressure.

	LP [kW]			HP [kW]		
Recycle ratio	50 %	70%	90 %	50 %	70 %	90 %
No added steam	3677	4947	6132	4209	5501	6785
30 % water content	3724	4872	6178	4208	5385	6758

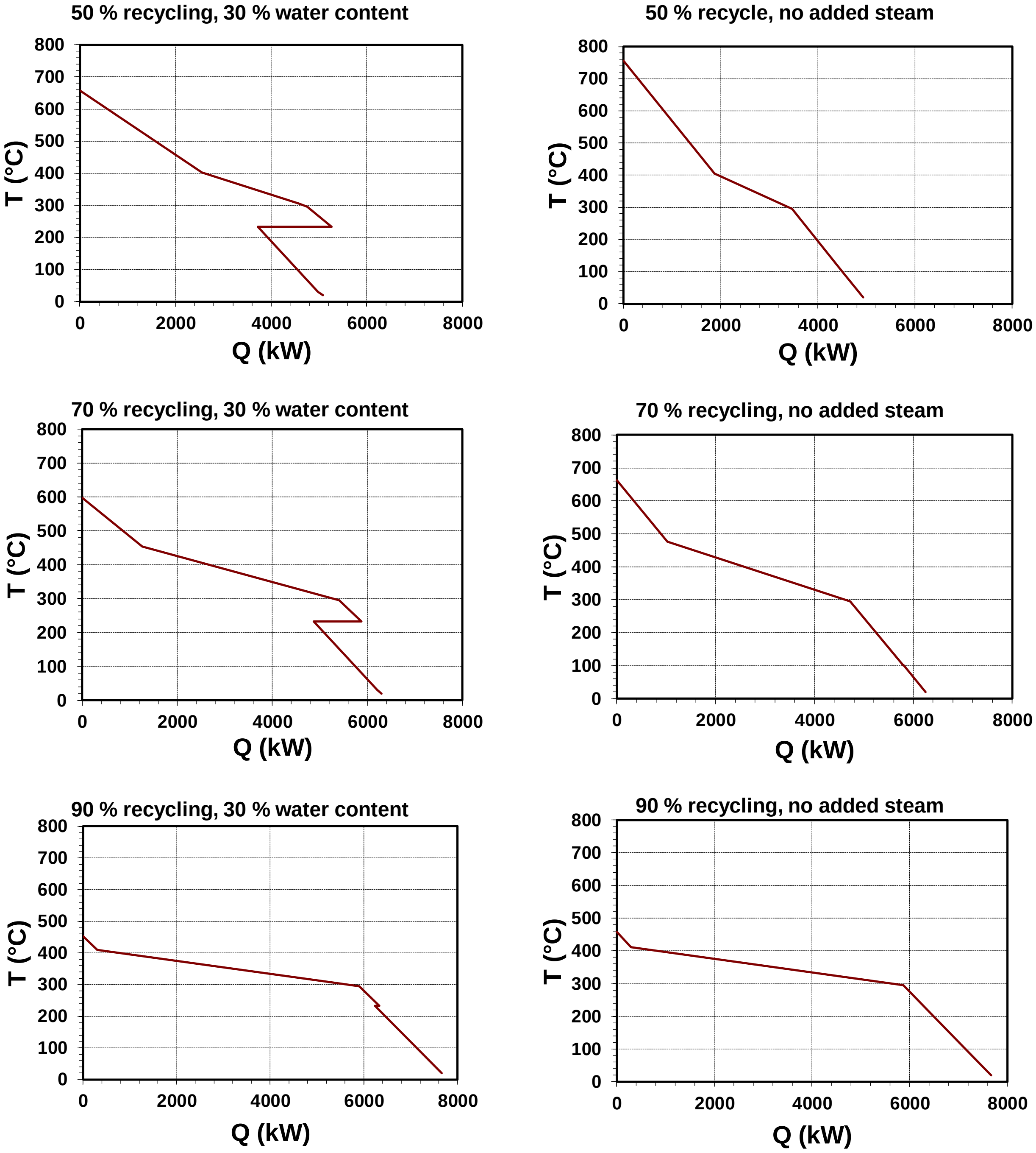


Figure 4.8 *Grand composite curves for the single adiabatic reactor with 30 % water content to the left and no added steam to the right.*

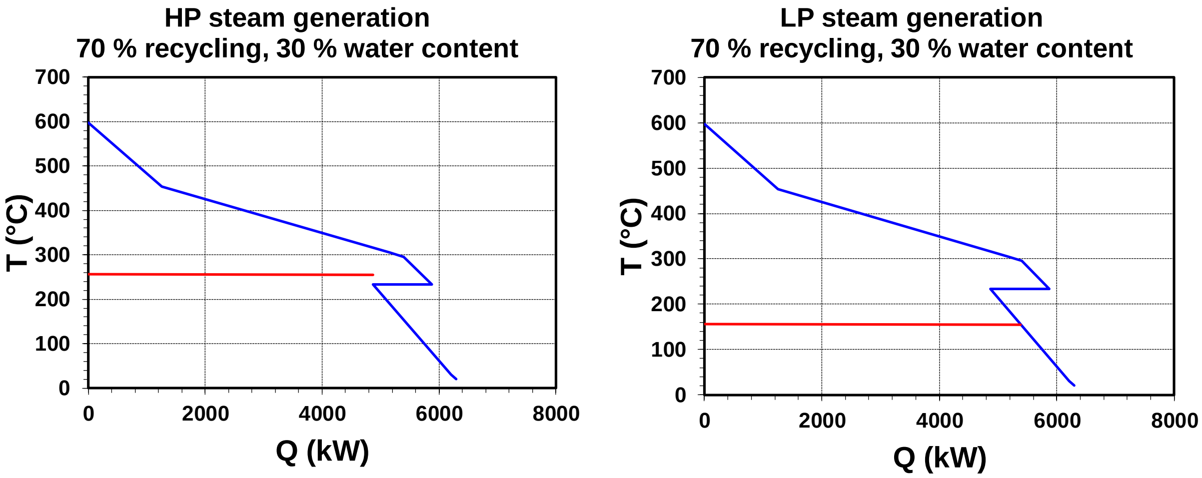


Figure 4.9 Back/foreground curves for the single adiabatic reactor with 30 % water content in the feed and 70 % recycling. The foreground has been fitted to achieve the maximum amount of HP or LP steam.

The possible steam generation is favoured by a high recycling ratio, for both LP and HP steam (see Figure 4.10) as it could be expected from the increasing heat content. The water content is affecting steam generation per unit of produced methane where no added steam gives better results. There is a higher generation of HP steam than LP for all levels of recycling. The reason that the mass flow is higher for HP steam than for LP steam even though the heat content is higher in LP steam is that ΔH_{vap} is smaller for HP steam.

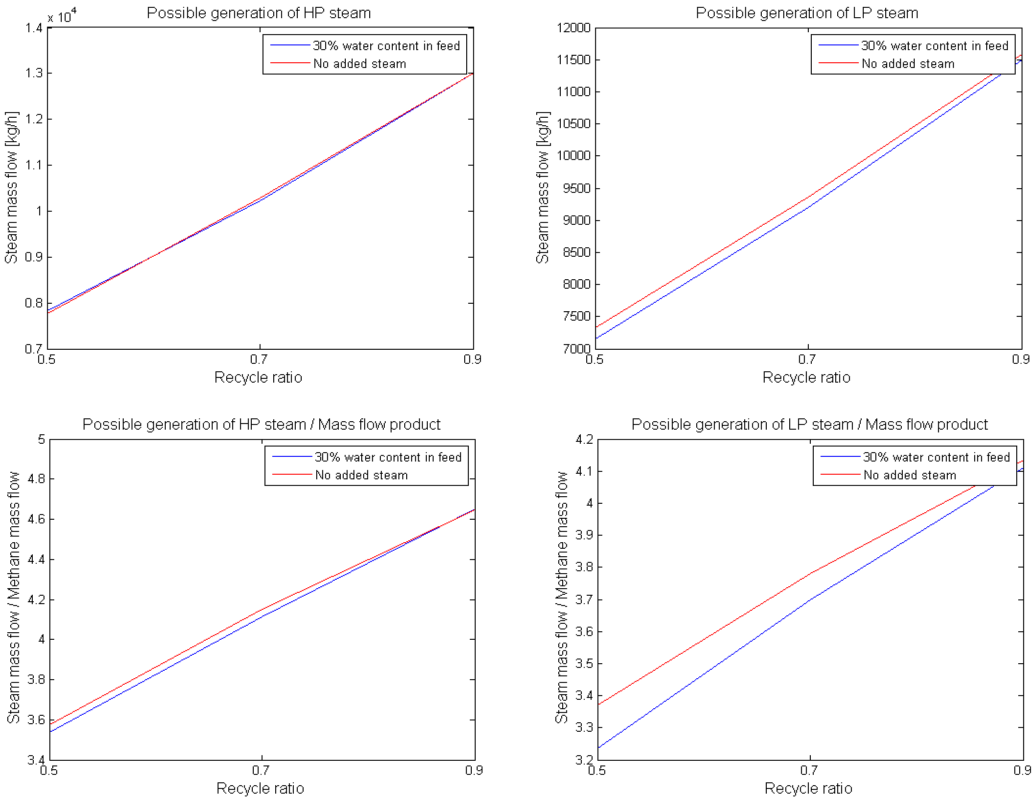


Figure 4.10 *The possible generation of HP steam (left) and LP steam (right) for different recycle ratios with the bottom figure scaled with the methane mass flow in the product.*

4.2.2 Adiabatic reactors with intermediate cooling

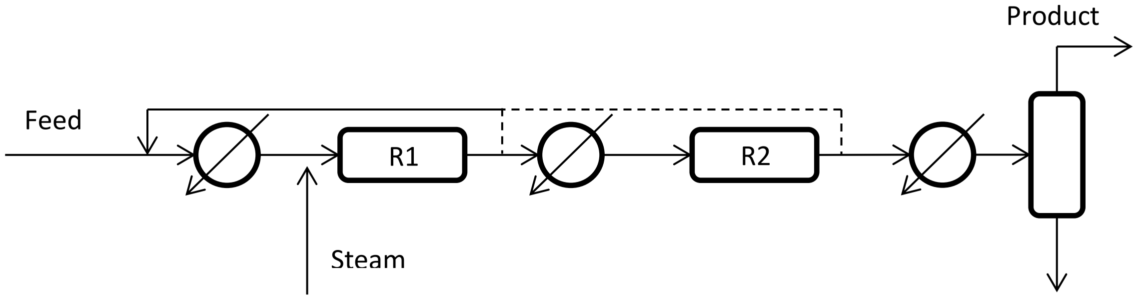


Figure 4.11 *Flow scheme for the two adiabatic reactors with intermediate cooling layout.*

For the layout with adiabatic reactors with intermediate cooling the number of reactor vessels was set to two. Two different configurations for the recycling stream were used, recycling after the first reactor or recycling after the second reactor. Recycling after the first reactor has the advantage of decreasing the size of the second reactor but the product stream from the second reactor has a higher methane content which means that the temperature control should be increased. The inlet temperature for the second reactor was set to 250 °C as found in the literature (Kopyscinski, et al., 2010).

4.2.2.1 Results

The configuration of the recycle stream and water content has been combined to one “concept” parameter to present the parameters effect on the criteria in an effective way. The three cases are:

1. Recycling from the first reactor with 30 % water content
2. Recycling from the first reactor without adding steam
3. Recycling from the second reactor with 30 % water content

The methane content is positively affected by the recycling rate for all three concepts, Figure 4.12, and the three cases appear to perform equally at the highest recycle ratio. At lower recycle ratios the third case is favoured followed by the first indicating that high water content is preferable. This is positive since low water content can yield to carbon formation.

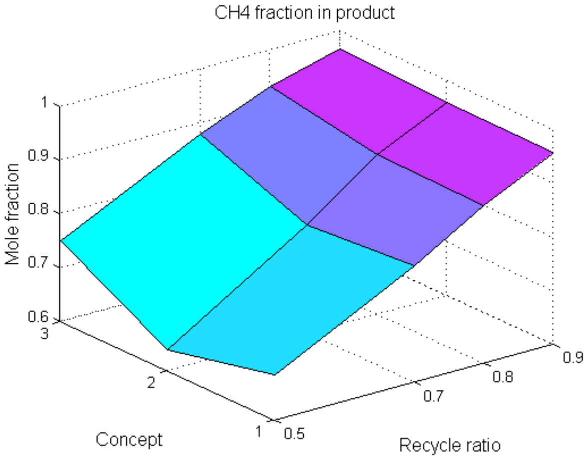


Figure 4.12 The mole fraction dependence on the recycle ratio for each concept.

The total reactor volume is also depending on the recycle ratio and similar conclusions can be drawn when looking at reactor length per unit of methane, Figure 4.13. The first and second cases are both better than the third which is explained by the configuration for the recycling stream. When the recycling stream is connected from the first reactor a much lower volume is needed for the second. The positive effect of lower water content is noticeable but it is small for low recycling rates and insignificant for high recycling rates.

The effect of the recycling ratio is larger for the third case where the highest recycling ratio gives more than three times the volume compared to the lowest recycling ratio.

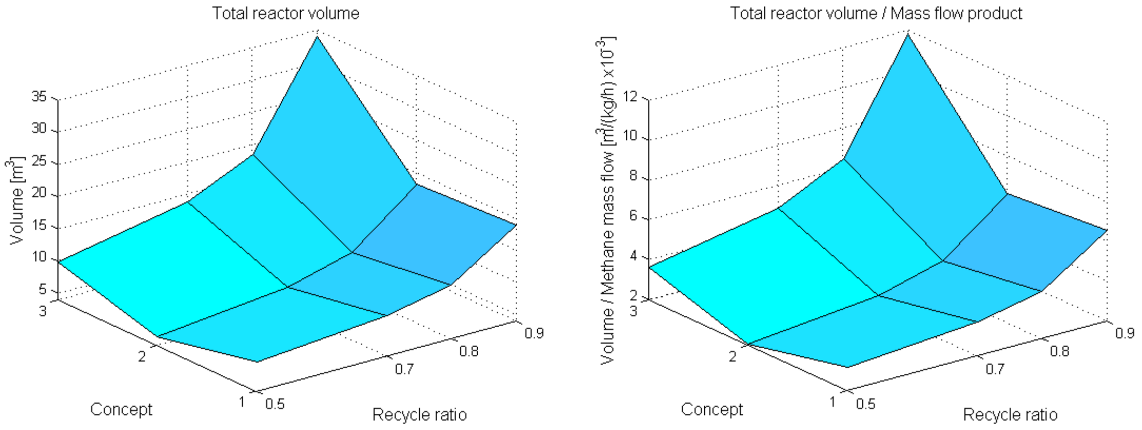


Figure 4.13 The reactor volume dependence on the recycle ratio for the different concepts.

Grand composite curves were constructed for all parameter variations and Figure 4.14 shows these curves for 50, 70 and 90 % recycling ratio and for the three concepts. Concept 1 and 2 behave similarly to a single adiabatic reactor but concept 3 differs for 90 % recycling. It can be seen that there is no added steam for this level of recycling which is due to the high water content in the recycling stream. The recycling stream has also such low temperature that the feed stream has to be heated even after mixing with the recycle stream.

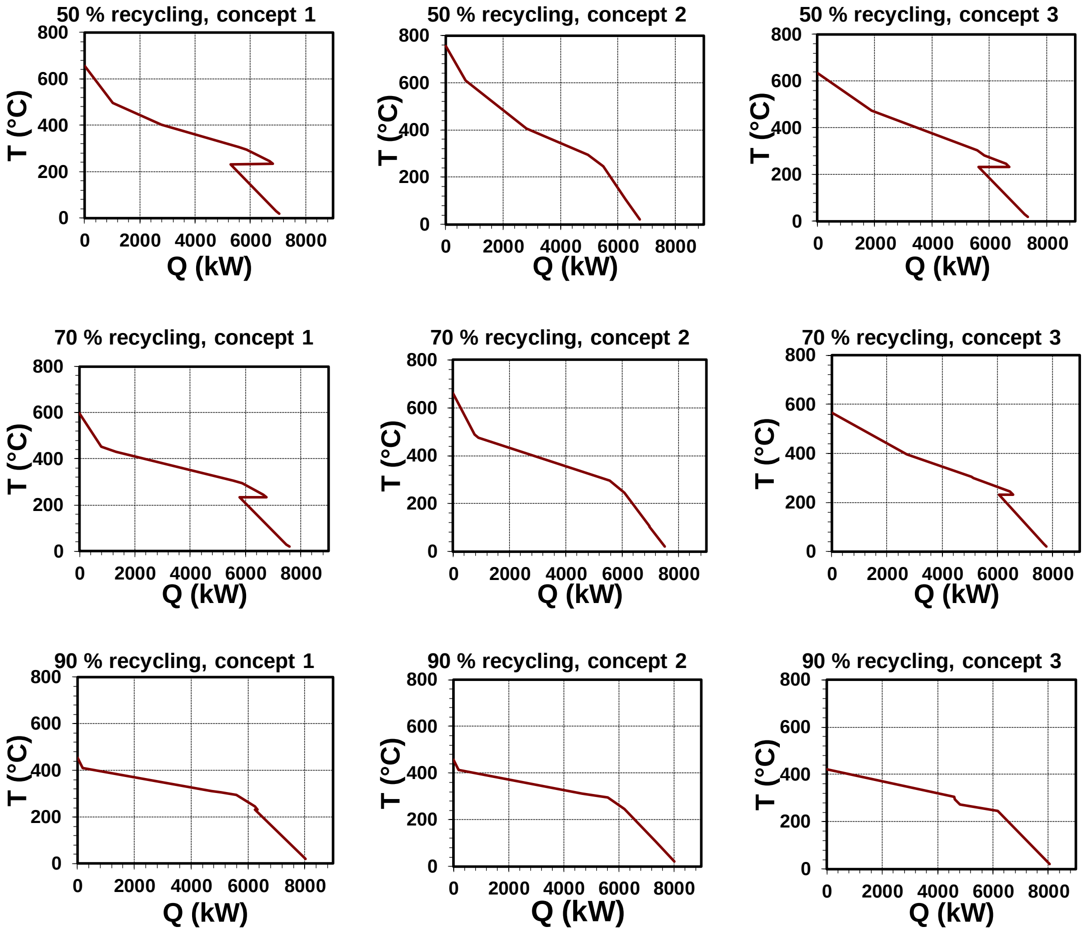


Figure 4.14 Grand composite curves for two adiabatic reactors with intermediate heating where the figures to the left is for concept 1, the middle for concept 2 and to the right concept 3.

The maximum amount of heat for steam generation was found in the same way as for the single adiabatic reactor. The heat loads for the different recycle ratios and concepts can be found in Table 4.10.

Table 4.10 Heat content in the maximum amount of generated steam for high pressure and low pressure.

	LP				HP			
Recycling	50	70	80	90	50	70	80	90
Concept 1	5912	6441	6703	6903	5272	5781	6037	6119
Concept 2	6000	6672	6911	6947	5386	6001	6173	6103
Concept 2	6250	6704	6865	6932	5628	6071	6058	5736

The generation of steam in the three cases changes noticeably and the recycle ratio is also highly important as shown in Figure 4.15. Both HP steam and LP steam generations are favoured in the third case (when recycling from the second reactor).

The HP steam generation is clearly affected by scaling the steam generation to the product flow with the exception for the first case where similar trends for the dependence on the recycle ratio which decreases with increasing level are obtained. In the second case a distinct peak at 70 % recycling is observed and then the HP specific production quickly decreases. In the third case a peak at 80 % recycling is observed, but the difference between 70 % and 80 % is small. The reason for the poor results for the highest recycle ratio for the third case is that the recycle stream temperature is too low to heat the feed stream sufficiently and therefore it must be heated by other means instead of being cooled to 300 °C. The decreasing trend at higher recycle ratios is also explained by that a higher recycle ratio gives a higher methane mole fraction in the product so when the actual generated steam is fairly constant the generated steam per mass flow product decreases.

The trends for the generation of LP steam is somewhat affected by scaling the results with the mass flow of produced methane but generally there is a lower effect of the recycle ratio than for HP steam generation.

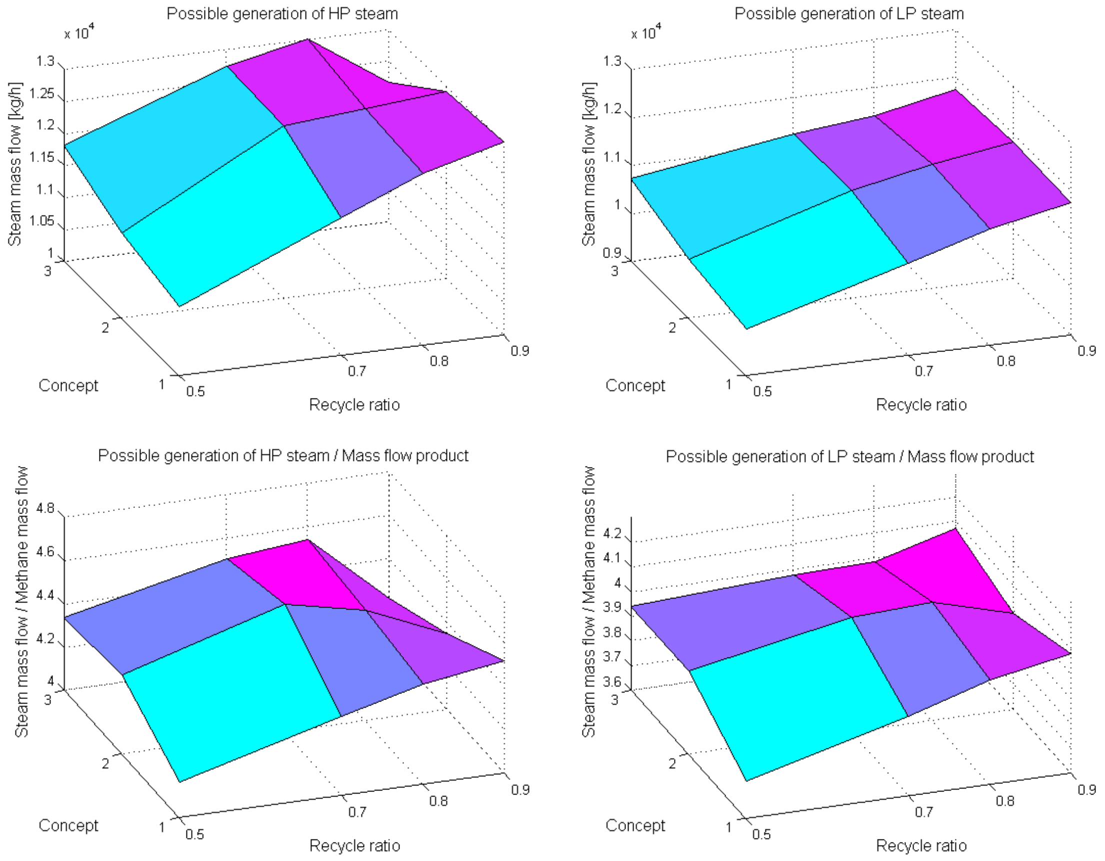


Figure 4.15 The possible fuel generation dependence on the recycle ratio for each concept.

For this layout with two reactors with intermediate cooling it is clear that a very high recycling ratio is not preferable since the volume gets high and the steam production gets either very low or insignificantly higher than for 80 % recycling. If the first and third cases are compared the volume lower is for the first but the steam generation is larger for the third. The second case is actually the best concept regarding the investigated criteria, but may be unsuitable if the water content is too low to avoid undesired reactions.

4.2.3 Adiabatic reactors with intermediate cooling and feed splitting

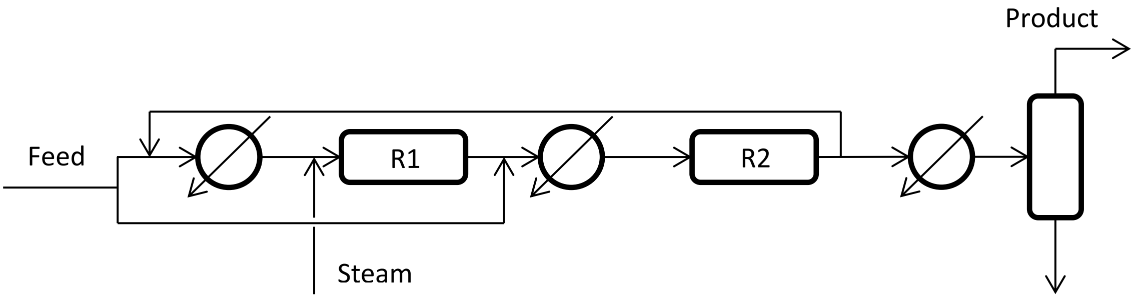


Figure 4.16 Flow scheme for the two adiabatic reactors with intermediate cooling and feed splitting layout.

The third layout was varied from the second layout by splitting the feed and injecting it after the first reactor. The recycling stream was set to be connected from the second reactor. The feed was split at 60, 70 and 80% to investigate the impact on total reactor volume, possible steam generation and product quality. The recycling ratio was varied between 50, 70, 80 and 90 % for the different feed ratios. The reactor stream was cooled to 250 °C before the second reactor but after the feed injection.

4.2.3.1 Results

The methane content is positively affected by the recycling rate for all feed ratios, as it can be seen in Figure 4.17. The feed ratio has no significant effect at high recycle levels, but for low a high feed ratio is favourable.

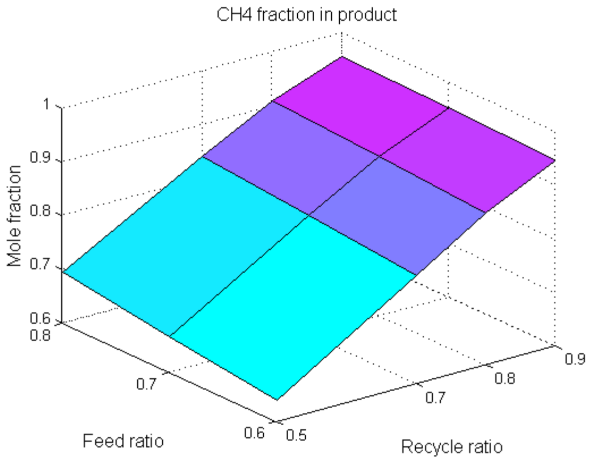


Figure 4.17 The mole fractions dependence on the recycle ratio and the feed ratio.

The total reactor volume follows the same pattern for the recycle ratio as for the two previous reactor layouts, i.e. it increases fast for high recycle ratios as shown in *Figure 4.18*. The Feed ratio does not have any significant effects. The scaled results do not show any major differences from the actual total volume.

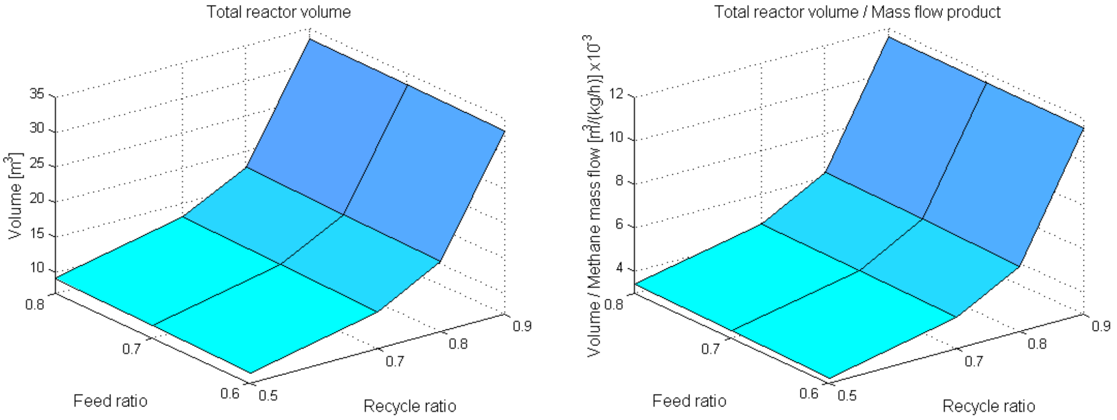


Figure 4.18 The reactor volume dependence on feed ratio and recycle ratio

Grand composite curves were constructed for all parameter variations and are shown for a feed ratio of 70 % into the first reactor in Figure 4.19. The greatest difference between recycle ratios is due to the fact that the added steam diminishes with increased recycling. The GCCs for the two other feed ratios behave in a similar matter and can be seen in Appendix C.

The possible steam generation for two adiabatic reactors with a split feed was calculated in the same way as for a single adiabatic reactor and two adiabatic reactors with intermediate cooling. The value of the heat load for the possible high pressure and low pressure steam can be found for the different cases in Table 4.11.

Table 4.11 Heat content in the maximum amount of generated steam for high pressure and low pressure.

	LP				**HP**			
Recycling	50 %	70 %	80 %	90 %	50 %	70 %	80 %	90 %
Feed ratio								
60 %	6049	6594	6052	6960	5587	6049	6052	5835
70 %	6014	6635	6869	6958	5471	6072	6067	5817
80 %	6105	6667	6874	6952	5539	6084	6074	5794

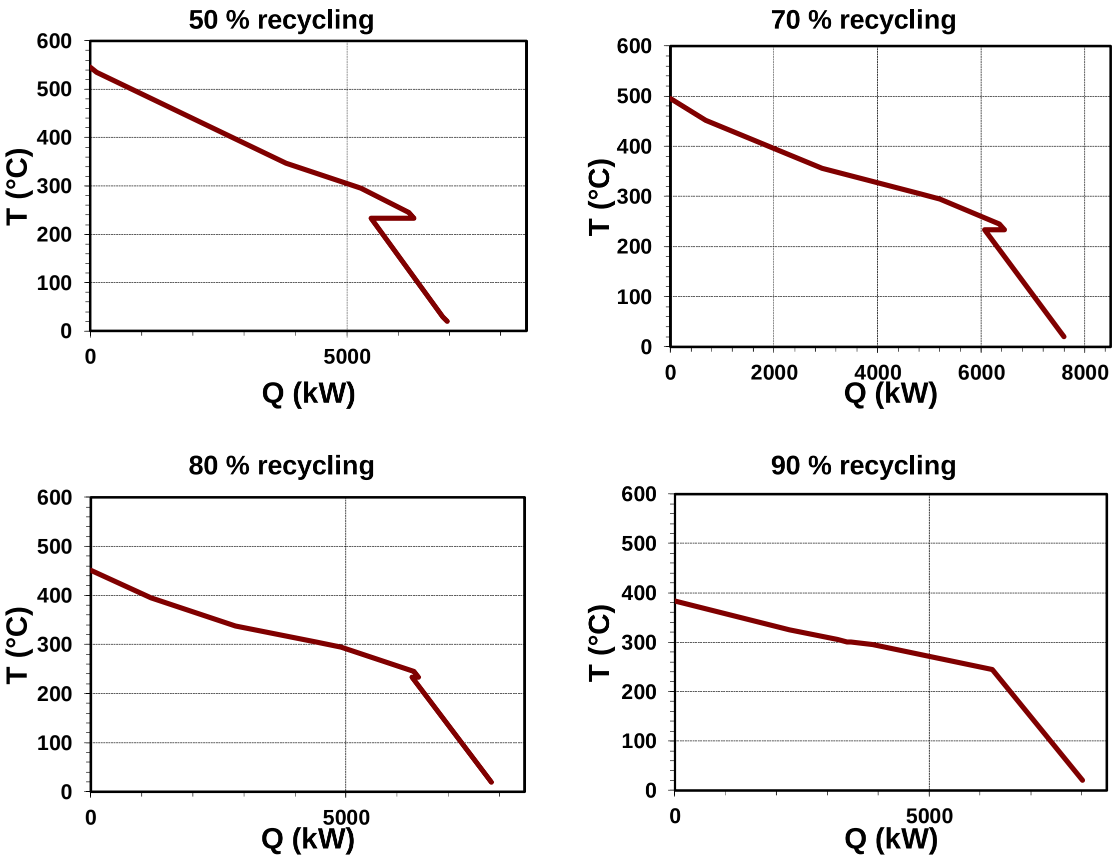


Figure 4.19 Grand composite curves for a feed ratio of 70 % into the first reactor

The feed split ratio and recycle ratio both affect the possible generation of steam, Figure 4.20. The recycle ratio has a larger impact on the steam production than the feed split ratio which becomes significant for low recycle ratios only. There is a distinct peak at 70-80% recycling for the generation of HP steam whereas the LP steam is favoured by a high recycle ratio.

When comparing the normal HP steam production and the HP steam production scaled by the methane product flow the peak for HP steam is shifted from 80 % to 70% recycling. It is also noticeable that the HP steam production is higher for the lowest recycle ratio than for the highest recycle ratio when scaling it to the product flow. This makes a low recycle ratio favourable for this layout since the total volume of the reactor is favoured by a low rate of recycling. The feed ratio does have a small effect at low levels of recycling with a local minimum at 70 % and a low feed ratio is favourable to a high. This indicated that there may be an interest to investigate lower feed split ratios.

The LP steam generation shows the same trends for both the normal steam generation and the methane product scaled steam generation. The effect from the feed ratio is more apparent for the scaled generation but still only significant for low recycle ratios. The LP steam generation is generally lower than the HP steam generation and this makes HP steam generation a better choice for this layout since LP steam generation is favoured by a high recycling rate which gives a large volume.

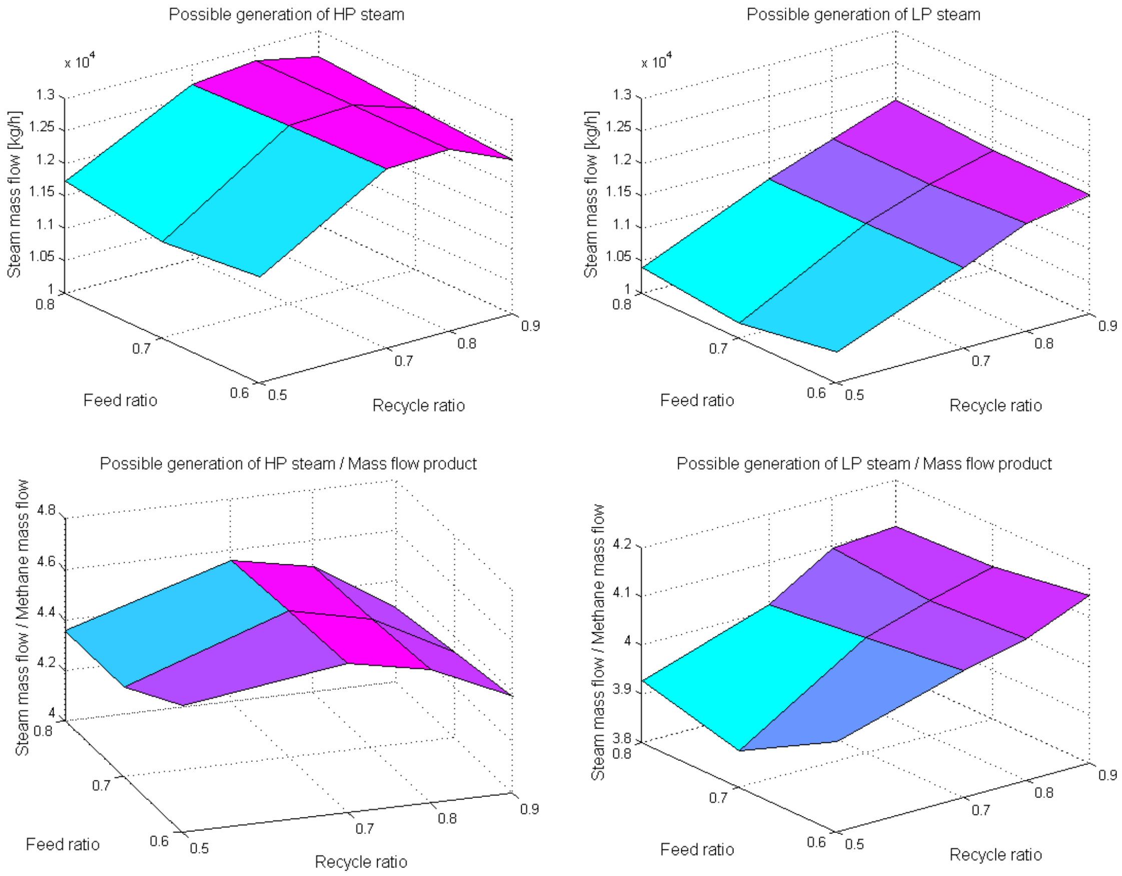


Figure 4.20 The possible fuel generation dependence on the recycle ratio and feed ratio.

4.2.4 Cooled single exothermic vessel reactor

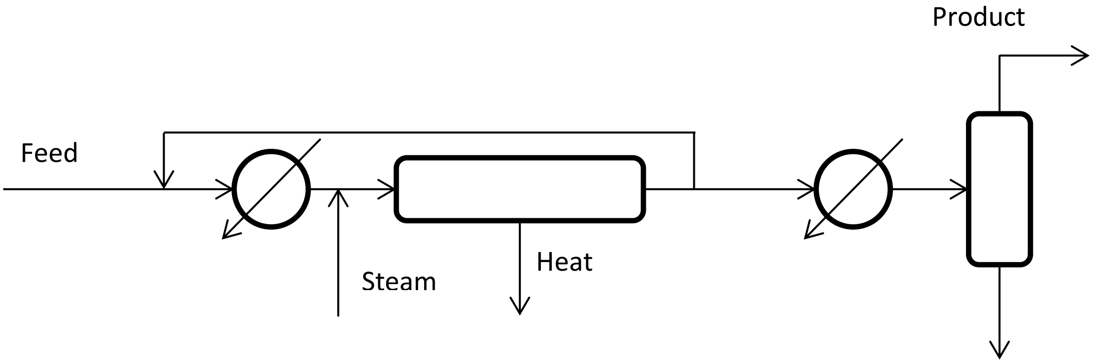


Figure 4.21 Flow scheme for the single cooled reactor layout.

The last layout varied the most from the other three since the reactor is not adiabatic but of a cooled type. The layout is similar to basic layout of the single adiabatic reactor with the difference that heat is taken directly from the reactor by steam generation. Another difference from the three above layouts is the fact that the cooled reactor does not reach equilibrium as quick as for the adiabatic ones and therefore was the reactor length becomes a much more significant parameter to investigate.

The length also affected the temperature of the product and a heat deficit can be observed for too long reactors due to that the temperature for the recycle stream was not sufficient to heat the feed to 300 °C. The reactor length was therefore limited to 1 m since the focus in this case study was limited to the cases when excess heat appears.

4.2.4.1 Results

The methane mole fraction is positively affected by the recycle ratio for both HP and LP steam generation, Figure 4.22. The mole fraction gets higher when the reactor is cooled with LP steam and the difference between HP and LP steam is fairly similar for all levels of recycling.

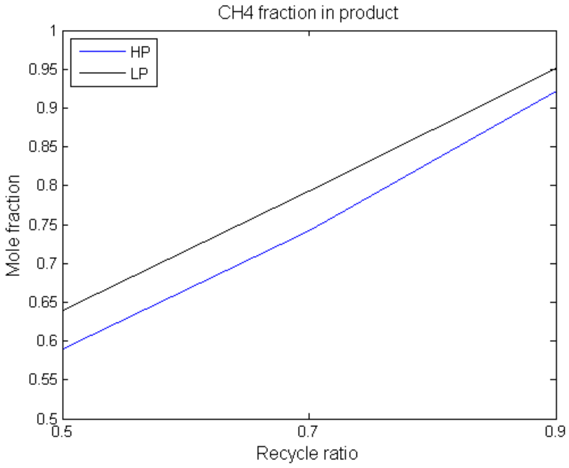


Figure 4.22 The mole fraction dependence on the recycle ratio for the two steam levels.

The reactor volume rises with the recycling rate and the difference between HP and LP steam is minimal, Figure 4.23. There is no change in trends for the recycling ratio dependence when scaling the volume with the methane mass flow in the product, only a small dampening effect on the increase from 70 % to 90 %.

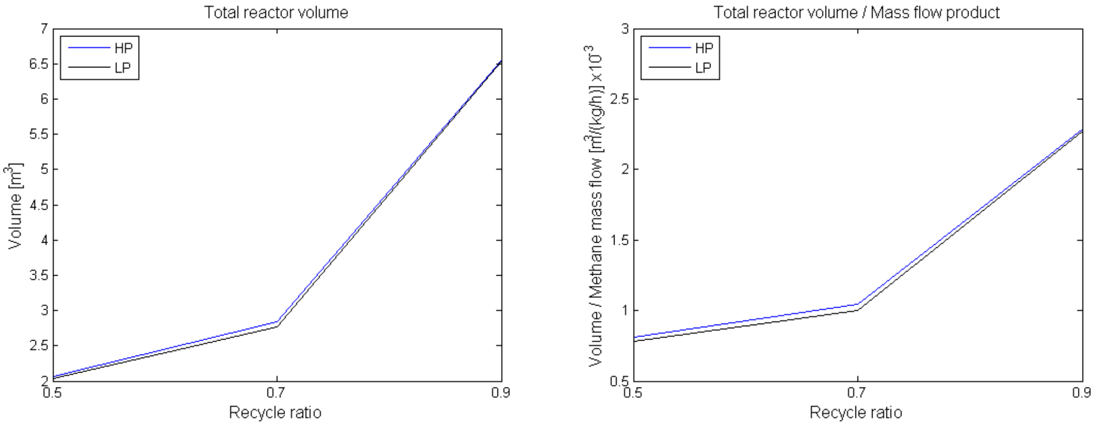


Figure 4.23 The total reactor volume dependence on the recycle ratio for the two steam levels.

The grand composite curves, Figure 4.24 shows similar trends for LP steam generation and HP steam generation for the different levels of recycling. The curves are also similar between LP steam and HP steam for each recycle level.

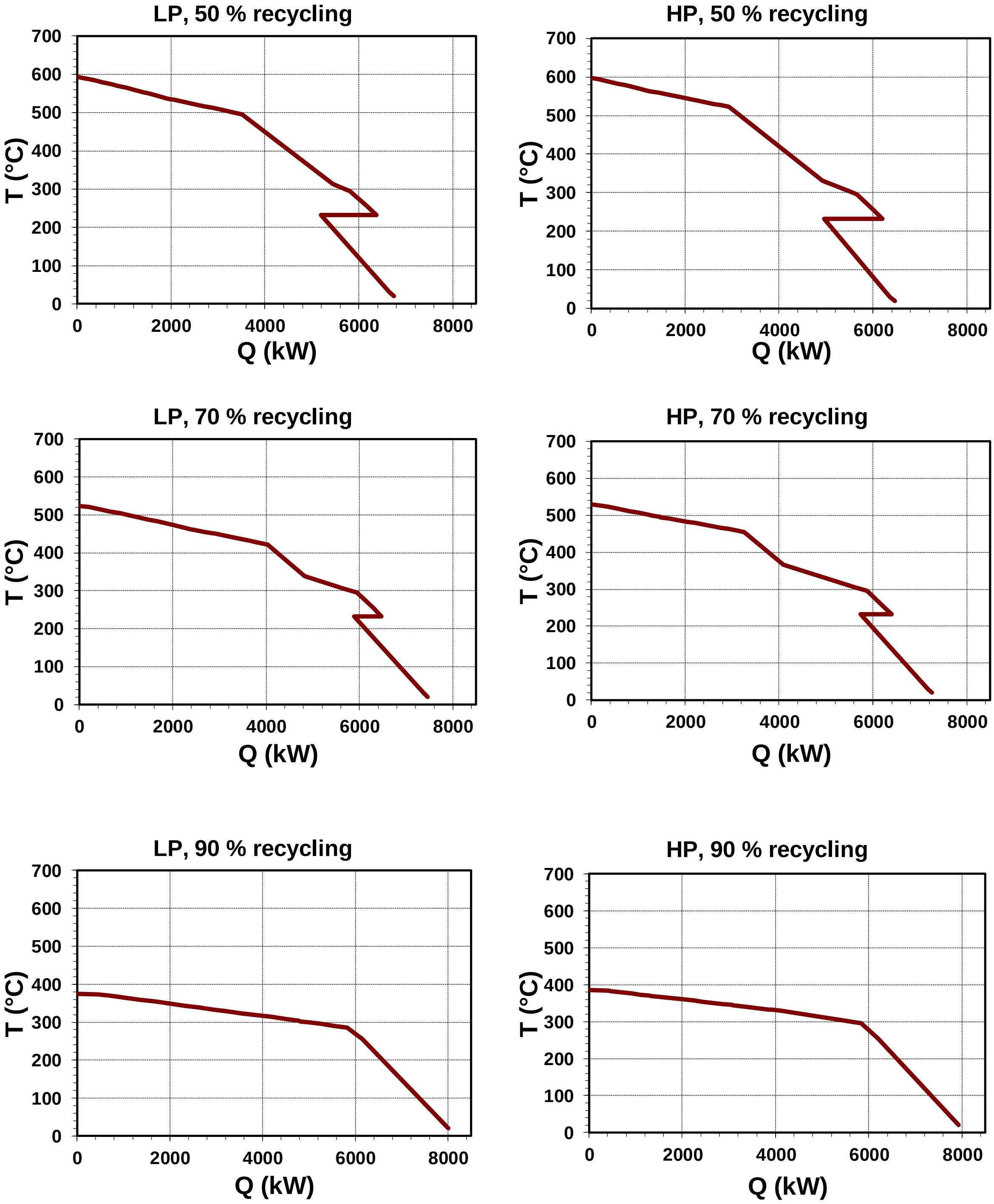


Figure 4.24 Grand composite curves for the reactor cooled by steam generation

Since steam is generated in the reactor and the reactor heat is not used for other type of heating[1], the total steam production was estimated by adding the steam produced by the reactor to that generated with extra available heat from the surrounding streams, this latter quantity being estimated by means of a GCSS that therefore omits the reactor. Similar background/foreground curves used for the analysis of the previous layouts were constructed for each set of parameter values. The steam levels were held at the same level used for the reactor cooling. Back/foreground curves for 70 % recycling for the material streams can be seen in Figure 4.25.

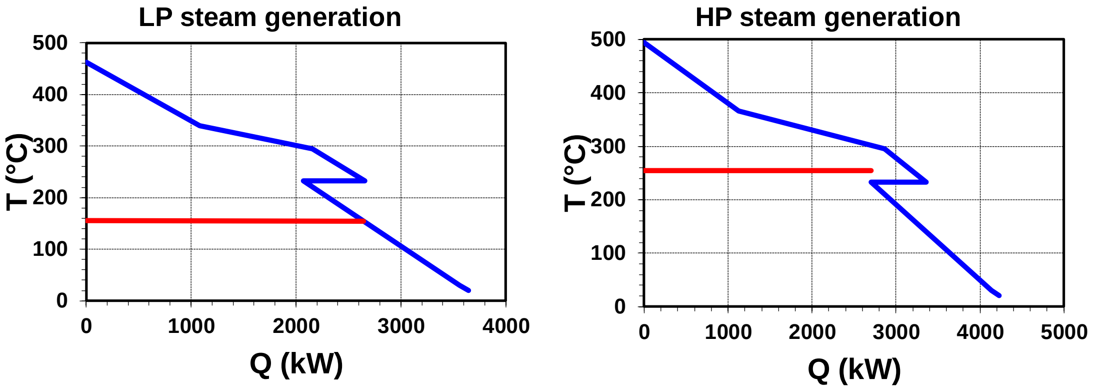


Figure 4.25 Back/foreground curves for LP and HP steam generation for a recycling rate at 70 %.

The total heat load for the generated steam can be found in Table 4.12.

Table 4.12 Heat content in the generated steam for different recycle ratios.

Recycling	50 %	70 %	90 %
LP steam [kW]	5758	6463	6943
HP steam [kW]	4961	5737	6205

Both LP steam generation and HP steam generation has a quite linear increase with increasing recycling ratio, Figure 4.26. The same general trends for the steam production appear when scaling the steam flow with the methane mass flow in the product.

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[1] Note that in principle, reactor heat could be used for heating a different stream than steam, but this would lead to a different type of heat transfer within the reactor and another kinetics would result.

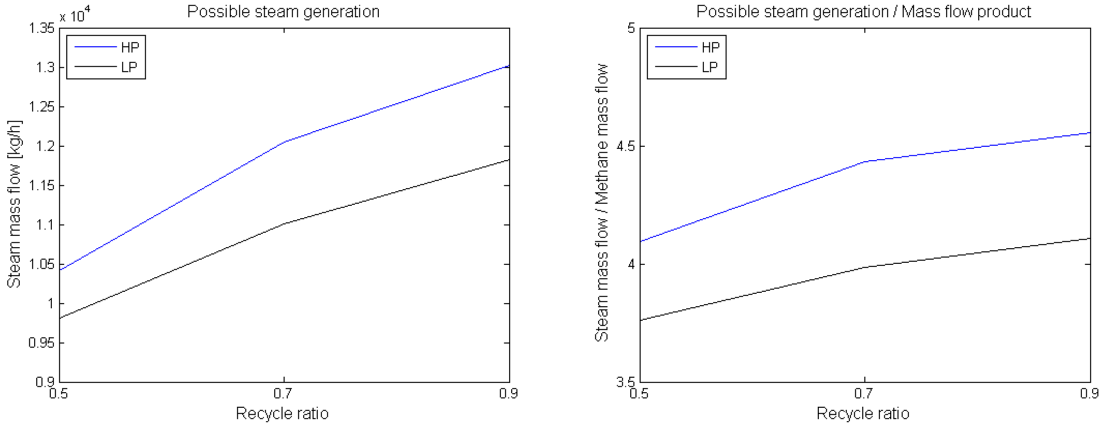

Figure 4.26 The possible steam generation for different recycle ratios for the two steam levels.

4.2.5 Discussing reactor length

The reactor length was quickly decided as an unimportant factor since that methanation in adiabatic reactors reaches equilibrium very quickly. The simulation of the reactors reaches equilibrium in the first few calculation steps and thus emphasises the unimportance of the length because the results was the same regardless of what length was used. Therefore was the length set to be the same for all reactors and the changes in volume would only be dependent on the changes in diameter. The final decision on a length of 2.5 meters for the adiabatic reactors was determined to fit the larges diameters, which were for the highest recycling. The diameters reached over 2 meters for a recycling rate of 90 % and it seemed appropriate to at least have a bit longer reactor than width.

For the cooled reactor this decided length became a problem. Since the cooling was simulated as only steam generation and not steam generation and then super heating was the cooling too efficient to have a long reactor. The cooling simply removed too much heat and left the recycling stream too cold to heat up the feed to the appropriate temperature. A shorter length of 1 m was decided to ensure that the outlet temperature from the reactor was not too low. Unfortunately was this a setback for the volume comparability between all designs.

4.2.6 Comparison between reactor designs

The lengths of the adiabatic reactors need to be adapted to be able to compare their reactor volume with the volumes of the cooled reactors. New simulations were done for a selection of the adiabatic layouts with a reactor length of 1 meter and no significant changes in the results were found.

The specific reactor volume and specific steam flow (per unit of produced methane) of the different layouts are plotted in Figure 4.27 and Figure 4.28. A good design should have a high steam production and a low volume.

These first two plots, show all the investigated cases for the different when considering HP steam generation and LP steam generation respectively. For HP steam generation, Figure 4.27 the majority of the cases is in the desirable corner.

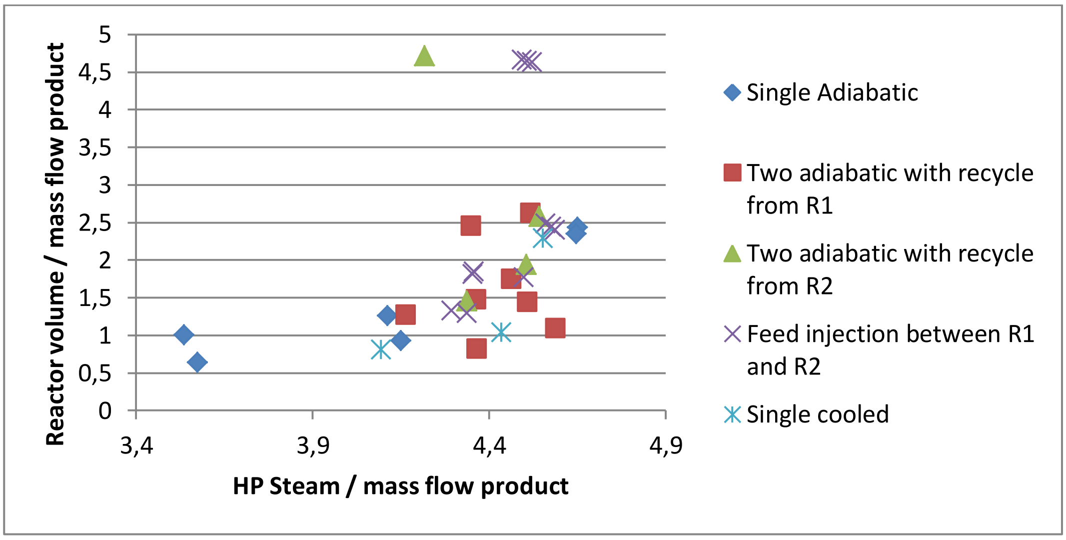

Figure 4.27 *Scaled reactor volume against the scaled HP steam generation for all different designs and parameters.*

LP steam generation, shown in Figure 4.28, follows the same trends as HP steam generation with the majority of the cases closely gathered at the bottom right corner. For both HP and LP steam generation the cooled reactor together with some of the cases for two adiabatic reactors with recycle from the firs reactor does have the lowest volumes together with high steam production.

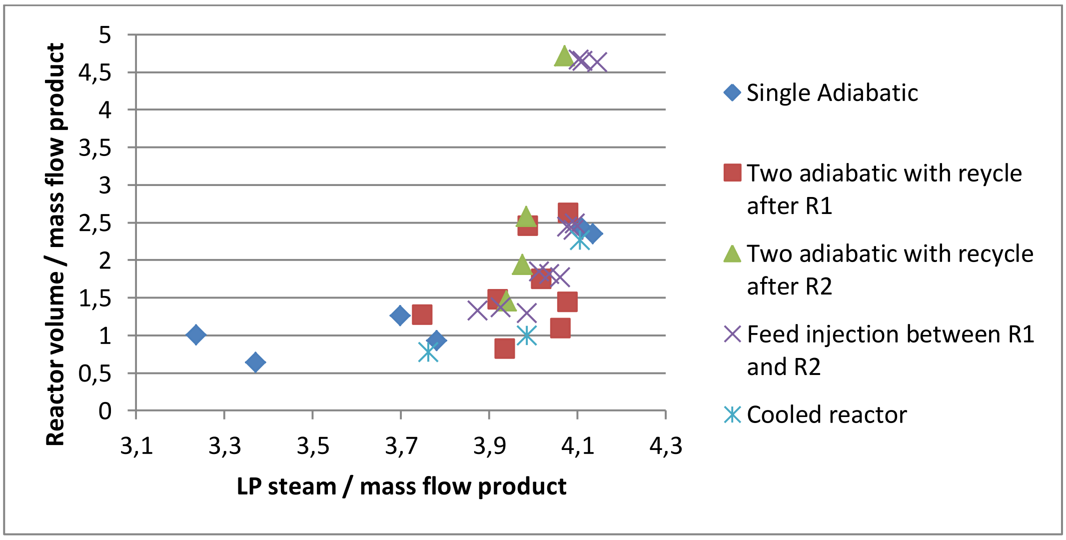

Figure 4.28 *Scaled reactor volume against the scaled LP steam generation for all different designs and parameters.*

For each layout the design parameters were limited to the recycling rate and choosing one level for the other design parameters to make the difference and similarities between the different layouts clearer. For the single adiabatic reactor and two adiabatic reactors with intermediate heating the cases with constant water content at 30 % were chosen. This was the case since a low water content may lead to carbon deposits. The cases with different connections for the recycling stream for the two adiabatic reactors are shown. For the third layout with two adiabatic reactors and a split feed the configurations with feed split ratio of 60 % are shown since they are marginally better than those with feed split ratio at 80 %.

For all designs the scaled volume increases with the recycle ratio.

If comparing the layout with two adiabatic reactors, for both HP and LP steam, Figure 4.29 and Figure 4.30 it can be seen that the layout with the recycle after R2 follows the layout with the earlier recycle but 50 % recycle corresponds to 70 % and so on. The configuration is not appropriate for a recycle of 90 %. The same connections can be made for the layout with a split feed that is injected between two reactors. The single adiabatic reactor is not an option for a recycle of 50 %.

No design stand out as significantly better than any other but the cooled reactor have generally the lowest reactor volume and maintaining a high steam production. The favourable recycling ratio is 70 % for both HP and LP steam generation for the cooled reactor since the steam generation increases quite a lot from 50 % to 70% recycling without increasing the volume so much, but from 70 % to 90 % does the volume increase fast without that much improvement on steam generation. For all layouts is high pressure steam generation favourable since it generates a higher quality of steam at a higher mass flow.

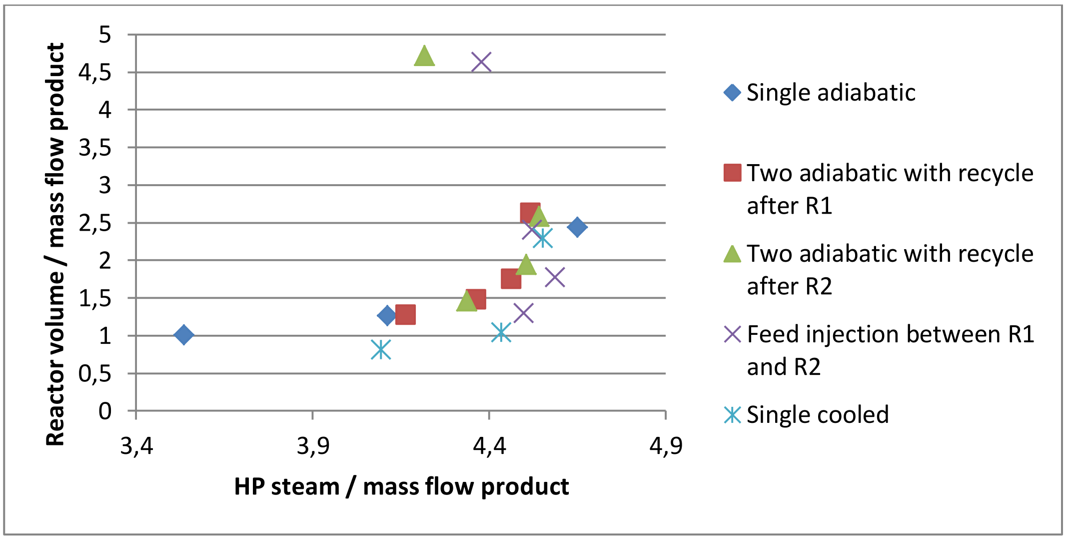

Figure 4.29 Scaled reactor volume against the scaled HP steam generation for a limited number of design parameters. All levels of recycling are present for each layout and the volume increases with increased recycle ratio.

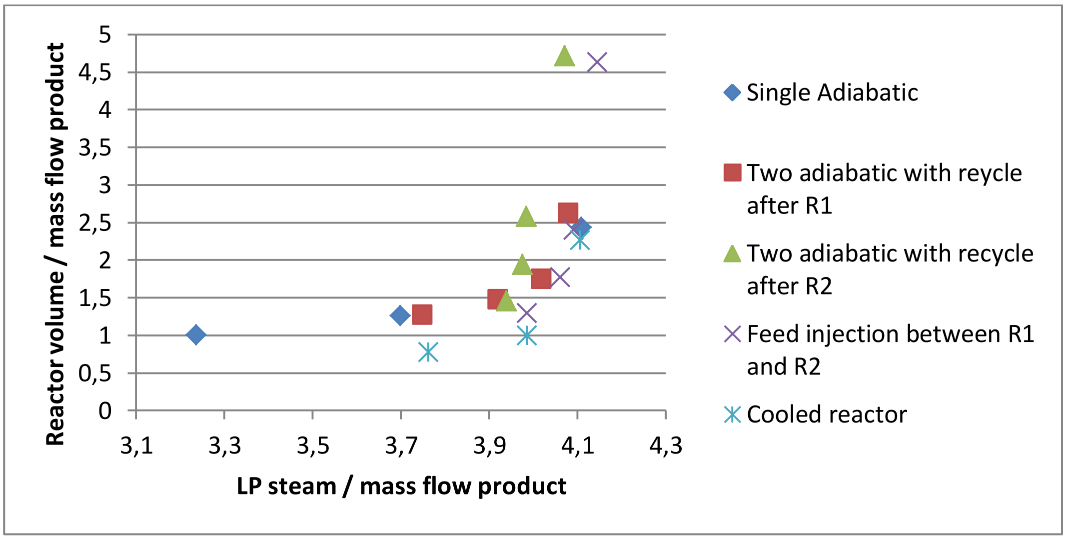

Figure 4.30 *Scaled reactor volume against the scaled LP steam generation for a limited number of design parameters. All levels of recycling are present for each layout and the volume increases with increased recycle ratio.*

5 Discussion

The amount of generated product affected the results surprisingly little; it was only one layout for the MEK case study that scaling with the product changed the dependence on a parameter. The reason for this was that the percentage changes in the amount of generated product for different conversions generally were smaller than the percentage changes on volume or fuel consumption for MEK or steam generation for methanation. Nonetheless could it be interesting to investigate different reactor layouts with a specified mass flow for the product.

One limitation for this master thesis is the focus on the reactor and adjacent streams. This is especially important to consider regarding the MEK case study where the energy requirement of the reactor is met with a furnace. The best design for the conditions of this thesis was a series of adiabatic reactors where the energy requirement could be met without any excess heat. This means that if the rest of the process, like the separation part needs energy more fuel is demanded. The adiabatic reactors are probably still a very good choice since the fuel demand is about half of the fuel demand for the other layouts.

The methanation is one of the final steps for SNG production and the results for the different reactor designs are quite close together. The importance of an optimized reactor layout to produce the largest amount of steam is questionable for the methanation unit since for the whole process of SNG production the cooling of the product gas from the gasification has the most amount of high quality heat. This since the gasifier works at very high temperatures. It is therefore probably more important to focus on the size and complexity of the reactor unit.

One main difference between the endothermic case study and the exothermic case study has been the speed of reaching the equilibrium. For MEK production was the equilibrium not reached and therefore could conversion be used as a design parameter, which was adjusted by changing the length of the reactor. Methanation on the other hand achieved equilibrium almost immediately. This means that the conversion is to be maximized by keeping the temperature low leaving temperature management by means of cooling and product recirculation as the most important design aspects. These differences cannot be made generally for endothermic and exothermic reactions since they depend on the kinetics for each special case.

6 Conclusions

Pinch analysis is not a sufficient tool to evaluate the best choice in utility temperatures for heated or cooled reactors because of the intrinsic relation between heat transfer and kinetics cannot be taken into account rigorously when selecting different type of utility streams. This makes it impossible to define an energy target for the utility consumption of a tubular reactor system independent of the specific design. Nonetheless pinch analysis can be used to evaluate energy consequences of different reactor design thus allowing to identify the most suitable configuration based on the trade-off between investment and energy targets.

In this study the reactor volume was considered as indication of capital investment while operating costs were associated with fuel consumption for the endothermic reactor and to steam generation (revenue) for the exothermic reactor case.

Concerning the specific case studies the results of this master thesis work show that

- For the production of MEK a series of adiabatic reactors with intermediate reheating is the best option
- For the synthesis of methane from syngas a single cooled reactor with steam generation is the best option.

The last result suggest that most probably a fluidized bed reactor could be the best solution for steam generation where a more effective energy transfer than a packed bed can be achieved. However the kinetics in fluidized bed reactors is different and therefore other trade-off between reactor size and steam generation can results.

Future works:

One very interesting aspect for both case studies to investigate is to examine the whole process and see how different reactor layouts affect the total energy requirements.

Future work on the methanation process should:

- Find a better kinetic model for the methanation
- Investigate fluidized bed reactors
- Investigate the steam to carbon ratio effect

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8 Appendix

Appendix A

The construction of the equilibrium curve for the MEK process.

$$\mathrm{r_A} = \frac{\mathrm{k_1 p_A p_K^{-1} - k_2 p_H}}{\mathrm{1 + K_A p_A + K_{AK} p_A p_K^{-1}}} \tag{A 1}$$

$$\mathrm{r_A} = 0 \tag{A 2}$$

$$\mathrm{k_1 p_A p_K^{-1} - k_2 p_H} = 0 \tag{A 3}$$

$$\frac{p_i}{P} = y_i = \frac{F_i}{F_{tot}} \tag{A 4}$$

Dividing ***(A 3)*** with P and using ***(A 4)*** gives:

$$k_1 \frac{F_A}{F_K} - k_2 \frac{F_H}{F_{tot}} P = 0 \tag{A 5}$$

The mass balances are:

$$F_A = F_{A0}\left(1 - X_{eq}\right) \tag{A 6}$$

$$F_K = F_H = F_{A0} X_{eq} \tag{A 7}$$

$$F_{tot} = F_A + F_K + F_H = F_{A0}\left(1 + X_{eq}\right) \tag{A 8}$$

Inserting ***(A 6) (A 7)*** and ***(A 8)*** in ***(A 5)*** gives:

$$k_1 \frac{1 - X_{eq}}{X_{eq}} - k_2 \frac{X_{eq}}{1 - X_{eq}} P = 0 \tag{A 9}$$

$$\left(1 - X_{eq}\right)\left(1 + X_{eq}\right) = \frac{k_2}{k_1} P {X_{eq}}^2 \tag{A 10}$$

$$X_{eq} = \sqrt{\frac{1}{1 + \frac{k_2}{k_1} P}} \tag{A 11}$$

X_{eq} is dependent on temperature from k_1 and k_2.

Temperature-conversion relationship for the energy balance

$$X_{EB} = \frac{\sum \Theta_i\, C_{P,i}(T - T_0)}{-[\Delta H_{Rx}(T_R) + \Delta C_P(T - T_R)]} \qquad \textit{(A 12)}$$

where $\Theta_i = C_{i0}/C_{A0}$ if A is set as the main reactant. In this case $\Delta C_P(T - T_R)$ can be seen as negligible with respect to $\Delta H_{Rx}(T_R)$ and the feed consist of only the reactant 2-butanol which means that equation ***(A 12)*** can be simplified to:

$$X_{EB} = \frac{C_{P,A}(T - T_0)}{-\Delta H_{Rx}(T_R)} \qquad \textit{(A 13)}$$

By plotting X_{EB} and $X_{eq}$the maximum possible conversion can be found for a specified feed temperature. If $C_{P,A}$ is set as a constant X_{EB} will be a linear function. To make the prediction of at which temperature a specific conversion will be obtained to correspond better with results from HYSYS $C_{P,A}$ was set to be temperature dependent. The temperature dependence was found by fitting a polynomial function to a series of values for $C_{P,A}$ at different temperatures. The equation ***(A 14)*** is valid for temperatures between 200°C and 500°C.

$$C_{P,A} = z_1T^3 + z_2T^2 + z_3T^1 + z_4 \qquad \textit{(A 14)}$$

z_1	z_2	z_3	z_4
$4.776 * 10^{-8}$	$-2.329 * 10^{-4}$	0.4248	5.757

T is given in K.

Appendix B

The construction of the equilibrium curve for CO methanation. The used method is described in more detail in Elements of Chemical Reaction Engineering by Fogler (Fogler, 2006, pp. 1021-1026)

$$3\mathrm{H_2} + \mathrm{CO} \leftrightarrow \mathrm{CH_4} + \mathrm{H_2O} \quad \Delta \mathrm{H_R^0} = -206\ \mathrm{kJ/mol} \tag{B 1}$$

The pressure equilibrium constant for CO methanation is:

$$K_p = \frac{p_{CH_4} p_{H_2O}}{p_{CO} p_{H_2}^3} \tag{B 2}$$

And the concentration equilibrium constant is:

$$K_c = \frac{C_{CH_4} C_{H_2O}}{C_{CO} C_{H_2}^3} \tag{B 3}$$

K_c and K_p are related by:

$$K_p = K_c (RT)^{\delta} \tag{B 4}$$

$$\delta = -2 \tag{B 5}$$

This lead to:

$$K_p = \frac{C_{CH_4} C_{H_2O}}{C_{CO} C_{H_2}^3 (RT)^2} \tag{B 6}$$

The mass balances if it $C_{H_2,o} = 3C_{CO,0}$:

$$C_{CH_4} = C_{CO,0} X_e \tag{B 7}$$

$$C_{H_2O} = C_{CO,0} X_e \tag{B 8}$$

$$C_{CO} = C_{CO,0}(1 - X_e) \tag{B 9}$$

$$C_{H_2} = 3C_{CO,0}(1 - X_e) \tag{B 10}$$

Inserted in ***(B 6)*** gives:

$$K_p = \frac{C_{CO,0} X_e C_{CO,0} X_e}{C_{CO,0}(1 - X_e)\big(3C_{CO,0}(1 - X_e)\big)^3 (RT)^2} \tag{B 11}$$

→
$$K_p(RT)^2 = \frac{{X_e}^2}{9(1-X_e)^4} \quad \textit{(B 12)}$$

Define:

$$A = 3\sqrt{K_p}(RT) \quad \textit{(B 13)}$$

Which gives after some rearranging ***(B 12)*** to be:

$$\mathrm{A} = \frac{X_e}{(1-X_e)^2} \quad \textit{(B 14)}$$

→
$$A(1-X_e)^2 = X_e \quad \textit{(B 15)}$$

→
$$A\left(1-2X_e+{X_e}^2\right) = X_e \quad \textit{(B 16)}$$

→
$${X_e}^2 - \left(2+\frac{1}{A}\right)X_e + 1 = 0 \quad \textit{(B 17)}$$

Set $B = 2 + \frac{1}{A}$ which gives:

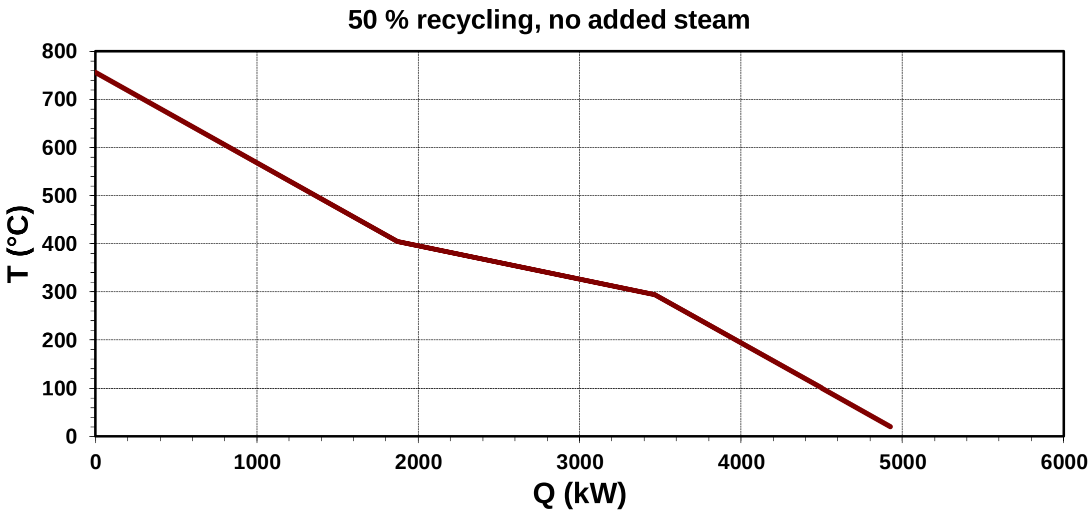
$$X_e = \frac{B}{2} \pm \sqrt{\left(\frac{B}{2}\right)^2 - 1} \quad \textit{(B 18)}$$

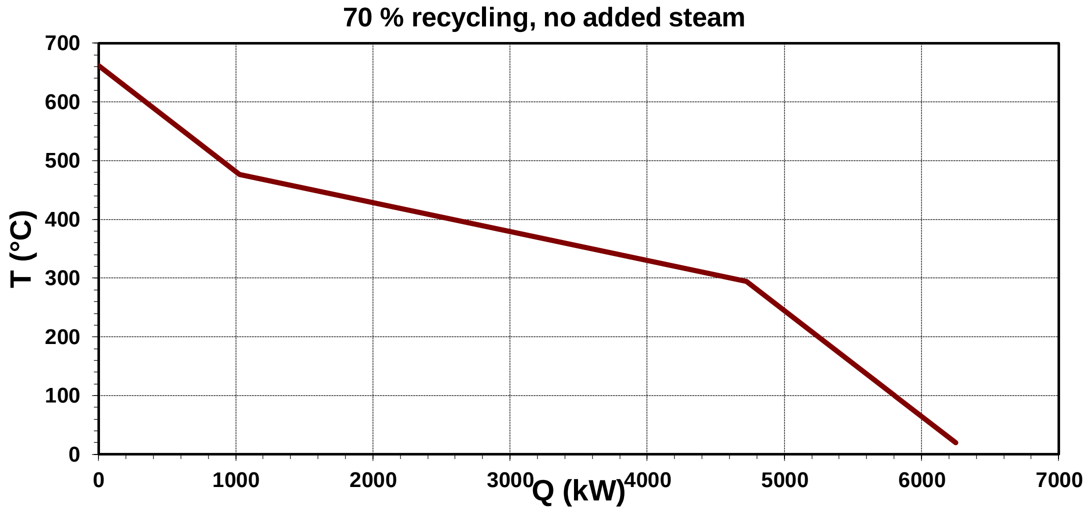
This is used in MatLab to calculate X_e for different temperatures for K_p given for CO methanation.

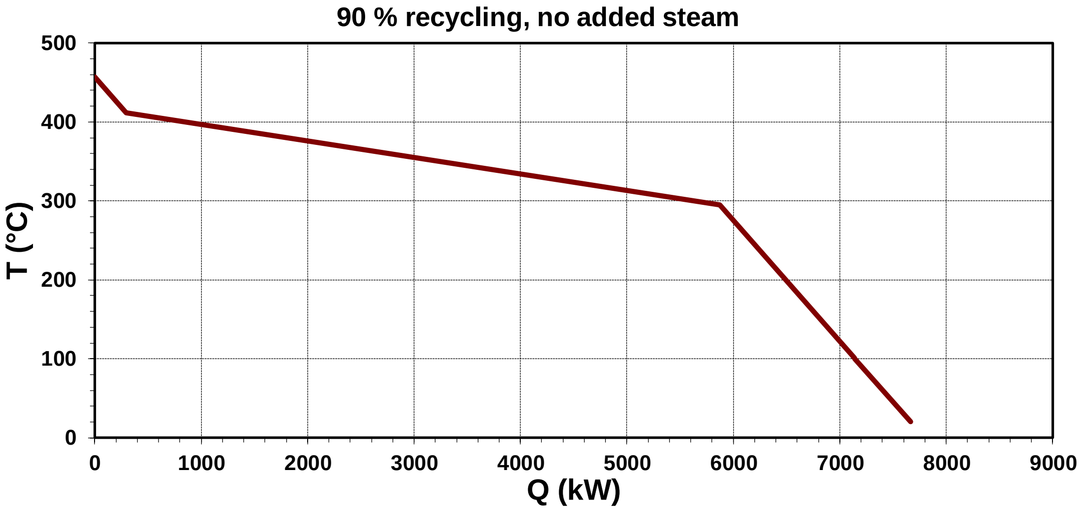
Appendix C

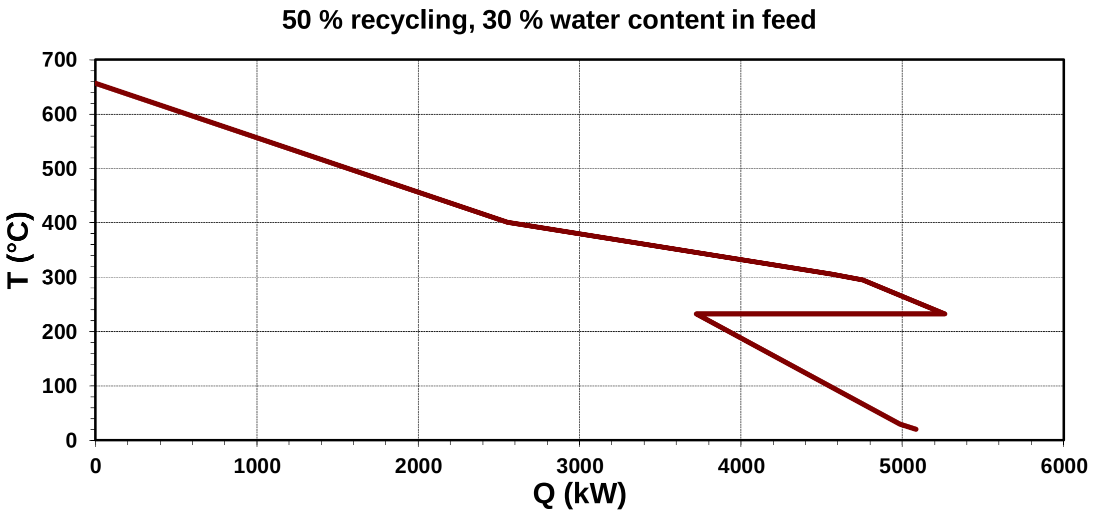
All grand composite curves for the methanation case study.

Single adiabatic reactor

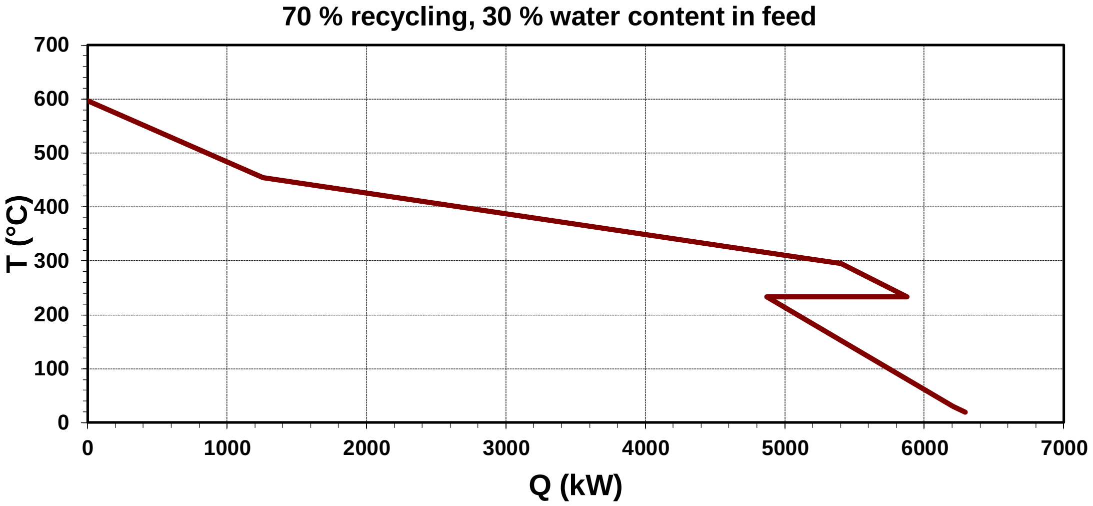




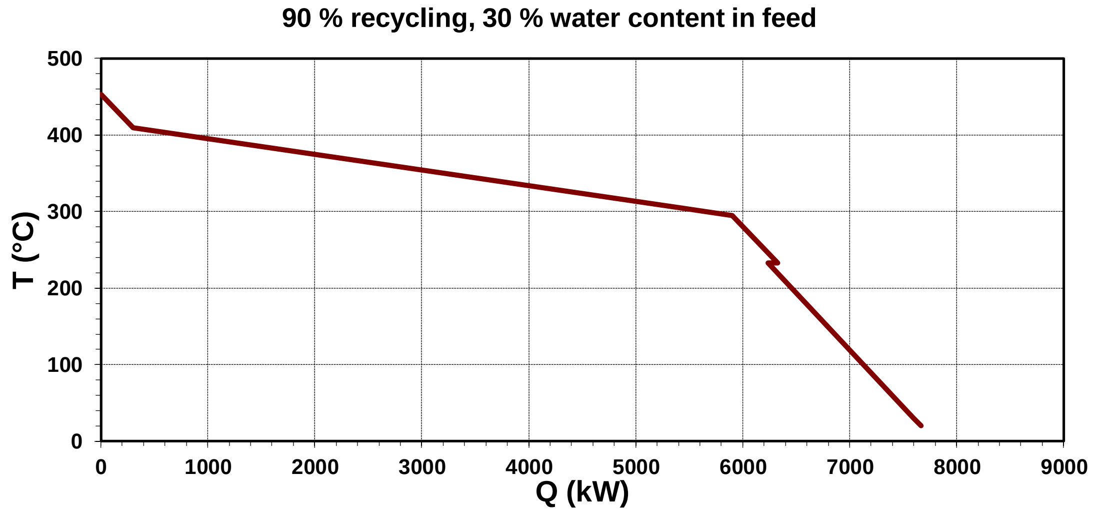




50 % recycling, 30 % water content in feed



70 % recycling, 30 % water content in feed

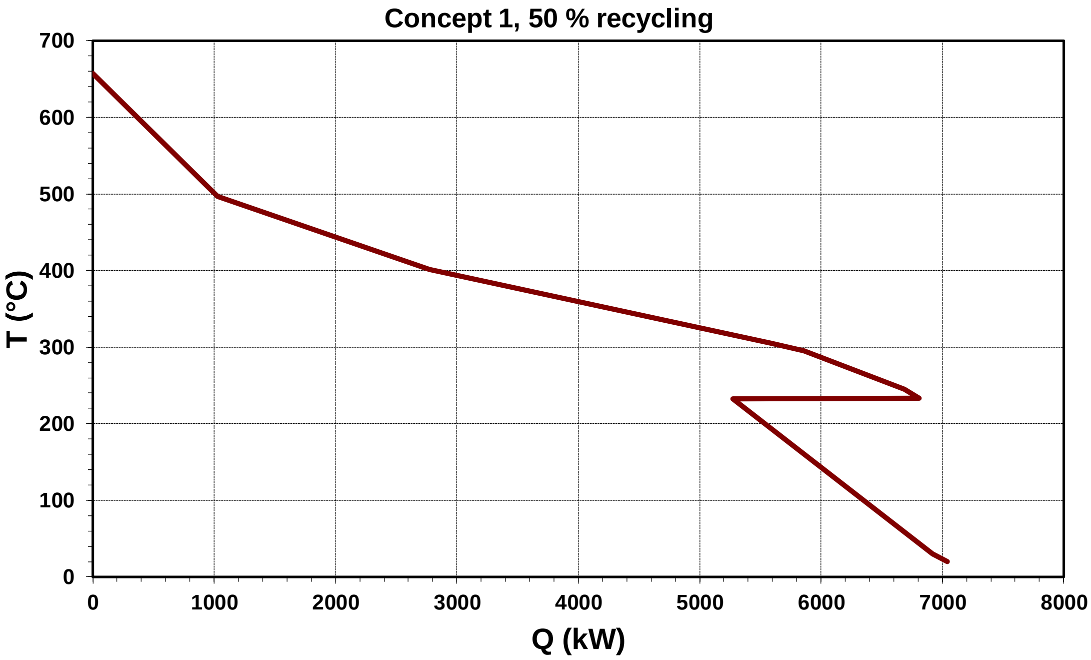


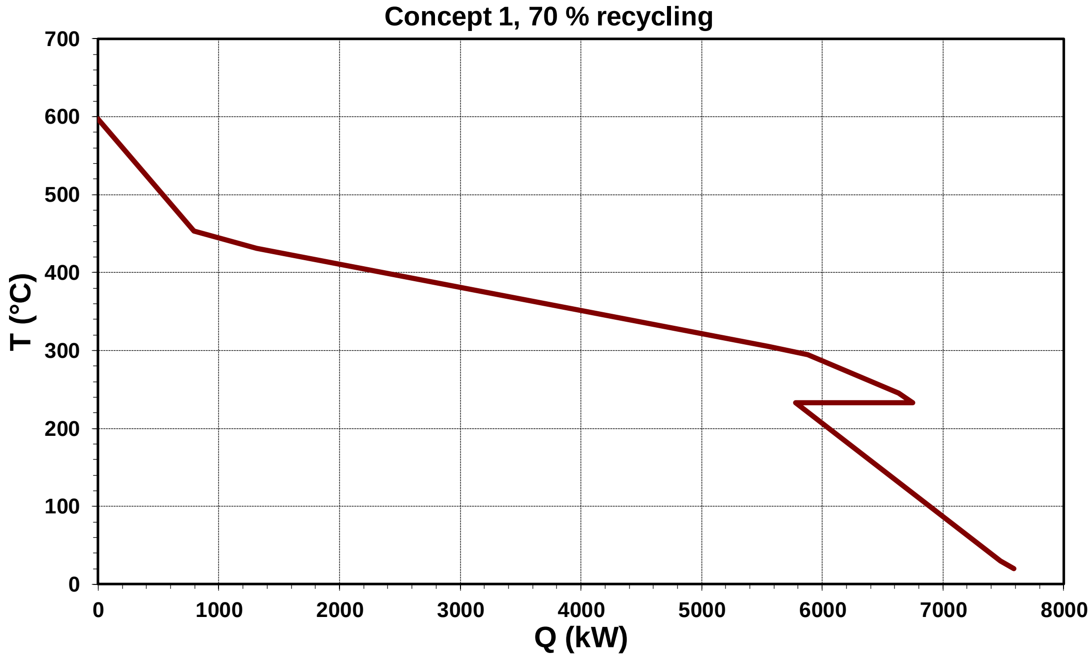
90 % recycling, 30 % water content in feed

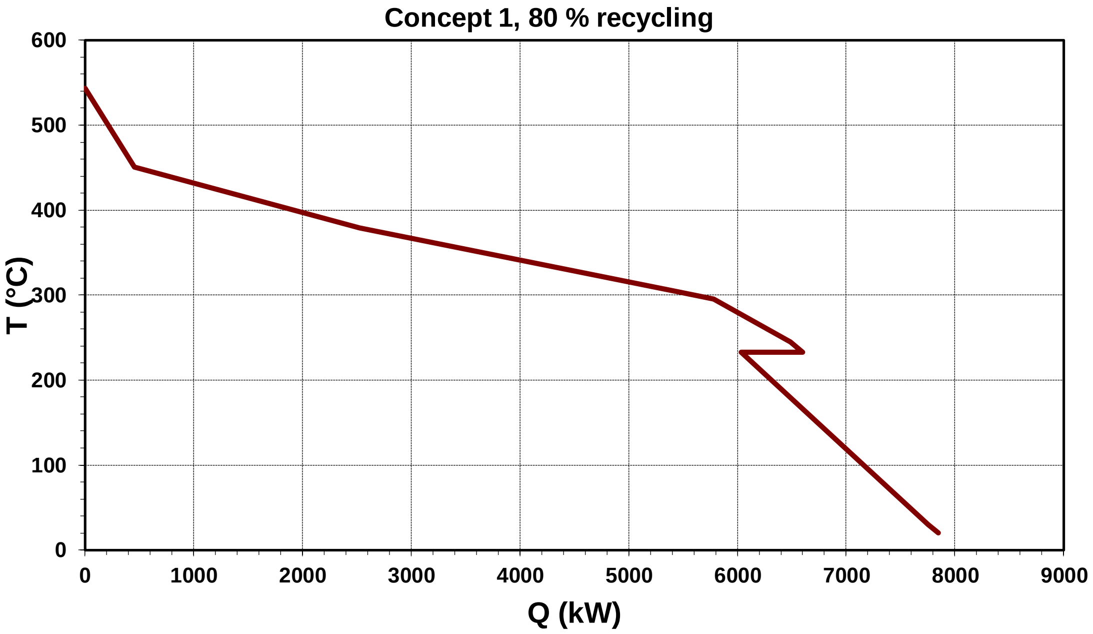
Adiabatic reactors with intermediate cooling

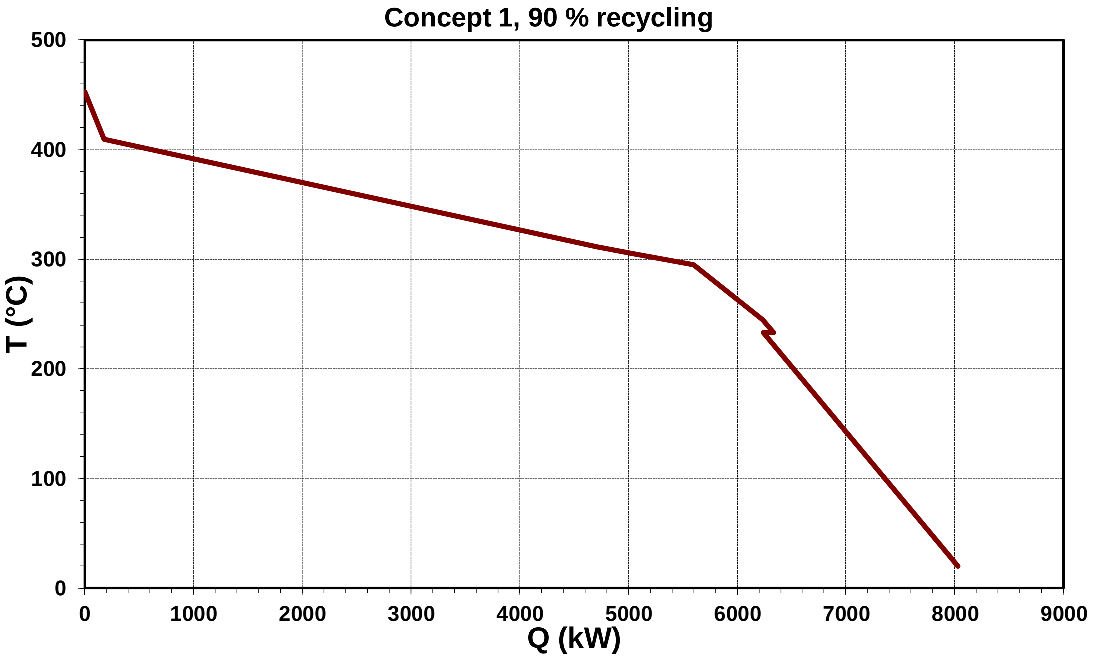
The three concepts:

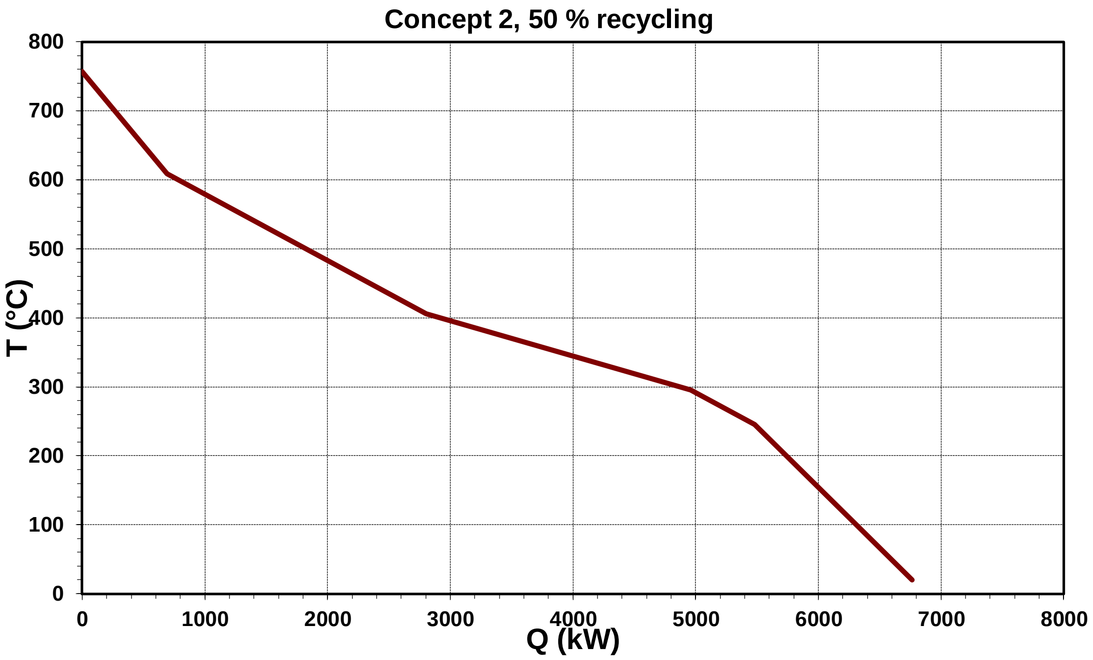
1. Recycling from the first reactor with 30 % water content
2. Recycling from the first reactor without adding steam
3. Recycling from the second reactor with 30 % water content

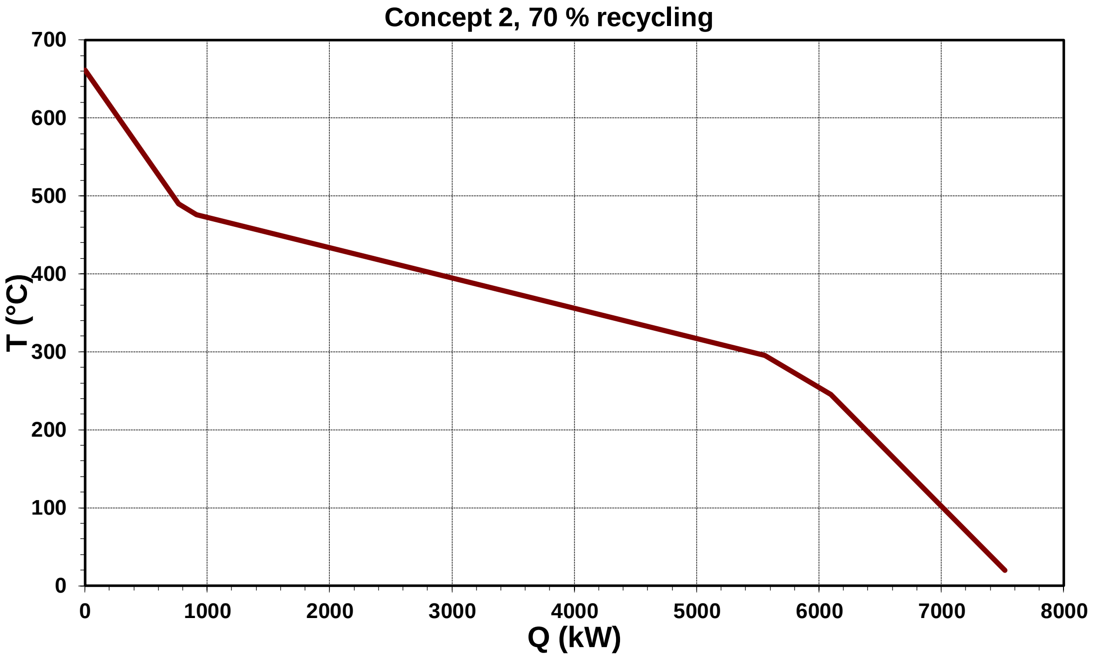


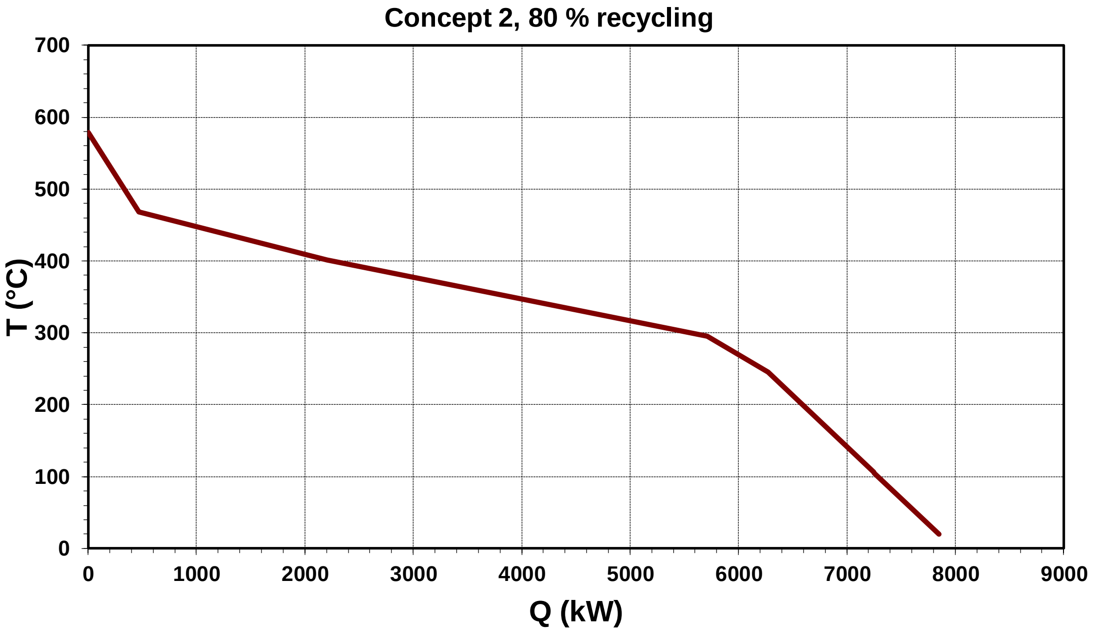


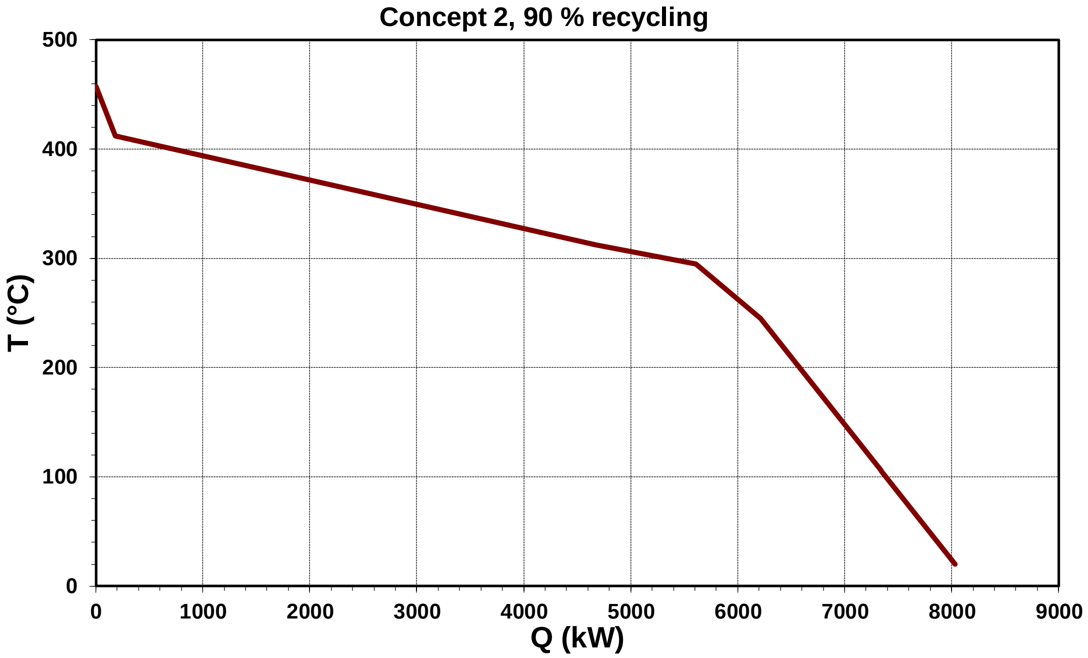

Concept 1, 80 % recycling
T (°C)
600
500
400
300
200
100
0
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
Q (kW)

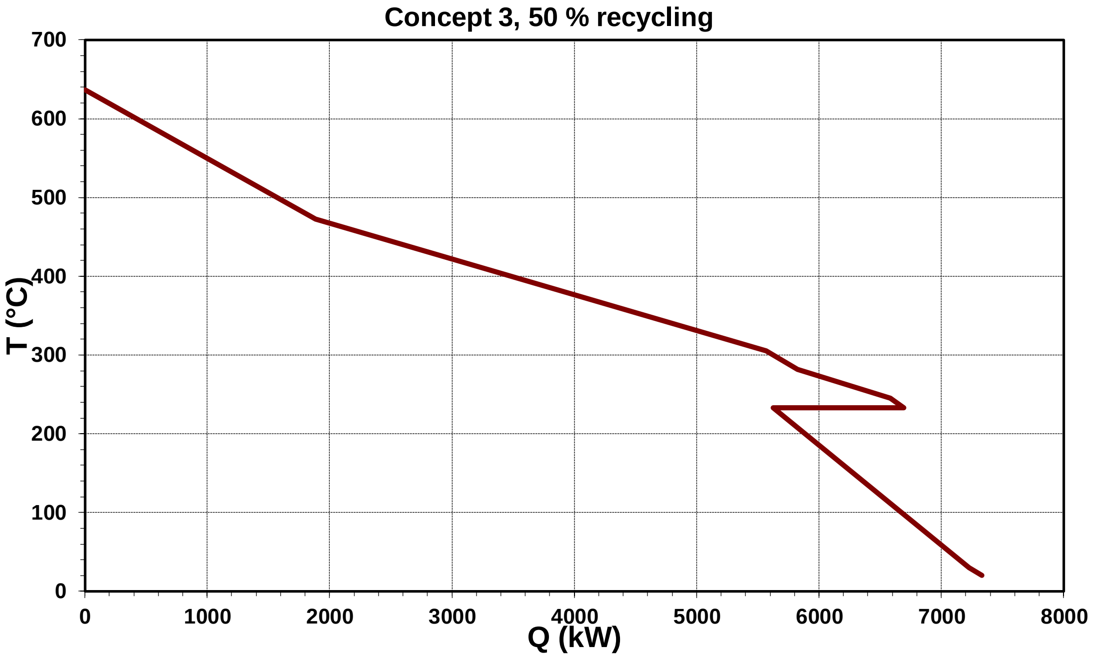

Concept 1, 90 % recycling
T (°C)
500
400
300
200
100
0
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
Q (kW)

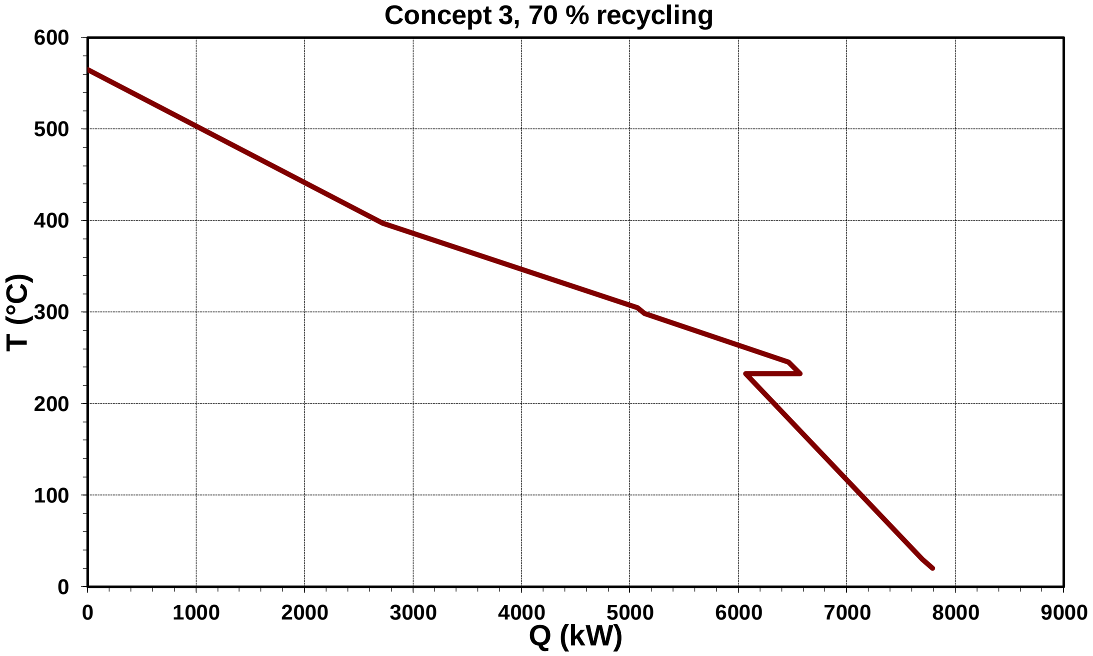

Concept 2, 50 % recycling
T (°C)
800
700
600
500
400
300
200
100
0
0
1000
2000
3000
4000
5000
6000
7000
8000
Q (kW)

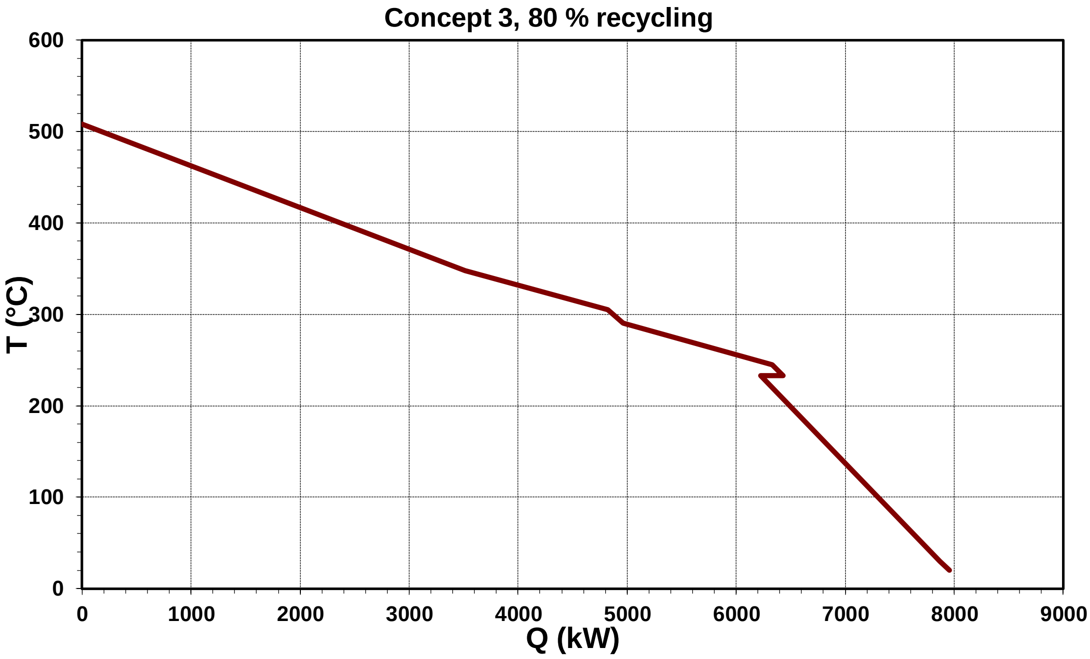

Concept 2, 70 % recycling
T (°C)
700
600
500
400
300
200
100
0
0
1000
2000
3000
4000
5000
6000
7000
8000
Q (kW)

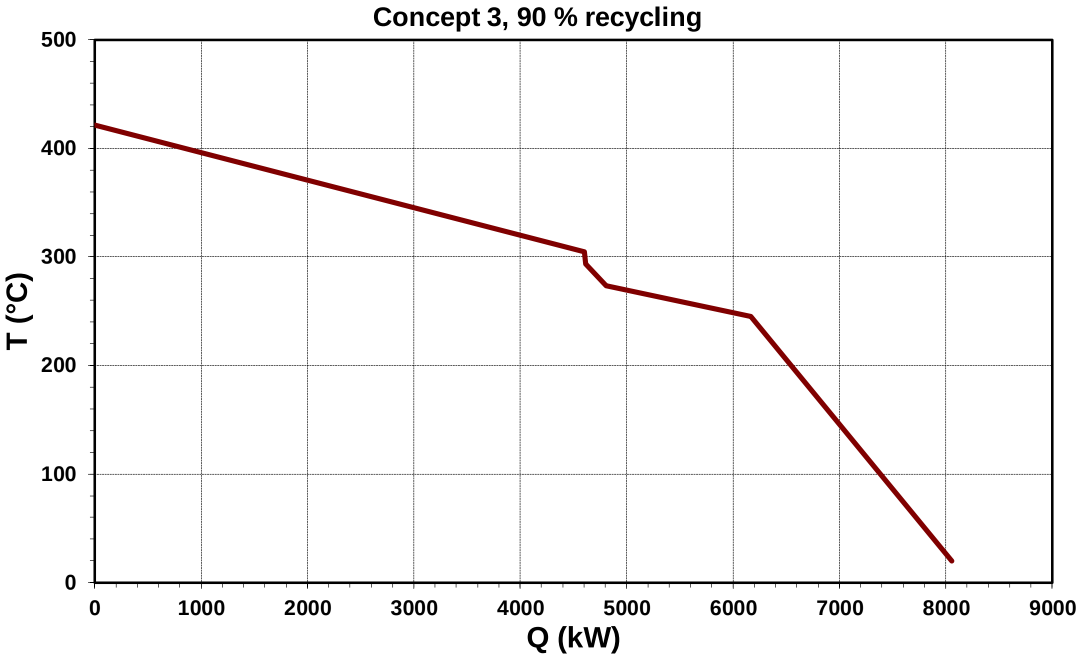

Concept 2, 80 % recycling
T (°C)
700
600
500
400
300
200
100
0
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
Q (kW)


Concept 2, 90 % recycling
T (°C)
500
400
300
200
100
0
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
Q (kW)

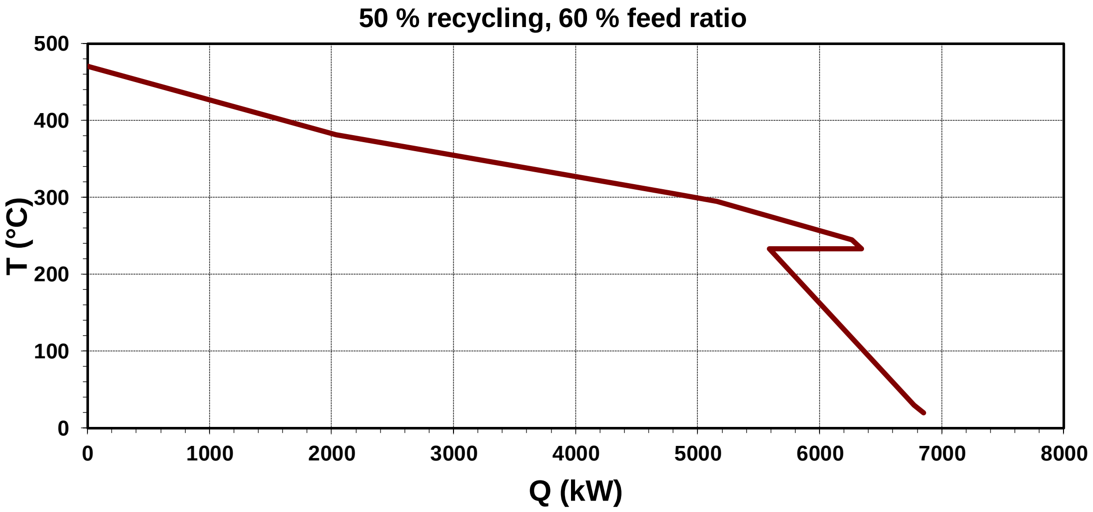

Concept 3, 50 % recycling
T (°C)
0
100
200
300
400
500
600
700
Q (kW)
0
1000
2000
3000
4000
5000
6000
7000
8000

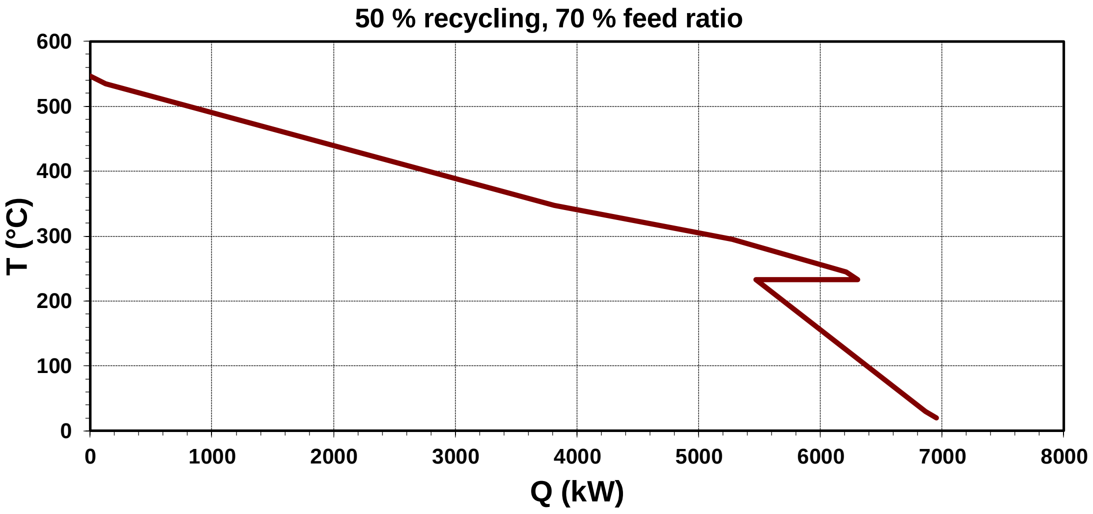

Concept 3, 70 % recycling
T (°C)
0
100
200
300
400
500
600
Q (kW)
0
1000
2000
3000
4000
5000
6000
7000
8000
9000

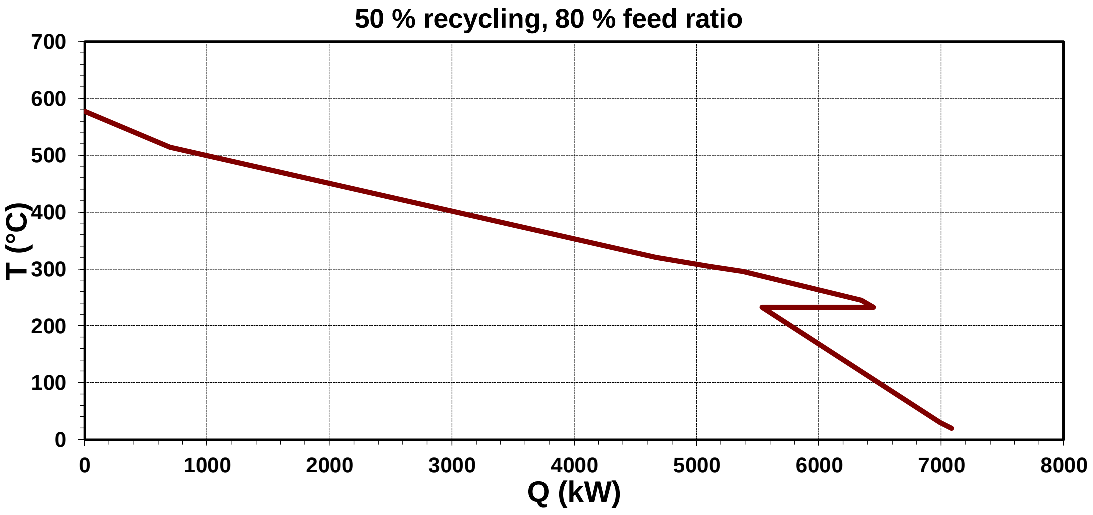

Concept 3, 80 % recycling
600
500
400
300
200
100
0
T (°C)
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
Q (kW)

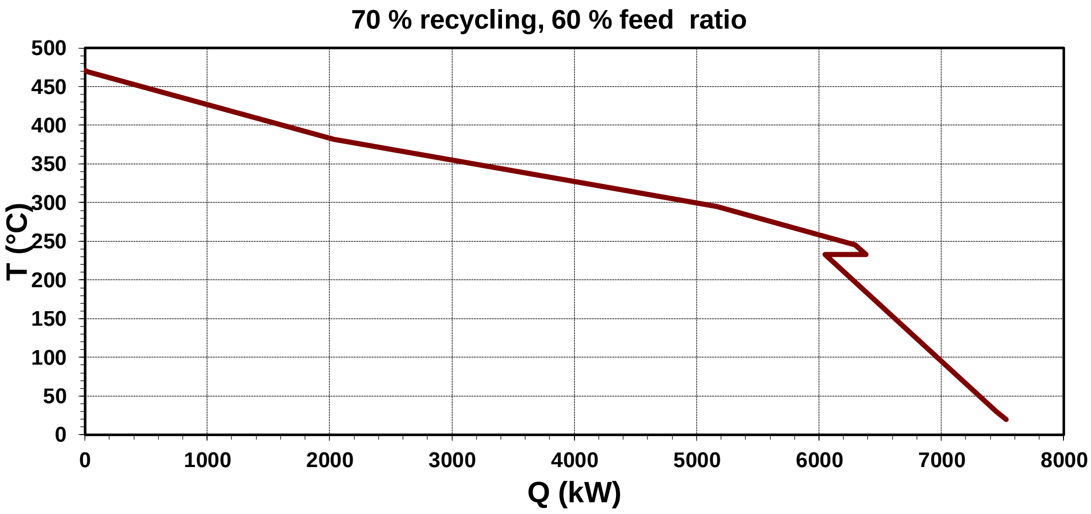

Concept 3, 90 % recycling
500
400
300
200
100
0
T (°C)
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
Q (kW)

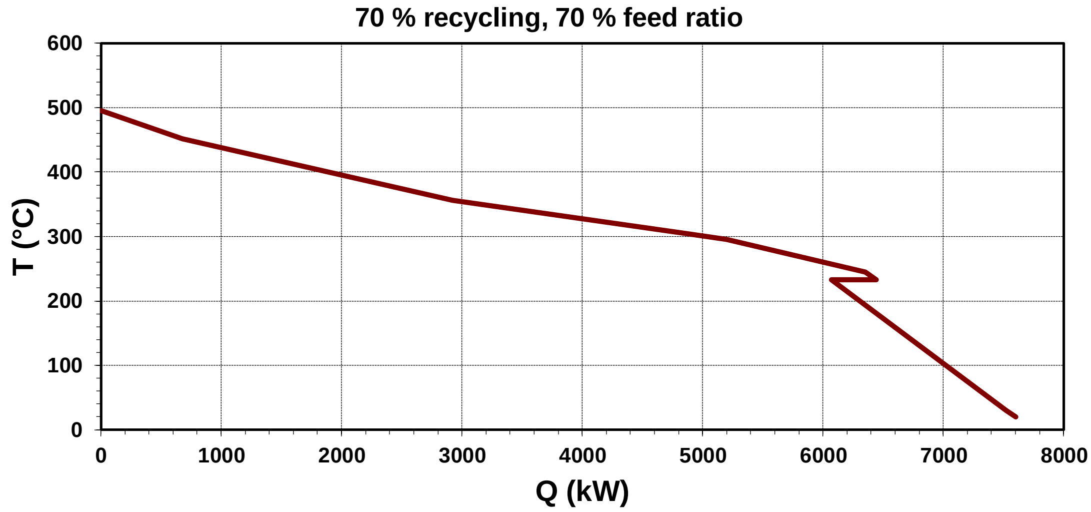
Adiabatic reactors with feed splitting

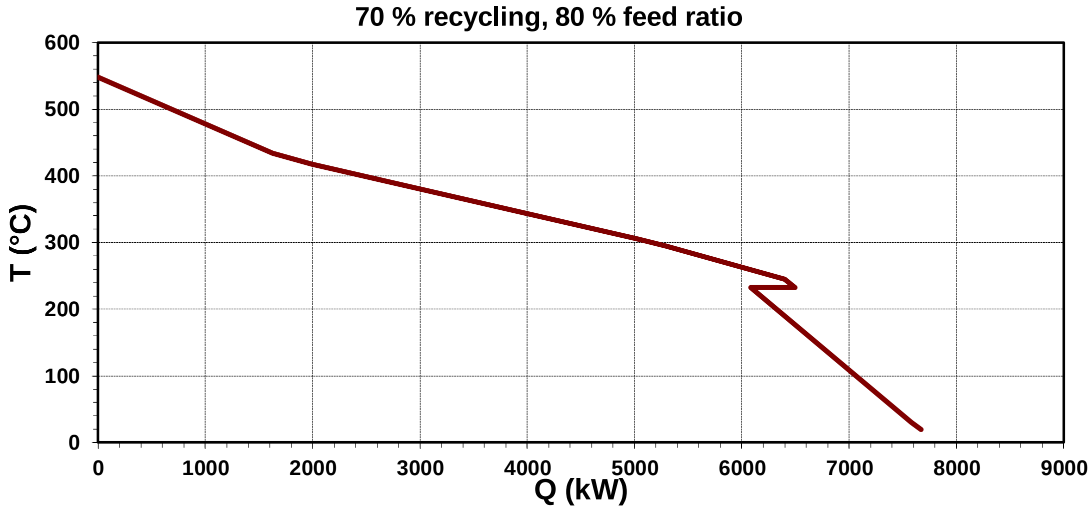




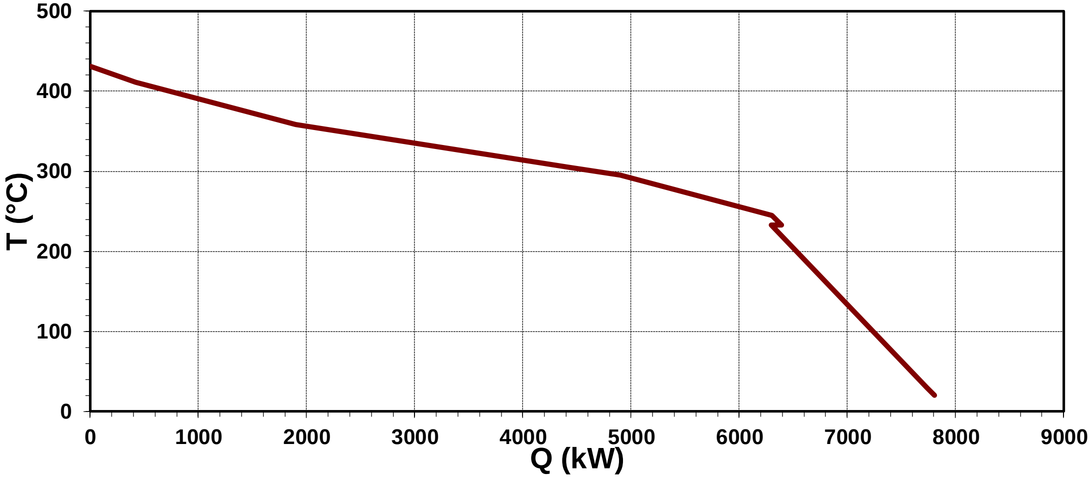



70 % recycling, 60 % feed ratio
T (°C)
500
450
400
350
300
250
200
150
100
50
0
0
1000
2000
3000
4000
5000
6000
7000
8000
Q (kW)

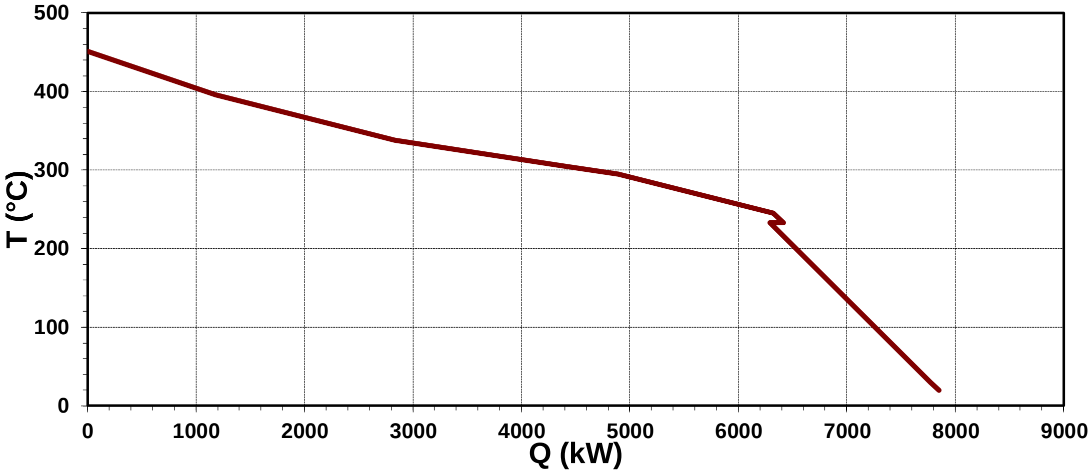

70 % recycling, 70 % feed ratio
T (°C)
600
500
400
300
200
100
0
0
1000
2000
3000
4000
5000
6000
7000
8000
Q (kW)


70 % recycling, 80 % feed ratio
T (°C)
600
500
400
300
200
100
0
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
Q (kW)

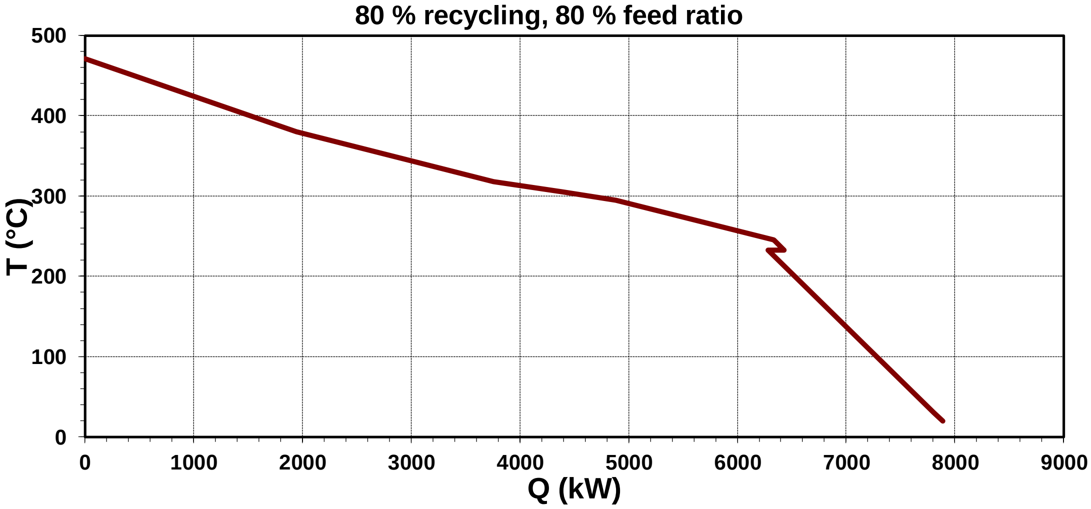
80 % recycling, 60 % feed ratio

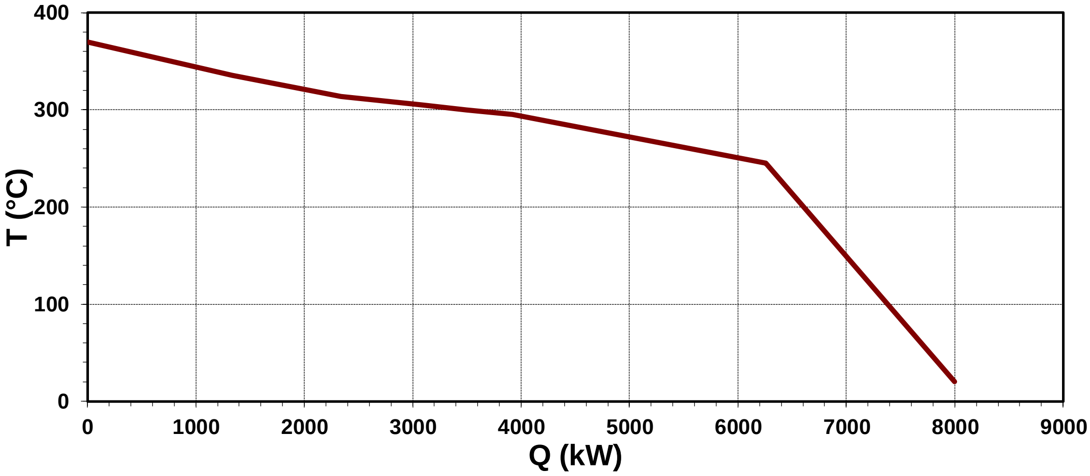


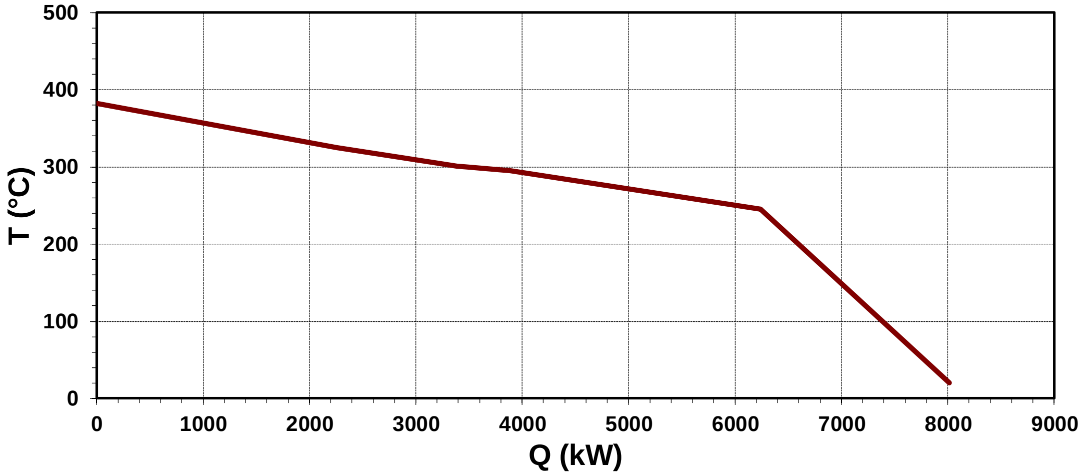
80 % recycling, 70 % feed ratio

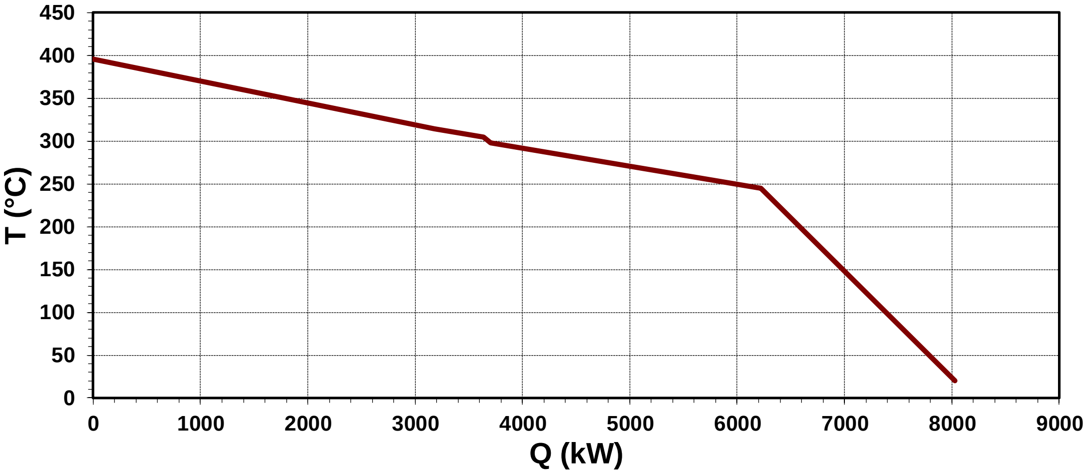


80 % recycling, 80 % feed ratio

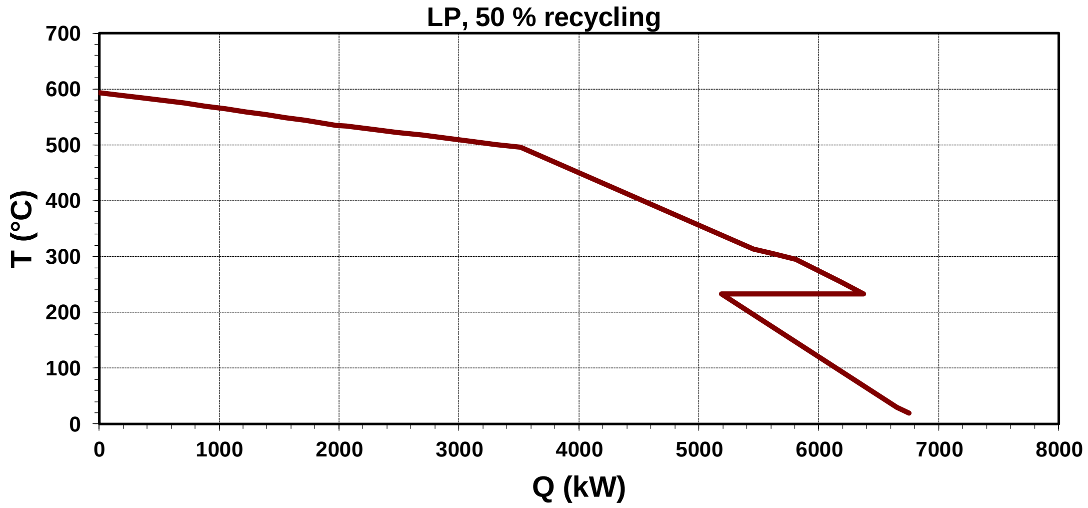


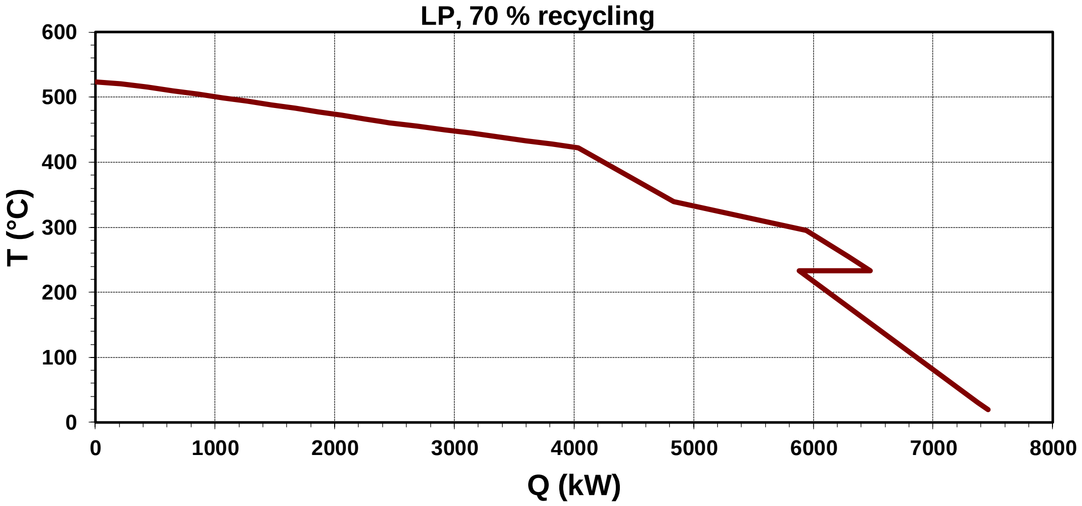

90 % recycling, 60 % feed ratio

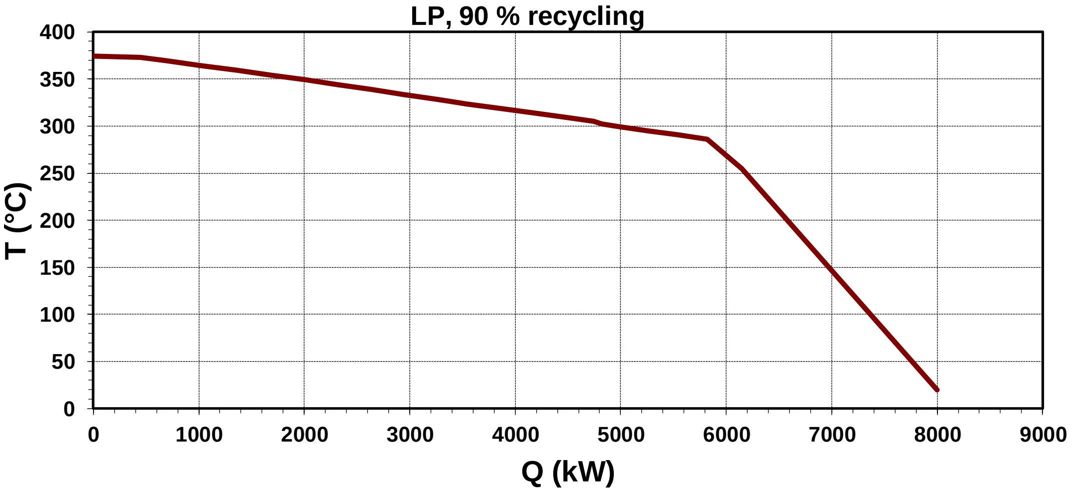

90 % recycling, 70 % feed ratio

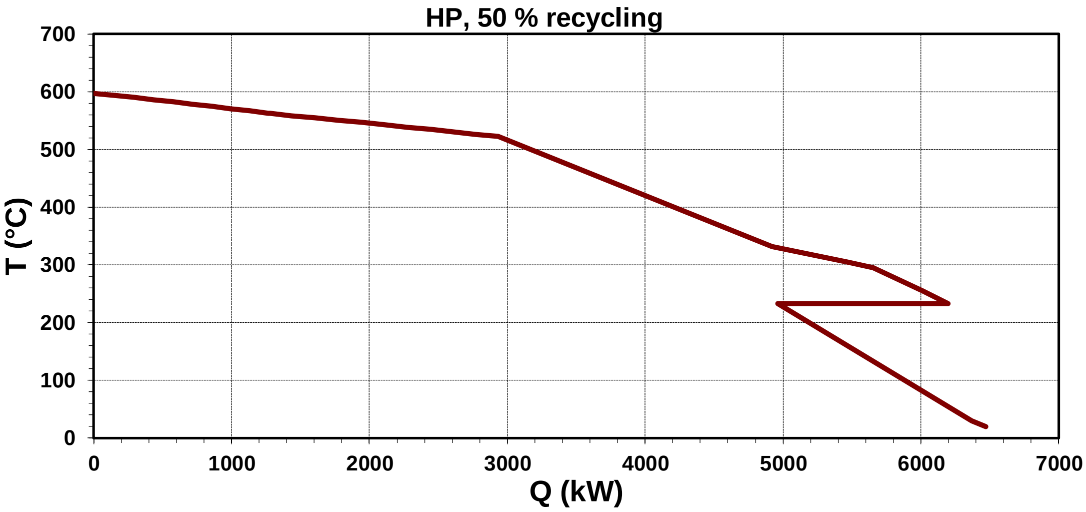

90 % recycling, 80 % feed ratio

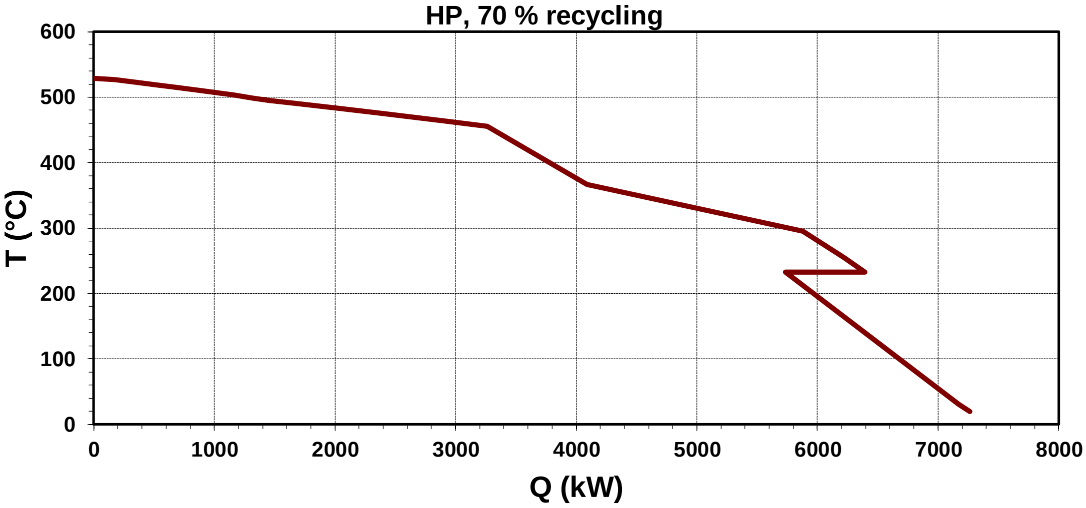
Cooled single reactor

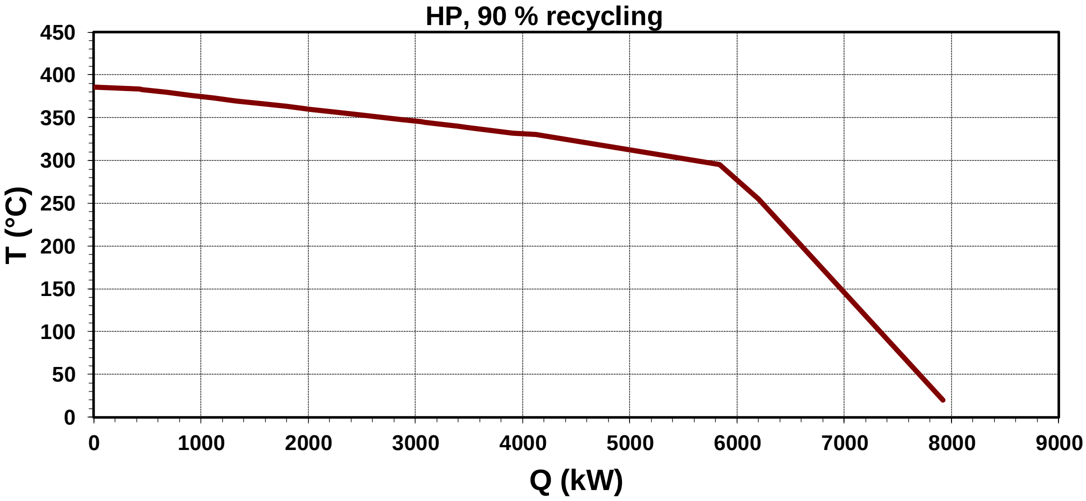







HP, 50 % recycling
T (°C)
700
600
500
400
300
200
100
0
0
1000
2000
3000
4000
5000
6000
7000
Q (kW)


HP, 70 % recycling
T (°C)
600
500
400
300
200
100
0
0
1000
2000
3000
4000
5000
6000
7000
8000
Q (kW)


HP, 90 % recycling
T (°C)
450
400
350
300
250
200
150
100
50
0
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
Q (kW)