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Chemical Quenching

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Preface

The present master thesis is an extension of specialization project and has been carried out at the Department of Chemical Engineering at the Norwegian University of Science and Technology (NTNU).

The work with the project started after personal meeting with my supervisor Professor Edd. A. Blekkan who proposed to investigate the opportunity of chemical quenching of synthesis gas by light hydrocarbons. The project idea has seemed very attractive and challenging because it promised a lot of interesting work.

Catalysis group at the Department of Chemical Engineering disposes experimental set-up *Pyrolyserigg* that has been moved to a new location at the Chemistry Hall D. *Pyrolyserigg* was placed previously at *Varmeteknisk Lab*, (NTNU). In connection with relocation, it was necessary to re-establish apparatus and perform a series of methane pyrolysis experiments in order to confirm that the *Pyrolyserigg* works properly. Verification tests were finished in the middle of February.

In order to perform quenching experiments, it was necessary to design and install a new quencher part for the cooling/quenching system. First, in the middle of March the modified quencher was installed and it was possible to continue with experiments. Further, a series of experimental problems (gas leakages, welding of connection ceram tube-quencher, problems with gas flows, problems with thermocouples, PC – problems, some problems with gas chromatograph) has occurred that slowed experimental work. Finally, one of the heating elements of high temperature furnace was broken.

Experiments with a synthesis gas were planned, but were not performed as a result of the events mentioned above. However, some practical knowledge were obtained that can form the basis for the future work if it will be decided to continue with the topic.

I wish to thank a lot my supervisor Professor Edd A. Blekkan and co-supervisor Torbjørn Gjervan for their participation in my work and supervision.

I am very thankful to all technical staff at the Department of Chemical Engineering that helped me with solving of practical tasks that have arisen during my project work.

Alexei Pylilo
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Abstract

The main objective of the present work was to investigate the opportunity for the use of light hydrocarbons as quenching agents to quench high temperature gas streams. When light hydrocarbon, for example propane, is introduced into a hot gas, for example synthesis gas, the cooling of hot gas will occur both by dilution and by endothermic reactions of hydrocarbon. Thus, the hot gas may be quenched to a lower temperature. At the same time, thermal energy present in the hot gas may be recovered in the form of desired products that are produced during hydrocarbon cracking. This type of quenching is called for *chemical quenching*. A proof-of-concept study would be performed, but was not completed because of problems with a realization of experimental conditions and problems with equipment.

Methane pyrolysis experiments were performed at high temperatures 1400 and 1450 °C. Short residence times and high dilution with hydrogen were applied in order to minimize coke formation. Methane conversions, selectivities and yields of products for different experimental conditions were calculated from the gas chromatographic analysis. The aim of pyrolysis experiments was to validate that the experimental set-up *Pyrolyserigg* works properly. This was done by comparison of experimental results with results that were obtained before on the same set-up and by comparison with a literature data.

After the work of *Pyrolyserigg* was verified, it was possible to modify existing cooling/quenching system. A new quencher part that gives opportunity to introduce a cold gas into hot gas, heated by high temperature furnace, was designed. The quencher part was designed in a way that the temperature of hot gas entering the quencher and temperature of cooled gas mixture leaving the quencher could be measured. Thus, quenching effect (temperature drop) could be measured.

Three types of experiments were performed after modification of cooling system: experiments with only hot inert gas (N₂), experiments with a hot nitrogen gas «quenched» by methane, and hot nitrogen gas quenched by propane. Hot gas temperature and gas flows were varying in order to study the modified system's behaviour.

Experiments with a hot nitrogen showed that there is a limit for maximum obtainable temperature inside the quencher, 1195 – 795 °C, for the given quencher design. A high temperature gradients between measurements points were registered that may be an indication of high heat losses. The temperature gradient increases with increasing gas temperature and decreases with increasing gas

flow.

Quenching effect (temperature drop) was measured in quenching experiments with propane, and expected temperature drop was calculated for the applied experimental conditions. Low measured temperature drop in quenching experiments indicates poor mixing of hot and cold gases. Quenching effect of propane introduction increases with increasing hot gas temperature because heat consumption by endothermic reactions increases, that is a consequence of increasing propane conversion.

A product mixture from quenching experiments with propane was analysed, and conversion of propane, yield and selectivities to products were calculated. Ethylene and propylene are considered to be most valuable products. Ethylene yield increases with conversion and is around 37 % at 100 % conversion. Propylene yield goes through a maximum at 55 % conversion and approaches zero at 100 % conversion.

The main identified problems for the proof of concept study are a poor gas mixing, high temperature gradients through the quencher and high heat loss from the quencher part. In addition, problems with connection ceramic tube – quencher at high temperature have occurred.

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1. INTRODUCTION

1.1 Increase in energy demand and use of natural resources

Economic growth and expansion of world's population are the two most important driving forces for the increasing use of natural resources and for the increasing world's energy demand. As amount of people with a more income increases, the production and consumption of energy will also increase [1]. The *International Energy Outlook 2011* (IEO) prepared by the U.S. Energy Information Administration predicts that the world's energy consumption will increase by 53 % from 2008 to 2035. This corresponds to 1.6 % increase per year. Developing countries will contribute for the main part of the rise in energy demand.[2]

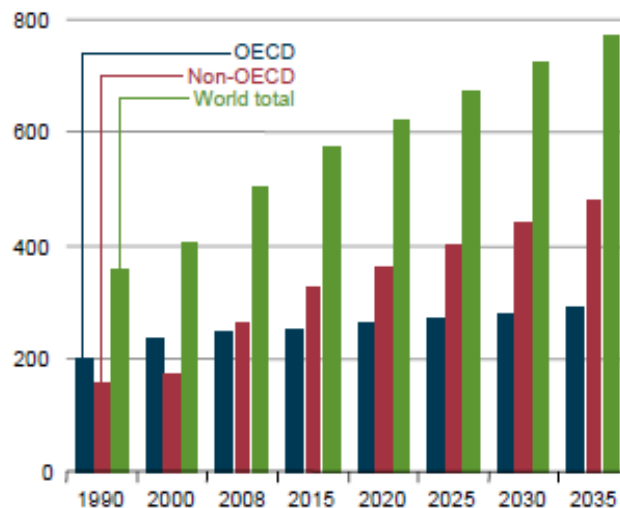


Figure 1.1 World energy consumption, 1990-2035 (quadrillion Btu)[2]
OECD – Organization for Economic Cooperation and Development (members)

According to IEO the consumption of natural gas, oil, coal and renewable resources will continue to increase in order to cover the world's energy demand. To meet the challenges of the future, it is an absolute necessity to develop new technologies and improve existing technologies for energy production and processing of natural resources.

1.2 Trends for more energy-efficient solutions

Saved energy is an earned energy. Improving energy efficiency of existing processes is one way to save or reduce energy consumption. Making a process more energy-efficient may often result in reduction of emissions and wastes from the process, reduction of operating cost and may give financial gains for the company. Many companies have a policies directed to reduce their emissions

and save energy consumption. Depending on particular process, different opportunities exist to make it more energy effective. In chemical industry improvement of processes producing chemicals can be reached by development and use of novel materials and catalysts. Energy efficiency may be increased by properly process design and process integration that maximize heat recovery and minimize energy consumption. Development of more sophisticated processes using advanced technologies is a trend and need of the future.

An example of successful energy-efficient solution is Combined Heat and Power plants (CHP). CHP plants produce electricity and heat in the form of steam that can be used as a process steam or used for district heating. CHP plants may reach electrical efficiencies of more than 50 % and total efficiency may be as high as 90 % [3].

Just to mention, when efficiency of a process is discussed, the term *energy efficiency* may be somewhat misleading if energy quality is not taken into account. Thus, when two or more process alternatives are compared, the exergy analysis should be performed to get an answer about which alternative is the best.

1.3 Synthesis gas production

Synthesis gas is a general name used to describe gas mixtures that contain various amounts of hydrogen and carbon monoxide. Other important components of synthesis gas mixture may be carbon dioxide, water and methane. Synthesis gas is a key intermediate for preparation of base chemicals like hydrogen, ammonia, methanol and Fischer-Tropsch fuels. In addition, it is used directly as a fuel gas in power generation by the gas turbine. Three main processes for the syngas production are steam reforming of natural gas, partial oxidation of heavy hydrocarbons with steam and oxygen, and gasification of coal.[4] Biomass gasification is also an important route for synthesis gas production that is in constant development.

Depending on the process configuration, the exit temperature of raw syngas out of reactor may vary significantly. Typical exit temperatures for different syngas production methods are given in Table 1.1

Table 1.1 Typical syngas outlet temperatures from reactor unit

	T _{exit} [°C]	Comment
Steam reforming of methane [4]	800-950	Higher temperature is preferred, but material constraints is limiting factor
Partial oxidation of heavy hydrocarbons [5],[6]	1300 - 1400	Contains particles of residual carbon and ash
Gasification of coal*[4],[7]	1300 - 1500	Ash (or slag) is in liquid form

*Entrained flow gasifier

As shown in Table 1.1 syngas is produced at high temperatures and contains a lot of energy in the form of heat. The heat should be removed in order to meet downstream applications. For the case when syngas is produced in entrained flow gasifier, it is possible to recover 5 – 25 % of the energy in the feed, relying on the applied technology [8].

Different configurations of syngas cooling and heat recovery system exist. The radiant and/or convective heat exchangers may be used in combination with direct quench systems, in which water or cool recycle gas are introduced into the hot raw synthesis gas. Afterwards, a heat recovery at lower temperatures occurs typically through a series of heat exchangers and different quality steam is produced.[7],[8]

In the case of coal gasification the outlet temperature of syngas is very high, and ash or (slag) is in liquid form. Fouling of downstream process equipment can be a serious problem, thus a quench is necessary to solidify the slag. Four main options is identified for quenching [7]:

2. Radiant syngas cooling
3. Water quench
4. Gas recycle quench
5. Chemical quench

Normally, a first step of syngas treatment is a quenching by one of methods mentioned above from 1500 °C to around 900 °C with a subsequent heat recovery in syngas coolers (fire tube boilers or water tube boilers) by steam production. During the water quench and gas recycle quench a thermal energy is degraded to a lower level and energy recovery is limited.

1.4 New way to energy recovery

In principle, the syngas or any other hot process stream may be quenched at the same time as thermal energy is used to produce other valuable products. For example, if light alkane is used as a quenching medium, the quenching will occur by dilution with cold alkane and by endothermic reactions of alkane. The valuable products will be a simple olefines and hydrogen. This may give a more effective heat utilization than the production of steam. The energy will be recovered in the form of valuable products. The quench process where quenching medium undergo chemical reactions may be referred as *chemical quench*. Chemical quench may be applied in combination with the heat recovery by steam and the total efficiency of the energy recovery may be increased. On the global level, the improvement of efficiency of syngas quenching may be an important step on the way to reduction of energy consumption

1.5 Background for the project: concept of chemical quenching

Background for the project was idea about chemical quenching. The concept of chemical quenching is not very widespread in industry and not so much literature was found about the topic. L. Dessau and H.-J. Spangenberg have performed studies of a plasma acetylene process. In this process the reactive mixture of H_2 , CH_4 , C_2H_4 and C_n compounds at the temperatures of about 2200 K was quenched by injection of liquid hydrocarbons such as gasoline or discrete n-alkanes. The process uses high enthalpy of hot gas mixture to convert quench-hydrocarbons to simple olefines. At the same time the reactive gas mixture is cooled very fast to avoid the consecutive reactions, such as coke formation. The quenching process with liquids can be divided in physical (formation, heating, evaporation of droplet) and chemical parts (cracking).[9]

One of the recent developments is a concept of chemical quenching of hot synthesis gas coming from an entrained-flow gasifier. The temperature of synthesis gas out from a such gasifier is around 1500 °C and synthesis gas should be cooled down to temperatures around 900 °C. This is because raw synthesis gas, produced from coal based feedstock, contains ash and slag on liquid form. These contaminants should be removed to protect downstream process equipment from fouling. By introducing a chemical quench or a second non-slugging gasification stage, the temperature out from gasifier can be reduced sufficiently, and ash or slag become sticky and easy to separate. At the same time the energy of the hot synthesis gas is used in endothermic reactions to gasify a second-stage feed. This results in increased cold gas efficiency. The quenching medium may be a dry feed

or slurry feed as in E-Gas process. In the case the feed is the coal-water slurry, the energy is used to heat up the quenching medium, to evaporate the water and for the pyrolysis of coal.[7],[10]

A similar principle has been demonstrated by *CHOREN* in so called Carbo-V[®] process. The charcoal produced in the first gasification stage of biomass is used as a quenching medium in the second gasification stage [11].

1.6 Scope of the work

Primary aim of the project work was to investigate if light hydrocarbons, for example propane, can be used as a quenching medium to quench very hot synthesis gas. Initial tests of the concept should be performed and quenching effect (temperature drop), conversion of used hydrocarbon, obtained products and other aspects should be studied.

Previous to this, it was necessary to perform a series of methane pyrolysis experiments in order to validate that the experimental set-up (Pyrolyserigg) is working properly, and to verify earlier experimental results from the methane pyrolysis. In order to perform quenching experiments the cooling system/cold finger was modified and new quencher part with opportunity for hydrocarbon injection was installed. A series of experiments with N₂ as a hot inert gas was performed with the purpose of study the behaviour of modified quencher. A series of experiments with hot N₂ quenched by propane was done to study the quencher performance.

Experiments with a hot syngas quenched by propane were planned, but were not done because one of the heating elements of the high temperature furnace was broken.

2. THEORY AND LITERATURE

2.1 General about quenching and quenching methods

Many processes for the preparation of chemicals are carried out at high temperatures. In some cases it is necessary with a rapid cooling of chemical substances or process flows. In this context the rapid cooling refers to a *quenching*. Depending on particular process the main objectives of quenching are heat recovery from process streams, temperature control in reactors, prevention of consecutive reactions, retention of product composition and increase in a process efficiency.[4]

Quenching can be direct or indirect, dependent on the way it is done. Indirect quenching is often used for the generation of high-pressure steam by special designed heat exchangers. In the case with indirect quenching there is no direct contact between heating medium and quenching medium. Direct quenching is associated with injection of solids, liquid or gas into the heating medium. Direct quenching can be very efficient and high cooling rates can be achieved.[4] The cooling rate is often a measure of performance of quenching process[12].

Sundstrom and DeMichiell have investigated the following quenching techniques: mixing with a cold gas, injection into a fluidized bed, contact with cold surface and evaporation of liquid spray. They concluded that all techniques are able to provide cooling rates greater than 10^6 °R/sec, but factors such as product recovery, energy recovery and scale-up should be considered, in selecting a technique. Gas mixing technique gave the fastest quenching rate. It is difficult to compare quenching methods because of the specific parameters associated with each method. In the Figure 2.1 a temperature decay curves are illustrated at typical quenching conditions.[13]

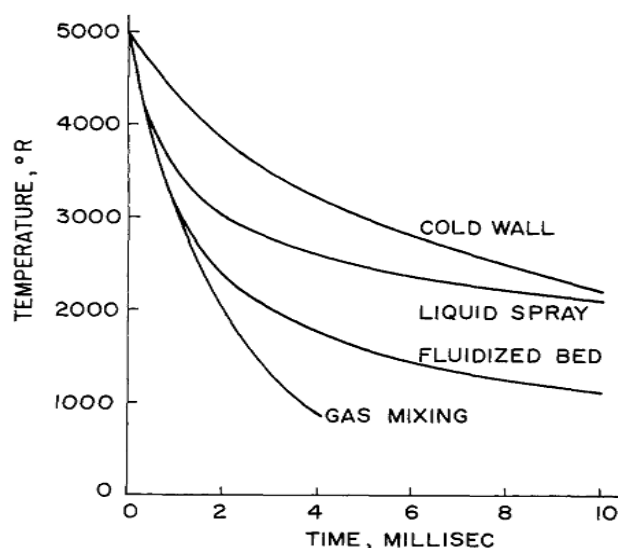


Figure 2.1 Temperature decay curves at typical quenching conditions [13]

In the case of coaxial mixing of hot and cold gases Figure 2.2, the most important factors for cooling rate were the diameter of the hot jet and the ratio of coaxial to jet velocity. A smaller hot jet diameter and higher velocity ratios increased the cooling rate by reduction the time necessary to establish turbulent mixing processes.[13]

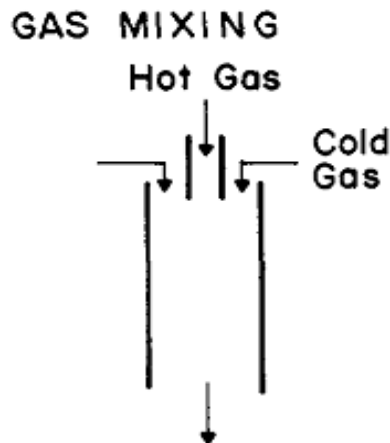


Figure 2.2 Schematic diagram of quenching by coaxial gas mixing [13]

Energy recovery is generally preferred at high temperatures. The high temperature conditions result in high driving forces for the heat exchange processes. At very high temperatures the material constraints can be a problem. During quenching by gas mixing or liquid spray the thermal energy present in the process stream is degraded to a lower level. In addition, dilution of the process stream by cooling medium occurs. The consequence of dilution may be an increase in separation costs of final gas stream. This problem can be avoided by using cold product stream as cooling medium by sending it in the return to the quencher. In principle the cooling medium can be a reactive component or mixture of reactive components that undergo endothermic reactions. In this case the quenching may result in reduction of temperature and production of desirable products. [13]

2.2.1 Gas mixing

Transport phenomena such as mass, heat and momentum transport should be considered when flows of hot and cold gases are mixed together. To obtain a high quenching effect, it is necessary with a rapid and completely mixing of hot and cold gases. The mixing of gases will occur mainly by to mechanisms: molecular diffusion and convective transport.

The molecular diffusion can be explained by the kinetic theory of gases. The gas molecules are in rapid random movement and often collide with each other because of their kinetic energy. Because

molecules move randomly in all directions, there are fluxes in all directions. When concentration gradients occur in the bulk gas phase, there is a net flux of molecules from a region with a high concentration to a region with a low concentration. The concentration gradient is a driving force for diffusion transport.[14] In the case when two gas flows in a tube in *laminar* regime and have the same velocity the mixing will occur mainly by molecular diffusion through the boundary layer.

On the other hand, the convective transport of gas occurs by the forced movement of the gas where the ensembles of molecules move in concerted and collective motion. The convective transport may occur at all scales that are larger than a few atoms. The cause for the convective mixing of the gas flow inside the tube or reactor is *viscous forces* and *shear stresses*. When gas velocity is sufficient high, the flow pattern is unstable and eddies or small packets of fluid particles are presented. These are moving in all direction and at all angles to the normal line of flow. When high degree of fluctuations exists, the gas flow is said to be in *turbulent* flow regime. In the turbulent flow regime the mixing of gases will occur mainly by convective transport.[14]

The mixing of hot and cold gas flows will depend on flow conditions such as temperature, gas velocities, viscosities, gas densities and geometry of mixing device. Turbulent flow regime will give a better gas mixing than laminar flow in which there is no lateral mixing of the gas.

2.2.2 Turbulent vs. laminar flow

To predict where a gas flow is in laminar or turbulent regime, the Reynolds number can be used, which is dimensionless. For *the tube geometry* the Reynolds number defined as:

$$N_{Re} = \frac{Dv\rho}{\mu} \quad (1)$$

Where

D – inner diameter of the tube	[m]
v – average velocity of the fluid	[m/s]
: defined as volumetric rate of flow divided by the cross – sectional area of the pipe	
ρ – fluid density	[kg/m ³]
μ – fluid viscosity	[Pa·s]

«For a straight circular pipe, when the value of Reynolds number is less than 2100, the flow is always laminar. When the value is over 4000, the flow will be turbulent, except in very special cases. In between – called the transition region – the flow can be viscous or turbulent, depending upon the apparatus detail, which can not be predicted». [14]

2.2.3 Velocity profiles in cylindrical tube

The knowledge about velocity profile of gas flow inside the tube (Quencher) can be important to explain the temperature measurements. For a simple tube geometry and laminar flow at steady state, the expression for velocity profile can be derived by making a shell momentum balance and using equation for the definition of viscosity. The following equations can be obtained [14]:

$$v_x = 2v_{x,av} \left[1 - \left(\frac{r}{R} \right)^2 \right] \quad (2)$$

$$v_{x,max} = 2v_{x,av} \quad (3)$$

Where

- v_x – flow velocity in x direction [m/s]
- $v_{x,av}$ – average flow velocity for a cross section [m/s]
- r – distance from the tube center in radial direction [m/s]
- R – tube inside radius [m]
- $v_{x,max}$ – maximum flow velocity in the tube center [m/s]

For the fluid flow the velocity profile is parabolic as represented in Figure 2.21

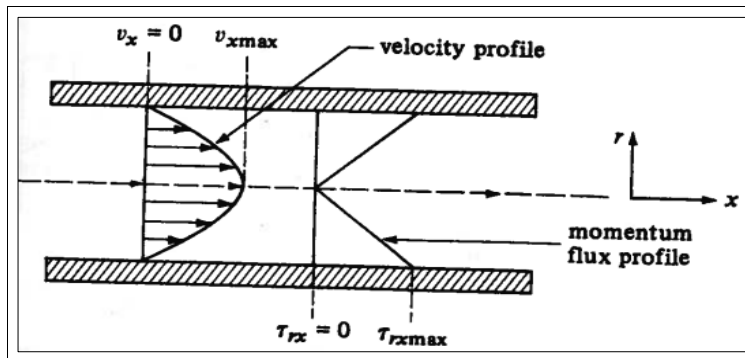


Figure 2.2.1 Velocity and momentum flux profiles for laminar flow in a tube [14]

It has been shown by experiments that fluid moving in the center of the tube is moving faster than the fluid near the walls. For laminar flow, the velocity profile is true parabola. The velocity at wall is zero. For turbulent flow the velocity profile is somewhat flattened in the center as shown in Figure below.[14]

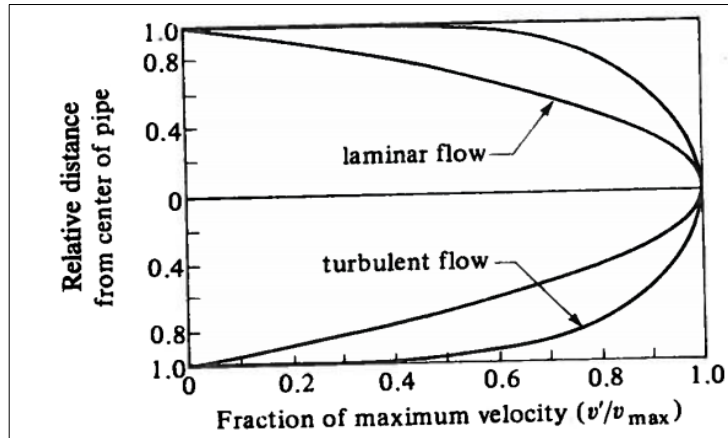


Figure 2.2.2 Velocity distribution of fluid across a tube [14]

A certain length of tube is necessary to establish a fully developed velocity profile at the entrance region of the tube. This length is called for *entry length*, L_e , and can be approximately calculated as (for laminar flow)

$$L_e = 0,0575DN_{Re} \quad (4)$$

For turbulent flow an approximation is that the entry length is nearly independent of the Reynolds number and is around 50 times of the tube diameter.[14]

2.2.4 Mass and energy balance over control volume, CV[14]

For heat-transfer systems, a steady state condition means that there is no temperature change at any given point and heat fluxes are constant over the time. With assumption about steady state, a simple *energy or heat balance* over control volume (CV) or over a system can be written on the form

$$\sum_i H_{in,i} - \sum_j \Delta H_{j,react} + Q = \sum_i H_{out,i} \quad (5)$$

Where

$H_{in,i}$	– enthalpy of flow of component i into the CV	[J/s]
$\Delta H_{j,react}$	– heat produced or consumed i reaction j	[J/s]
Q	– net heat added or removed from CV	[J/s]
$H_{out,i}$	– enthalpy of flow of component i out of CV	[J/s]

A sketch over the region of quencher considered as CV is illustrated in the Figure 2.2.3

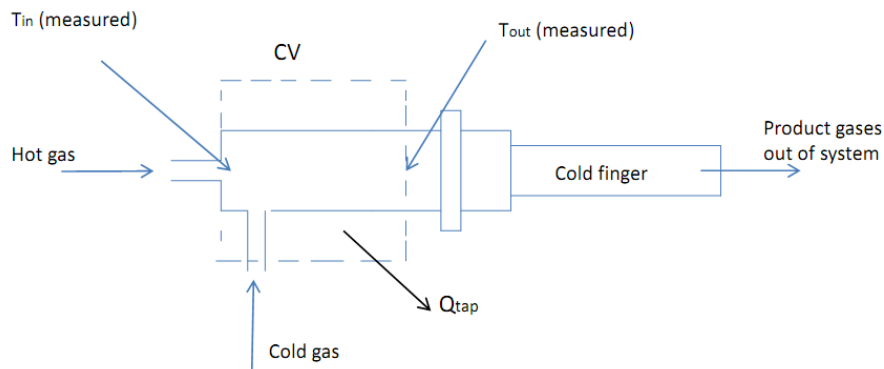


Figure 2.2.3 Control Volume (CV) considered in the heat and mass balances. The boundaries in axial direction are at temperature measurement points

The enthalpy of flows of components defined as:

$$H_{in,i} = F_{in,i} C p_i (T_{in} - T^0) \quad (6a)$$

$$H_{out,i} = F_{out,i} C p_i (T_{out} - T^0) \quad (6b)$$

Where

$F_{in,i}$ – molar flow of component i into CV	[mol/s]
$C p_i$ – heat capacity of component i	[J/mol·K]
T_{in} – flow temperature into CV	[K]
T_{out} – flow temperature out of CV	[K]
T^0 – reference temperature at standard conditions	[K]

$F_{in,i}$ is calculated, using ideal gas law, from the volumetric flow of component i, given by MFC:

$$F_{in,i} = \frac{P V_{in,i}}{R T} \quad (7)$$

Where

P – standard pressure	[Pa]
$V_{in,i}$ – volumetric flow of component I	[Nm ³ /s]
T – temperature at standard conditions	[K]
R – universal gas constant	[J/mol·K]

The flow of component i out of CV is calculated using experimental data for conversion of component i:

NB! The component i will to some extent react outside of CV. This means that the obtainable conversion inside the CV is lower than conversion predicted by experiments. This can be a source of error for heat balance over CV.

$$F_{out,i} = F_{in,i} (1 - X_i) \quad \text{Where } X_i \text{ – total conversion of component i}$$

2.2.5 Calculation of heat loss over CV

When approximately steady state condition for cooling system is reached, the *heat loose* over CV to the surroundings can be calculated. The temperature is measured for the gas flows in and out of CV. There is no reaction, since only inert hot gas is introduced during the heating period. The heat loose is a difference between enthalpies of incoming and out coming gas flows:

$$Q_{lose} = \sum_i F_{out,i} C_{p_i} (T_{out} - T^0) - \sum_i F_{in,i} C_{p_i} (T_{in} - T^0) \quad (8)$$

The calculated heat loss is a heat loss at actual experimental conditions and will be dependent on amount of gas passing CV, the gas temperature and isolation layer around the quencher.

When reacting or inert cold gas are introduced into the quencher, the established temperature profile through the cooling system and CV, will change. The heat loss will also be changed. It will probably be reduced because of reduction of temperature. However, this change is considered to be negligible and heat loss is assumed to be constant.

When heat loss over CV and conversions to products (product flows) are known, it is possible to calculate *expected temperature* out of CV. This is a way to calculate *expected quenching effect* (temperature drop) of cold gas injection.

By rearranging equation (8), the *expected temperature* out of CV calculated as

$$T_{out} = T^0 + \frac{\sum_i F_{in,i} C_{p_i} (T_{in} - T^0) - \sum_j \Delta H_{j,react} + Q_{lose}}{\sum_i F_{out,i} C_{p_i}} = \frac{\sum_i H_{out,i}}{\sum_i F_{out,i} C_{p_i}} \quad (9)$$

2.3 General about hydrocarbons pyrolysis

Pyrolysis or thermal cracking of hydrocarbons is a widely applied process. When hydrocarbons from natural gases, refinery gases or petroleum are heated up to a sufficient high temperature, thermal cracking take place. When pyrolysis of hydrocarbons occurs in the presence of steam, steam acts as a diluents, the process called for *steam cracking*. The higher alkanes are converted to olefines in a high yields. The final product mixture is complex, but ethene is considered to be the main product. Depending on feedstock and working conditions many other olefines and aromatics are produced: propene, butenes, butadiene, benzene, toluene, etc. In addition, it can be formed a less valuable products such as methane, heavy pyrolytic naphthas and coke. The coke formation should

normally be avoided because of associated fouling problems.[4],[15]

Steam cracking of hydrocarbons is a high temperature process, depending on feedstock a temperatures higher than 600 °C are applied [15]. Because the overall process is endothermic, considerable heat input at high temperature level is necessary. The primary reactions in hydrocarbon pyrolysis are dehydrogenation of alkanes and cracking of long chain alkanes to lower alkenes and alkanes:



The primary products of pyrolysis may undergo secondary reactions like further pyrolysis, dehydrogenation, condensation and coke formation.[4] Thermal decomposition of hydrocarbons can be described by free-radical mechanism and using a set of elementary reactions. For example, it was used 35 reversible and 1 irreversible elementary reactions to describe pyrolysis of methane in temperature range 1200 – 1500 °C [16]. L. Dessau has used 38 equation in reaction kinetic modelling of n-hexane, when it was used as a quenching agent for high temperature conversion of methane [9].

In general, smaller alkanes are more stable than higher alkanes. Thus, the pyrolysis of smaller alkanes requires a higher temperature and higher heat input to obtain a given conversion. Both dehydrogenation reactions and cracking reactions produce two molecules for every converting alkane molecule. As a consequence, the conversion of alkanes is dependent on the partial pressures of reactant and products.[4] The Figure 2.3.1 illustrates how the equilibrium conversion for some alkanes is affected by temperature and total pressure.

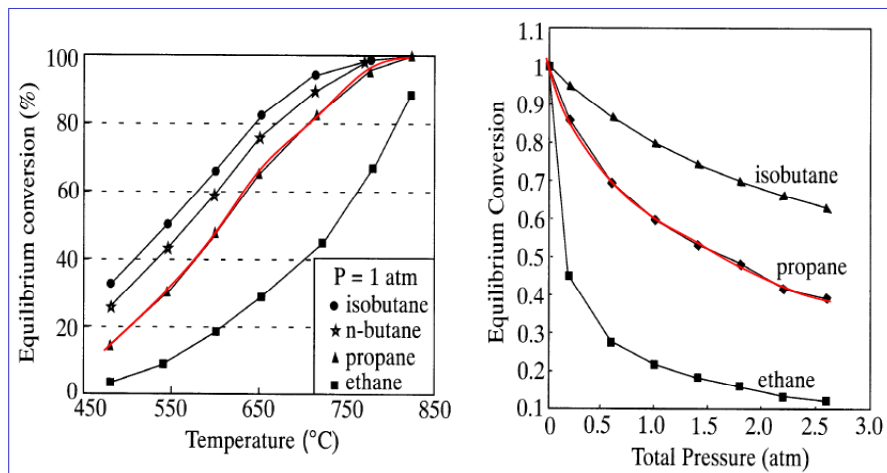


Figure 2.3.1 Equilibrium conversion of smaller alkanes [20]

Surface effects

The experimental results of methane pyrolysis and pyrolysis of other hydrocarbons may be affected by the surface effects like heterogeneous reactions, occurring on the reactor wall. To minimize these surface effects, the surface-to-volume ratio S/V of reactor should be kept low.[16]

Makarov et al. studied methane pyrolysis in a flow system in the temperature range 815-1100 °C. They concluded that at S/V ratios less than 20 cm⁻¹ only homogeneous reactions were present. This means no surface effect. At S/V ratios greater than 10⁴ cm⁻¹ homogeneous reactions were depressed.[16]

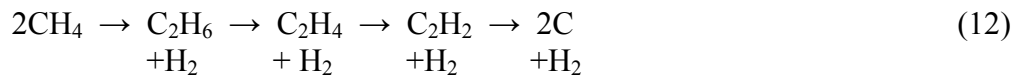
The surface effects will also be dependent on catalytic activity of the surface, and therefore, on the type of material used in reactor. The reaction rates are higher in iron than in quartz or gold reactors. *The tendency to coking is higher in iron, monel or cobalt than in quartz, porcelain, silver or gold reactors.* The pyrolysis of n-alkanes in a stainless steel reactor favour formation of ethene versus methane and propene, than pyrolysis in quartz reactor working at comparable conditions.[15]

The deposition of coke on the reactor surface may be a serious problem in the pyrolysis studies because the surface property is changed continuously as coke is formed [15]. In addition, an uncontrolled coke formation may cause the plugging of the system.

Other possibility to minimize the surface effects is the passivation of inner surface with surface-active agents [15]. [17] has used CS₂ to deactivate chromium steel when thermal cracking of propane was studied. [21] has used mixture of N₂, H₂ and CH₄ to passivate the ceramic reactor after the coke burn-off.

2.3.1 Pyrolysis of methane

Ola Olsvik has studied the conversion of methane into C₂ compounds at the temperature region (1000 – 1500 °C). At temperatures above 600 °C thermodynamic equilibrium favour formation of C and H₂, thus the residence time inside reaction zone become an important parameter to consider. The quenching step of methane pyrolysis is also important for product distribution. *“The pyrolysis of methane may be described as stepwise dehydrogenation at high temperature”*[16]:



The main products of methane pyrolysis are ethyne, ethene, benzene, hydrogen and carbon. Ethane is the primary product. Ethene, ethyne and benzene are secondary products, and at high residence times tar and coke are also produced. The dilution by inert gas and applied short residence times, reduce the opportunity for condensation reactions and formation of heavier compounds. [16]

The pyrolysis of methane is explained by free radical mechanisms. The formation of methyl radical and hydrogen radical is an initiation step. The reaction has high activation energy and supposed to be rate-determining [16]:



The overall reaction rate of methane can be considered as a 1. order reaction [16],[22]:

$$r = k \cdot C_{\text{CH}_4} \quad (14)$$

The methane conversion and the ratio of ethyne to ethene have been shown to increase with increasing temperature. The Figure 2.3.2 shows how conversion vary as a function of residence time for different temperatures.

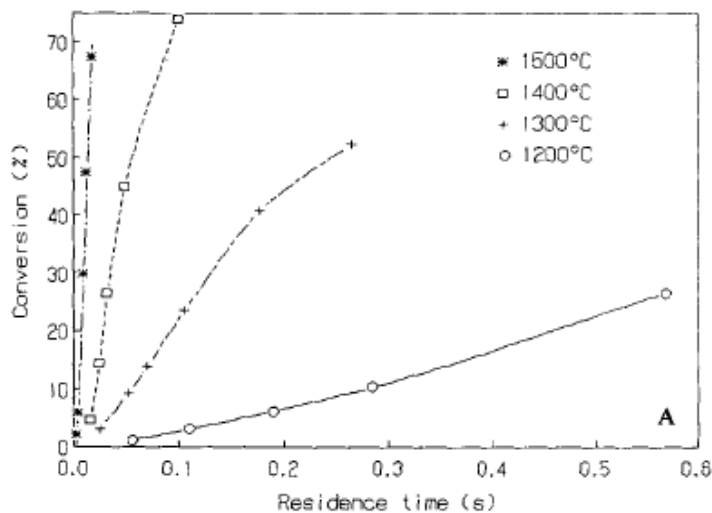


Figure 2.3.2 Conversion vs. Residence time for different temperatures. $P_{\text{tot}} = 1 \text{ bar}$, $d_i = 9 \text{ mm}$, except at $1500 \text{ }^\circ\text{C}$ where $d_i = 4 \text{ mm}$, $\text{H}_2:\text{CH}_4 = 2:1$ [16]

The Figure 2.3.3 shows how the maximum yields of products: ethyne, ethene and benzene vary with

increasing temperature.

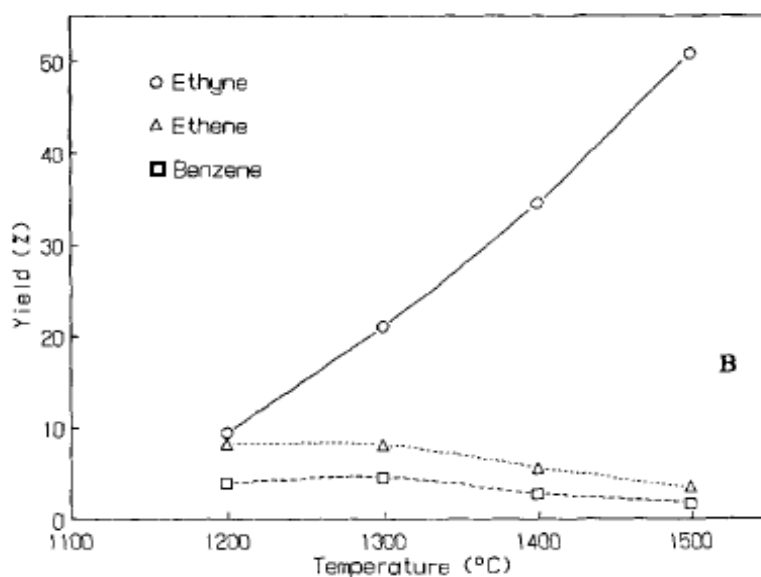


Figure 2.3.3 Yields as a function of temperature, $H_2:CH_4 = 2:1$ [16]

“The rate of pyrolysis decreases markedly in the presence of hydrogen”[22]. Hydrogen dilution has an important effect on the kinetics of the methane pyrolysis. The effect of hydrogen dilution becomes more important at higher reaction temperatures. Hydrogen strongly depresses carbon formation and increases the yield of ethyne [16],[22]. The Figure 2.3.4 illustrates how the conversion depends on hydrogen dilution for different residence times.

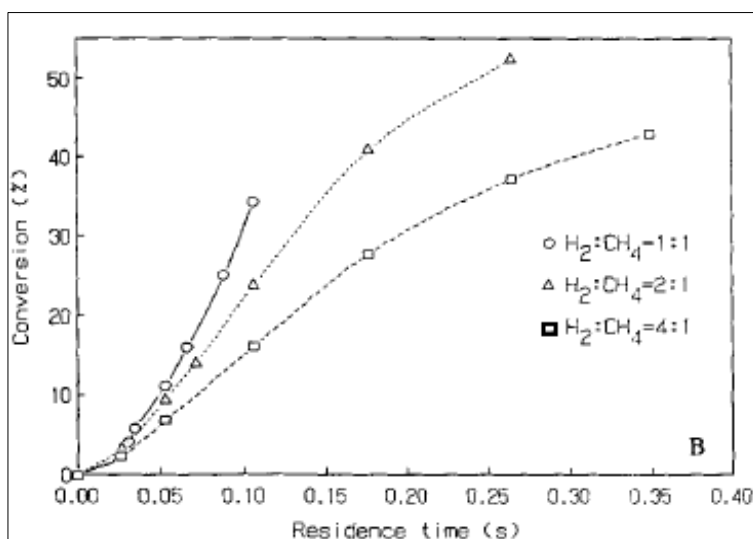


Figure 2.3.4 Conversion of methane as a function of residence time for different hydrogen dilutions. $T = 1300\text{ °C}$ [16]

2.3.2 Thermal cracking of propane

G. Buekens and F. Froment [17] have performed studies of pyrolysis of propane for temperature region between 625 and 850 °C, and near the atmospheric pressure. They concluded that the main products of thermal cracking of propane are methane, ethylene, propylene and hydrogen. “*Ethane is also partly a primary product, but it is produced in much smaller quantities*”. In addition, butenes, butadiene and aromatics are formed.[17]

Cracking of propane can be explained by two parallel decomposition reactions [17]:

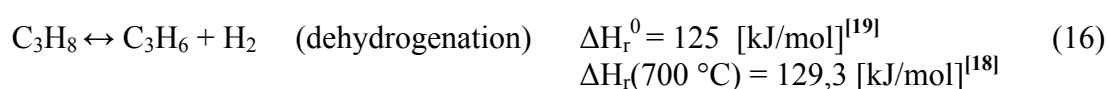
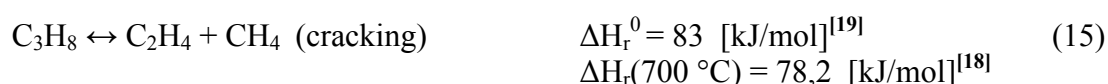


Table 2.1 illustrate selectivities to primary products at zero conversion for several temperature ranges.

Table 2.1 Primary product distribution at Zero Conversion [17]

(Moles formed per 100 moles of propane cracked)				
	675/ 700° C.	725/ 750° C.	775/ 800° C.	825/ 850° C.
Methane	47	47	49	48
Ethylene	48	49	50	50
Ethane	0.7	1.1	1.4	3.2
Hydrogen	52	52	51	53
Propylene	52	51	49	47

As conversion of propane is increasing, the selectivity for ethylene and methane is also increasing, but selectivity toward propane is decreasing. The Figure 2.3.5 illustrates how selectivities to primary products change with increasing conversion for temperature region 725 – 750 °C. [17]

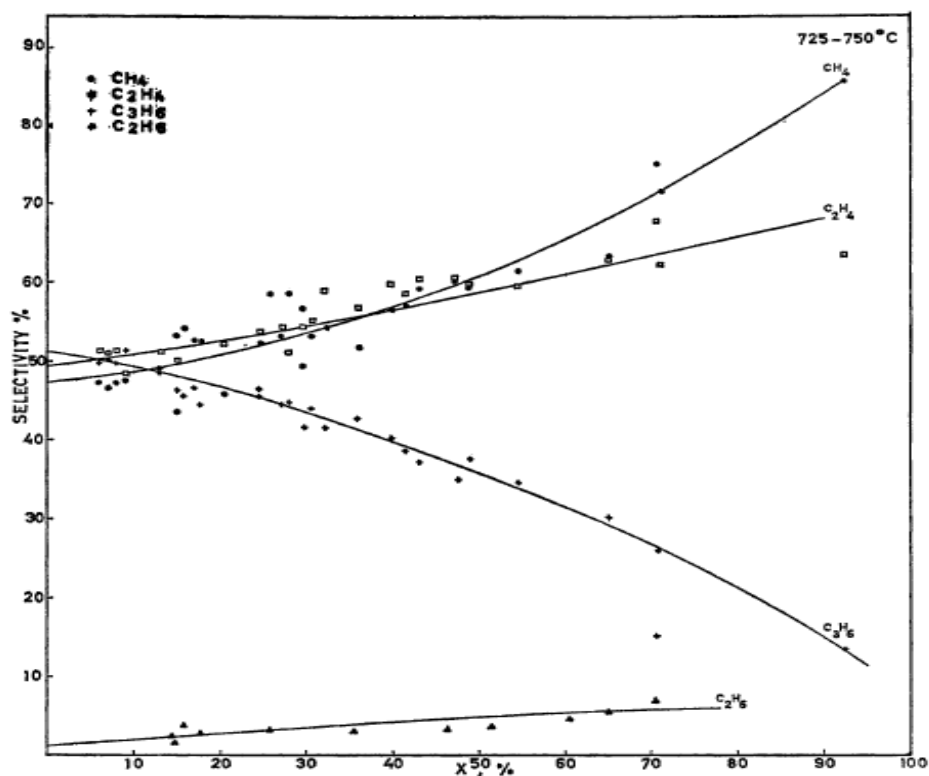


Figure 2.3.5 Selectivity diagram. (Temperature 725 – 750 °C) [17]

V.R. Choundary and V.H. Rane [18] have investigated thermal cracking and non catalytic oxidative conversion of propane *in the presence of steam* at various process conditions. They concluded that the thermal cracking of propane happens to a considerable level only at high temperatures (>700 °C). At lower temperatures the conversion was very small (< 7 %). At temperatures higher than 700 °C, the propane conversion and selectivity for propylene increased markedly. The selectivity for ethylene and methane decreased with increasing temperature, Figure 2.3.6. The coke formation on the reactor walls and/or a tarlike product on the cooler parts of reactor was observed.[18]

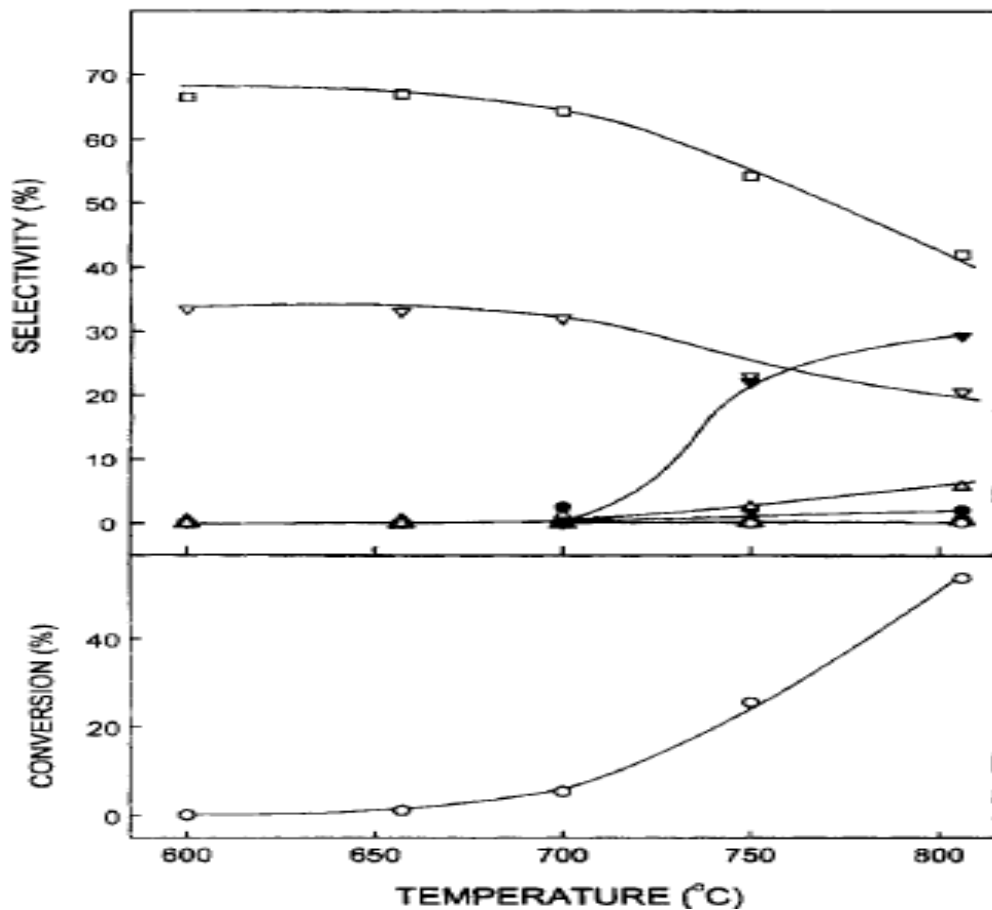


Figure 2.3.6 Influence of temperature on the thermal cracking of propane [18]

Feed = a mixture of propane, steam, and thiophene;
 $H_2O/C_3H_8 = 0.5$; thiophene/ $C_3H_8 = 10^{-4}$; and GHSV =
 $3,000 \text{ h}^{-1}$. \blacktriangle —CO; \circ —CO₂; ∇ —CH₄; \square —C₂H₄;
 \bullet —C₂H₆; \blacktriangledown —C₃H₆; \triangle —C₄₊.

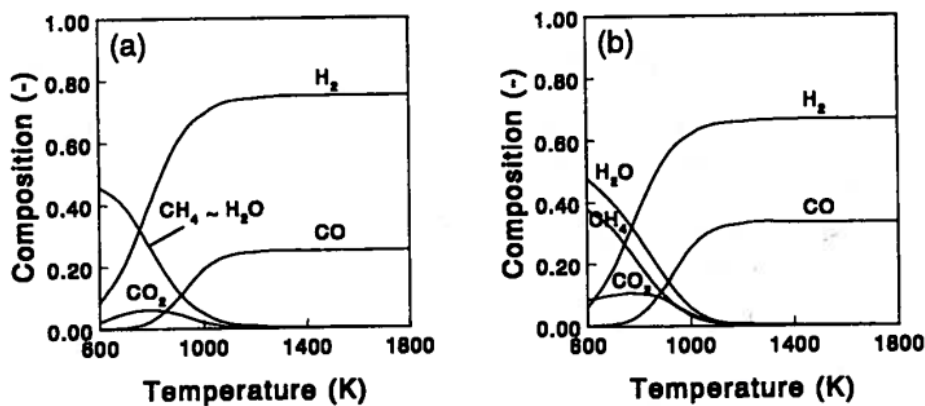
2.4 Synthesis gas: Reactions and thermodynamic data

Table 2.2 presents the main reactions for the production of syngas by steam reforming. Almost the same reactions may be used to describe the coal and biomass gasification. Because different feedstock have a different composition, the various ratios of $H_2O/CH_4(C)$ and $O_2/CH_4(C)$ are applied for syngas production. The reactions equations in table 2.2 are not independent.[4] The synthesis gas system may be described by only three of independent equations [20].

Table 2.2 Reactions during methane conversion with steam and/or oxygen [4]

Reaction	ΔH_{298}^0 (kJ/mol)	
$\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 3\text{H}_2$	206	(1)
$\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$	-41	(2)
$\text{CH}_4 + \text{CO}_2 \rightleftharpoons 2\text{CO} + 2\text{H}_2$	247	(3)
$\text{CH}_4 \rightleftharpoons \text{C} + 2\text{H}_2$	75	(4)
$2\text{CO} \rightleftharpoons \text{C} + \text{CO}_2$	-173	(5)
$\text{CH}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2$	-36	(6)
$\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$	-803	(7)
$\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2$	-284	(8)
$\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$	-242	(9)

The Figure 2.4.1 shows the thermodynamic equilibrium for the steam reforming of methane and for the partial oxidation of methane in the case with stoichiometric feed and 1 bar pressure.



Figur 2.4.1 Equilibrium gas composition at 1 bar as a function of temperature (a) steam reforming of methane; $\text{H}_2\text{O}/\text{CH}_4 = 1$ mol/mol; (b) partial oxidation of methane; $\text{O}_2/\text{CH}_4 = 0.5$ mol/mol [4]

From the figure above can be concluded that the synthesis gas mixtures can be quenched to approximately 1000 K without considerable change in equilibrium gas composition.

2.5 Temperature measurements at high temperature

Temperature measurement at high temperature can be a difficult task, and significant errors can occur. Temperature gradients are the main driving force for the heat transfer. Heat transfer may occur by conduction, convection or radiation. In many cases more than one of heat transfer mechanisms are involved.[14] Processes performed at high temperatures can give a rise to a high temperature gradients in measurement field/points. The consequence may be a wrong temperature measurement or wrong interpretation of the measurement.

In the case, when temperature measurement of flowing gas in a tube is taken by temperature sensor

(thermocouple), both the convective heat transfer and heat transfer by radiation should be taken into account. When hot gas is passing the sensor, the convective heat exchange will occur between the sensor and the gas, and heat exchange by radiation will take place between the sensor and the wall of the tube. The sensor will indicate a temperature between true gas and wall surface temperatures. The Figure 2.5.1 shows how heat is transferred, where the wall temperature T_w is lower than the true gas temperature T_g , ($T_w < T_g$). T_p is a measured temperature. [14]

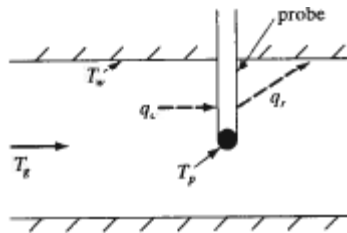


Figure 2.5.1 Temperature measurement of a gas showing radiative and convective heat transfer for a sensor. [14]

At steady state conditions a net heat balance for the sensor can be written as [14]

$$q_c = q_r \quad (17)$$

Where q_c – rate of convective heat transfer to the sensor from the gas [J/s]
 q_r – net radiation heat from the sensor to the wall [J/s]

The convective heat transfer can be expressed as

$$q_c = h_c A_p (T_g - T_p) \quad (18)$$

and heat transfer by radiation can be expressed as

$$q_r = \varepsilon \sigma A_p (T_p^4 - T_w^4) \quad (19)$$

Where h_c – convective heat transfer coefficient [W/m²·K]
 A_p – surface area of the sensor [m²]
 ε – emissivity of the sensor surface, < 1
 σ – constant [W/m²·K⁴]

(17) can also be written on the form

$$T_g - T_p = \frac{\varepsilon \sigma (T_p^4 - T_w^4)}{h_c} \quad (20)$$

The difference between true gas temperature and measured temperature can be calculated by trial and error, when all parameters are known.

However, the coefficient h_c is a function of the system geometry, fluid properties, temperature difference between gas and sensor, and flow velocity. True gas temperature T_g will also be dependent on flow conditions like gas velocity profile and will vary in radial direction when

temperature gradient is present. For turbulent flow the temperature is more uniform in the bulk gas flow because of turbulent mixing, occurring on some distance from the tube wall. For laminar flow conditions, the temperature gradient will be more definite in radial direction.[14]

Emissivity ϵ is the ratio of the emissive power of a surface to that of perfect black body. The surface emits a radiation, depending on its temperature. For all real materials the emissivity is lower than one, $\epsilon < 1$. Emissivity for polished metal surface is low and high for oxidized surface.[14]

During continuously temperature measurements, the surface of the sensor may be exposed to conditions that will change its emissivity. For example, the surface may be oxidized or coke deposits may be formed on the surface.

Both convective heat transfer to the sensor and radiant heat exchange with the wall, and as consequence the measured temperature may vary significantly with a flow conditions. High temperature «gives» high temperature gradients. That all can affect the temperature measurements.

3. APPARATUS AND PROCEDURES

3.1 Pyrolysis equipment: Pyrolyserigg

Pyrolyserigg is a platform that gives opportunity to perform experiments with gases at high temperature reaction conditions, up to 1500 °C. The main parts of the platform include electrical furnace, power supply-and control system, gas lines, gas storage cylinders, quenching system of hot gas mixture, equipment for analysis of product gases (GC-gas chromatograph) and gas alarm system. The platform is connected to central ventilation system in order to get the product gases out of the facility and to avoid accumulation of the gases inside the platform by eventual leakage. A schematic diagram of experimental apparatus is shown in Figure 3.1.1, and picture of the pyrolyserigg is shown in Figure 3.1.2

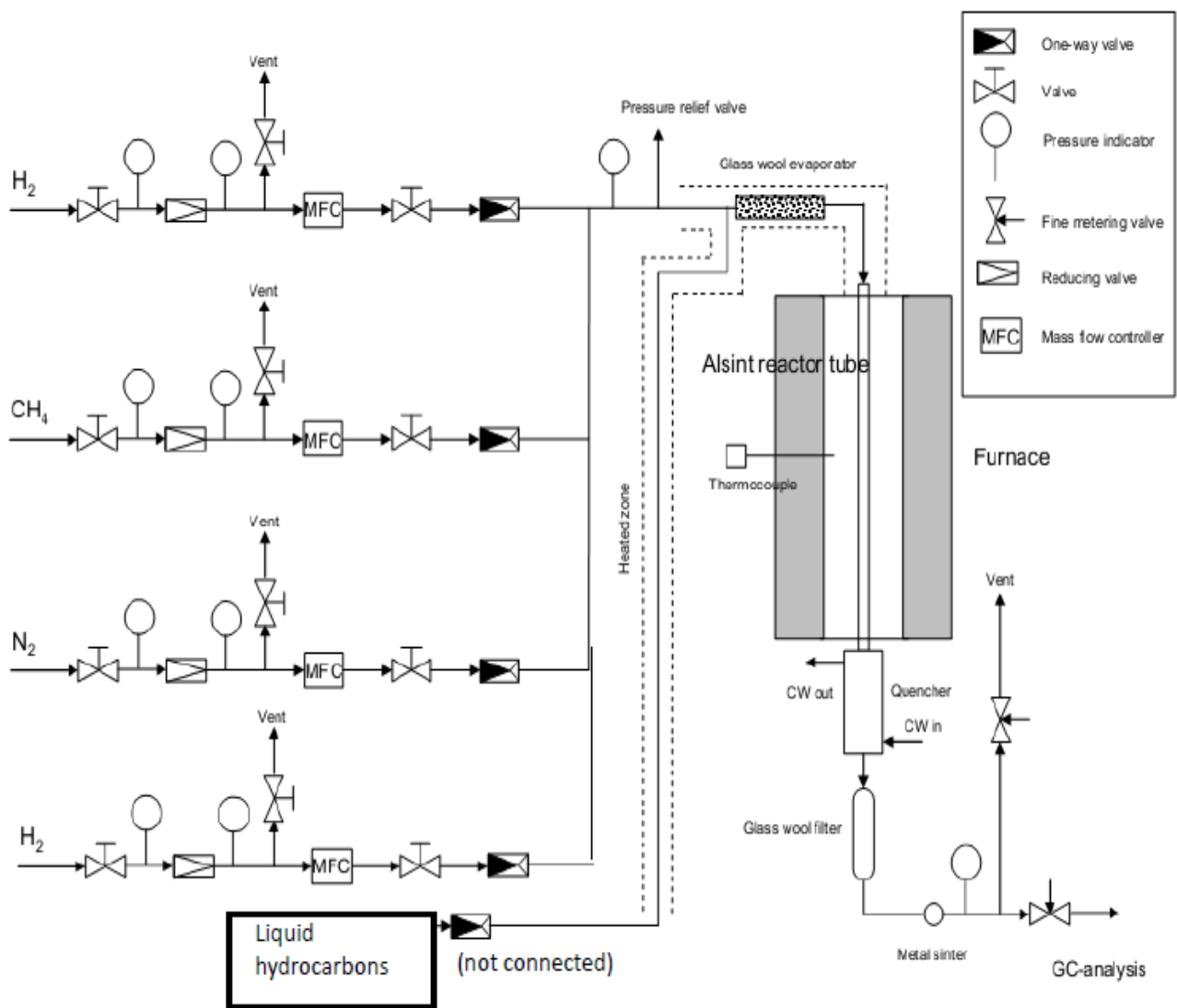


Figure 3.1.1 A schematic diagram of experimental apparatus with some modifications [21]



Figure 3.1.2 Pyrolyserigg and temperature control box to the write

3.1.2 Electrical furnace

The electrical furnace (Kanthal) has a vertical length of 60 cm and gives a total power output of 7 kW. The furnace is placed inside the rig in such a way that a ventilation aperture located above the furnace. This is done with regard to ensure a safe operation, since the probability for leakage in connections with the reactor tube is high. The furnace has two small apertures on the side. These are used to set thermocouples S-type (Rh-Pt) for temperature measurement and control. Schematic drawing of the furnace is in Appendix D



Figure 3.1.3: Electrical Furnace

3.1.2 Temperature regulation

Power supply and temperature control are provided by the «regulation box», which was delivered by Siemens. It was found out that temperature control is best at high temperatures. At temperatures

lower than approx. 1000 °C the temperature inside the furnace is unstable and swings with amplitude of approx. 30 °C in the measurement point. This is probably due to programming of «regulation box».

3.1.3 Gas lines

As shown in Figure 3.1.1, the gas supply to the reactor may occur by four gas lines. During experiments the gases were metered from storage cylinders, placed outside the rig. Two of gas lines (H₂, CH₄) are connected to central gas supply system with opportunity to provide gases from this system. At the moment of experimental work, the central gas supply system was not in use, with exception of technical air which was supplied to GC. If necessary, the line for introduction of liquid hydrocarbons to the reactor may be easily connected.

In experiments after modification of the quenching system, the “nitrogen line” was connected directly to the modified quencher and was used to introduce quenching gas.

3.1.4 Cooling system (Quencher/Cold finger)

The main path of the cooling system is the Quencher/Cold finger. The gas mixture from the reactor outlet passes through the quencher where a rapid cooling of the gas mixture happens. The quencher is of indirect type and water is used as a quenching medium. The quencher is connected to the central cooling system through which the cooling water is circulating. After that methane pyrolysis experiments were completed, the cooling system was modified. The sketch of quencher used in methane pyrolysis experiments is shown in the Figure 3.1.4.

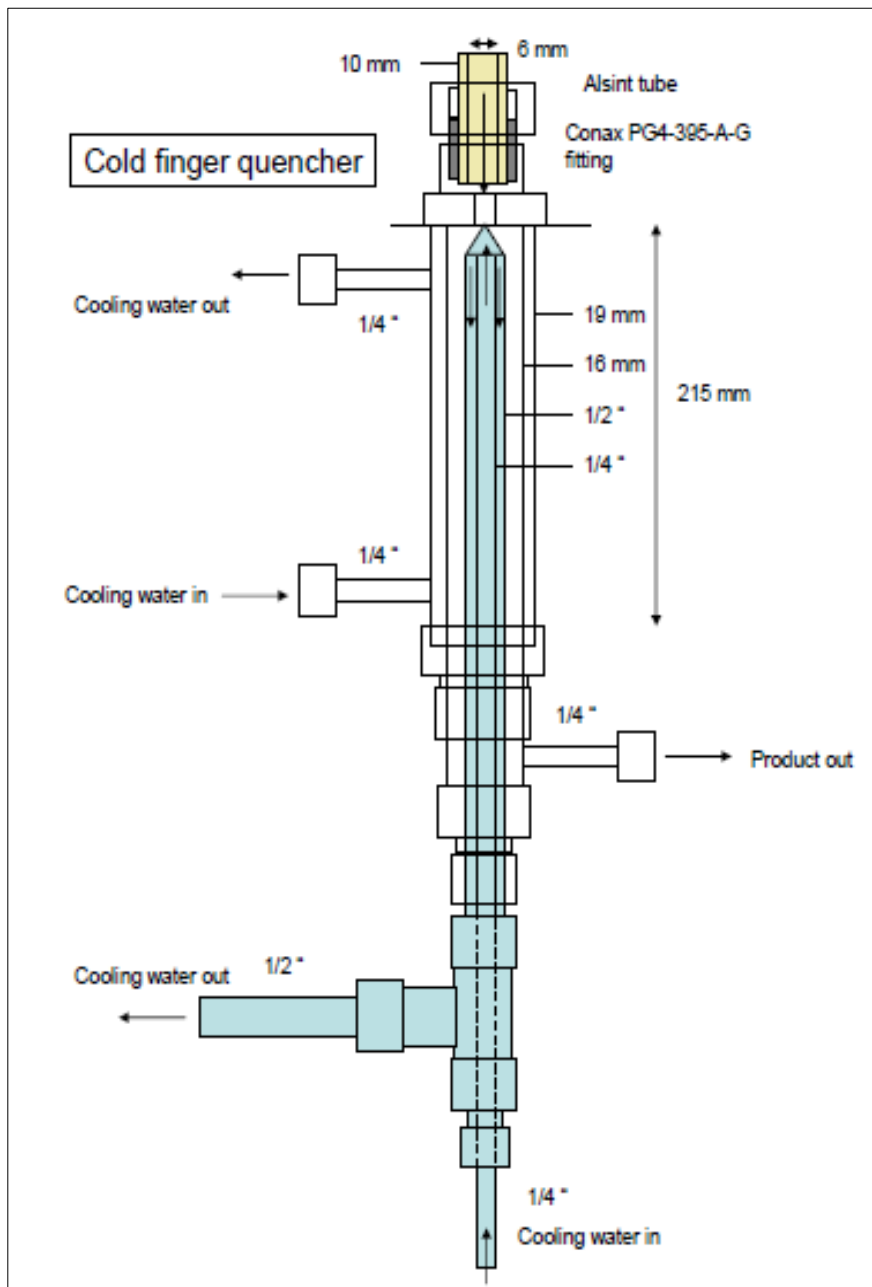


Figure 3.1.4 Quencher [21]

3.2 Analysis equipment

3.2.1 Gas Chromatograph (GC)

Gas chromatograph is a device for analysis of product gases. The GC is of the type (HP 5890 Series 2) equipped with a Thermal Conductivity Detector (TCD) (Carbosieve S-2) and a Flame Ionization Detector (FID) (GS-Q). The GC is the old device and some problems have occurred during its exploitation. Some of valves are not working, but it is still possible to use GC.

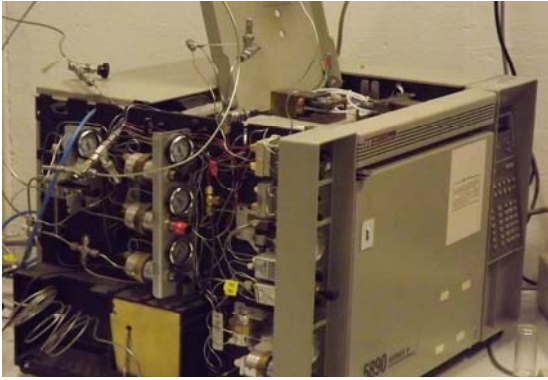


Figure 3.2.1 GC- Gas Chromatograph

3.2.2 Temperature measurements

One thermocouple S-type (Rh-Pt) was placed in upper aperture on the furnace, sticking approximately 5 mm from the inside wall. The thermocouple was connected to the “regulation box” which controlled temperature inside the furnace. It was observed that at high temperatures small displacement in thermocouple's position gave impact on measured temperature. Another S-type thermocouple was placed in lower aperture and was connected to the temperature Logger.

Temperature measurements inside modified quencher were taken by two K - type thermocouples, placed approximately in the middle of the quencher.

Temperature measurements during experiments were saved on PC with exception of Runs 4-12 for methane pyrolysis. The PC was out of stand.

3.3 Pyrolysis of methane

One of suggestions in the end of specialization project [23], which form the basis for the present work, was to continue with methane pyrolysis. The pyrolysis experiments have been repeated because of some inconsistencies during experiments in the specialization project. The experimental conditions were chosen in the way to verify the results that was obtained before[21], and are listed in Table 3.1.

Table 3.1: Experimental runs. Reaction temperature, feed composition by MFC, inner diameter of the reactor tube, residence time (at normal conditions), reactor pressure (during GC-analysis) for different runs.

Run/ Prøve	Temp. [° C]*	Temp. (logger)	CH ₄ [Nml/min]	H ₂ [Nml/min]	N ₂ [Nml/min]	d _i [mm]	P _{inlet} ** [barg]	τ*** [ms]
1	1450	1488-1495	150	3600	140	3	2,2-3,2	49
2	1450	1493-1503	250	3500	140	3	1,6-2,4	49
3	1450	1498-1512	500	3435	140	3	1,3	47
4	1450	--	100	3650	140	3	0,8	49
5	1450	--	150	3600	140	3	0,8	49
6	1450	--	250	3500	140	3	0,8	49
7	1450	--	400	3350	140	3	0,9	49
13	1450	--	500	3250	140	3	1,2	49
8	1400	--	100	3650	140	3	1,0	49
9	1400	--	150	3600	140	3	1,0	49
10	1400	--	250	3500	140	3	1,0	49
11	1400	--	400	3350	140	3	1,1	49
12	1400	--	500	3250	140	3	1,2	49

* Temperature is given as reference temperature at upper measurement point at furnace wall (thermocouple sticking approximately 5 mm from the inside wall of furnace)

** Reactor pressure varied during GC-analyses for Runs 1 and 2. The results from these runs are not taken into account.

***Residence time is calculated, based on estimation of reaction zone from specialization project [23]

3.3.1 Procedure: methane pyrolysis

Pyrolyserigg is equipment that was used for the methane pyrolysis. Gas flows of CH₄, H₂ and N₂ were adjusted by mass flow controllers (MFC) accordingly to planned Runs and in a way to give the same residence time. High dilution with hydrogen and short residence time were applied in order to avoid formation of coke. Two GC – analyses of feed gas were taken for each gas mixture composition. The furnace was heated up to setpoint temperature. After 5-10 minutes 1. GC – analyse was initiated. Three GC – analyses of product gas mixture were taken for each Run. Temperature inside furnace, pressure to the reactor inlet and outlet were registered for each GC – analysis.

Experiments were started with a lowest methane concentration and nitrogen flow was held constant. The alsint ceramic tube with inner diameter 3 mm was used as a reactor. The product gases were quenched at the reactor outlet by annular water – cooled quencher. After passing the quencher, product gases were filtered for coke particles in a box filled with a glass wool and afterwards, in a metal sinter (15 microns).

When pyrolysis experiment was finished a small flow of N₂ (50 Nml/min) was used to purge the gas lines in approx. 30 min.

3.3.2 Procedure: reactor regeneration

In Runs 1-2 pressure build-up at reactor inlet was observed. This is an indication of extensive coke formation and plugging of the reactor tube. Reactor was regenerated by burning off coke in air.

The methane storage cylinder was replaced by the air storage cylinder. The gas lines were emptied of gas previously. After run 1 the reactor regeneration was performed by procedure given by [21]: (20 Nml/min) of air diluted in N₂ (250 Nml/min) at 1000 °C. Decoking was very slow, no marked pressure decrease after four hours with regeneration.

It was decided to increase flow of air to (80 Nml/min) and temperature to 1100 °C. Cold water was disconnected during decoking. Decoking was finished when pressure at reactor inlet was 0,2 barg. The last regeneration procedure was applied after Runs 2 and 3.

[21] has mentioned that the Grafoil sealant may be exposed to oxidation when high flow of air is used.

3.4 Modification of cooling system

After the methane pyrolysis experiments were completed and the work of the Pyrolyserigg was verified, the cooling system could be modified in order to perform *quenching experiments* with hydrocarbons. The quencher with opportunity to introduce hydrocarbons into hot gas has been designed. It was mentioned in [23] that the quencher design is of great importance in order to study the quenching concept. The quencher should be designed in a way that gives a good gas mixing properties, minimal heat losses to the room (operate in adiabatic regime), opportunity for temperature measurement of outcoming gases and opportunity to remove coke deposits.

In the absence of practical knowledge about how such quencher could be constructed, a start point was to make a simplest possible design. A sketch of the proposed quencher design is shown in the figure below.

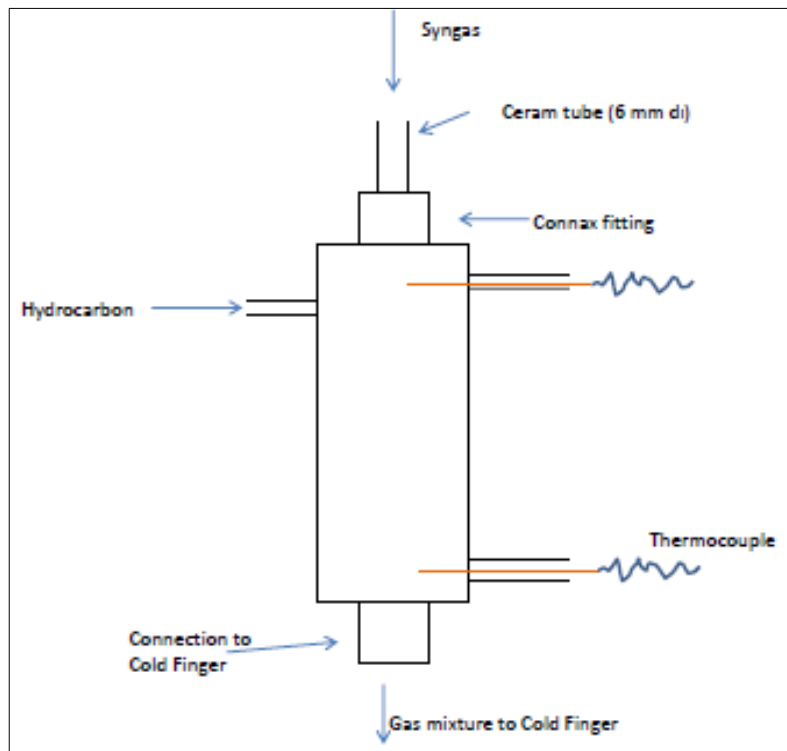


Figure 3.4.1 A sketch of proposed quencher design

This type of design should give opportunity to introduce cold hydrocarbon into hot gas that is heated by high temperature furnace. At the same time, the temperature of the injected hot gas and temperature at the outlet of the quencher could be measured. It was also proposed to install a nozzle at the hydrocarbon inlet or use some packing material inside the quencher to improve gas mixing. This idea was dropped because of expected coke formation that would result in plugging of the quencher and/or hydrocarbon inlet.

The following aspects were considered for the choice of material of construction: tolerance for high temperature, surface effects and easy-to-handle. Quartz or steel were proposed as materials. Quartz material tolerates high temperatures and surface effects are reduced in comparison to steel. The surface effects were considered to be of minor importance for the study of quenching concept at this stage. Stainless steel was chosen as material of construction because it is easy-to-handle and its tolerance to high temperatures. A path of *Connax* fitting was welded to the one end of the steel tube to provide connection with a ceramic tube. On the other end of the tube a *Swagelok* fitting was welded to connect the new quencher to the «cold finger». Ports for thermocouples and hydrocarbon inlet were also welded to the tube as shown on the sketch above.

It was also necessary to modify the «cold finger». A piece of tube with a *Swagelok* fitting was welded to the upper path of «cold finger». The inner part of the old quencher – actually, the *cold finger* was removed. This was done because of limitation in vertical length that could be applied.

Otherwise, the furnace should be lifted up.

After removal of the inner part, the cooling of gases inside the «cold finger» would occur only by outer shell, and *cold wall* quenching would be less effective. However, it was expected that the hot gas would be quenched by hydrocarbon in the upper section, previously. A detailed sketch of the modified cooling system (new quencher part + modified «cold finger») is shown in Figure 3.4.2.

3.4.1 Volumes of different sections of the cooling system

The cooling system can be divided into three sections:

1. section is a CV defined as in chapter 2.2.4. Ideally, the direct quenching of hot gas by hydrocarbon should be performed inside this section.
2. section is a volume between CV and «cold finger». This section can be considered as «died volume» because temperature measured above the section. The section should be minimal. Initially, it was not planned to have this section: lower point for temperature measurement should be placed write above «cold finger».
3. section is volume where the gas mixture is cooled indirect by water. The gas mixture should be at approximately room temperature when it leaves this zone.

Table 3.2: *Calculated volumes and residence times for different sections inside cooling system*

	Volume [ml]	Residence time [ms] at gas flow 6250 [Nml/min]
Section 1	31,4	301
Section 2	43	413
Section 3	43	413

3.4.2 Detailed sketch of the modified cooling system

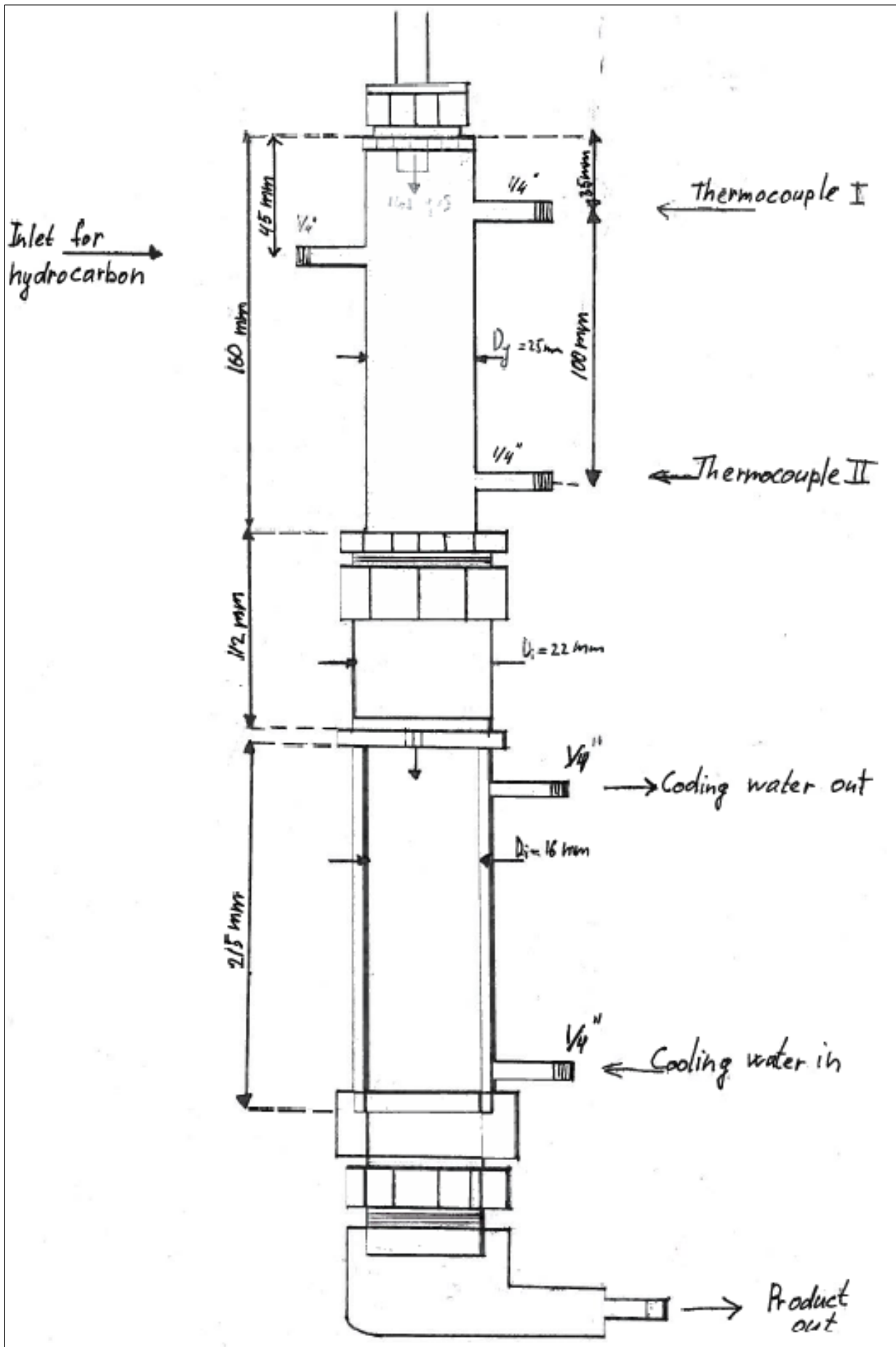


Figure 3.4.2 A detailed sketch of modified cooling system.

3.5 Experiments with a hot inert gas – nitrogen, «quenched» by methane or propane

After modification of cooling system was finished and new quencher was installed, a set of experiments with a hot inert gas (N_2) was performed. Three types of experiments were made: experiments with only nitrogen gas, experiments with nitrogen gas «quenched» by methane and nitrogen gas quenched by propane. Experiments, where *synthesis gas* should be quenched by propane were planned, but were not performed, because the furnace has been out of stand.

1) N_2 gas was heated up in alsint tube, ($d_i=3$ mm) in the furnace at different setpoint temperatures, ranged from 1000 to 1450 °C, and was send through the cooling system. Different gas flows were applied, 100 – 7500 [Nml/min]. Temperature variations in two measurement points inside the quencher were measured and registered by temperature Logger. The pressures into reactor system and out of reactor system were registered. The main purpose of experiments with inert nitrogen was to study the system's behaviour.

2) In experiment with methane, a cooling effect of introduction of cold inert was investigated. It was expected that the methane acts as inert at applied conditions, and that the cooling of hot nitrogen flow will occur mainly by dilution with cold methane.

The furnace was heated up to setpoint temperature 1200 °C. The N_2 flow was setting to 6250 [Nml/min]. After one hour, approximately a steady state condition was reached, $T_1=908$ °C $T_2=605$ °C. Than, CH_4 at room temperature, 506 [Nml/min] was introduced to the quencher. Two GC – analyses were taken afterwards. GC – analyses confirmed that the methane acts as inert.

NB! (T_1 - temperature at upper measurement point; T_2 – temperature at lower measurement point inside Quencher)

30 min after the methane was introduced, $T_1=903$ °C and $T_2=623$ °C. Its mean that temperature drop at upper point is 5 °C and temperature increase at lower point is 18 °C. The methane flow was stopped.

The N_2 flow was reduced to appr. 2500 [Nml/min]. After 20 minutes $T_1=810$ °C and $T_2=490$ °C. Again, 506 [Nml/min] methane was introduced and no cooling effect was observed.

3) Since experiments with methane did not give expected cooling effect, it was proposed to use propane as a quenching gas. The quenching would occur both by dilution and by endothermic reactions of propane.

The MFC, used for methane gas, was calibrated for propane. A maximum obtainable propane flow with this MFC was 246 [Nml/min]. As in the case of experiment with methane, the furnace was heated up to 1200 °C and nitrogen flow was setting to 6250 [Nml/min]. After 1,5 hour appr. steady state was reached, $T_1=897$ °C and $T_2=608$ °C. Then, 246 [Nml/min] of propane gas was introduced to the quencher.

90 minutes later, $T_1=895$ °C and $T_2=621$ °C. Again, no cooling effect was observed. GC - analyses were failed at this experiment: problems with sample injection.

It was decided to increase the temperature of hot nitrogen and use higher propane flows in later experiments. It was expected that cooling effect would increase because of higher dilution with cold gas and higher conversions of propane at higher temperature. It was also necessary to change MFC for propane with a MFC that could give higher flows. Experimental conditions in experiments where hot nitrogen was «quenched» by propane and GC – analyses of product gases were taken, are summarized in Table 3.3

Table 3.3: Experimental conditions in Nitrogen/Propane experiments (alsint tube used for heating up N_2 , $d_i = 6$ mm)

Run	Temperature [°C] ⁱ⁾	T_1 [°C] ⁱⁱ⁾	T_2 [°C] ⁱⁱ⁾	N2 [Nml/min]	Propane [Nml/min]	P_{inlet} [barg]	τ [ms] ⁱⁱⁱ⁾
14	1200	902-898	606-616	6250	246	0,6	290
15	1200	902-904	606-626	6250	143	0,6	295
16	1200	906-885	605-584	6250	445	0,6	281
17	1200	906-863	605-522	6250	998	0,6	260
18	1300	976-971	667-661	6250	143	0,6	295
19	1300	976-964	667-640	6250	246	0,6	290
20	1300	976-951	667-613	6250	445	0,6	281
21	1300	976-926	667-552	6250	998	0,7	260
22*	1450	1186-1175	774-769	6250	143	0,6	295
23	1450	1193-1071	745-611	6250	998	0,6	260
24	1450	1193-1061	745-661	6250	445	0,6	281

3. Setpoint temperature to the furnace

4. Measured temperature in upper and lower points inside quencher, given on the form (xxx-yyy), where xxx is a temperature at «steady state»: before propane is introduced.
yyy is a temperature registered during the last GC – analysis for the run, after propane introduction.

5. Residence time for the gas mixture inside CV - defined as in chapter 2.2.4

* Run 22, only 1 GC – analysis is taken; problem with propane flow (probably because of plugging of inlet or MFC failed)

4. RESULTS

4.1 Pyrolysis of methane: Conversions, Selectivities and Yields

The main objectives of the pyrolysis experiments were to verify the results, obtained in earlier experiments, and to validate that the *Pyrolyserigg* work properly. Methane conversions, selectivities and yields of products for different experimental conditions were calculated from gas chromatographic analysis. Methane concentration present in the figures below is calculated from TCD – measurements of feed gas mixture.

Three *Sets* of Runs accordingly to Table 3.1 were done: i) Runs 1,2,3
 ii) Runs 4,5,6,7,13
 iii) Runs 8,9,10,11,12

The Figures 4.1.1 and 4.1.2 show how methane conversion increases with an increase of methane concentration at temperatures 1400 °C and 1450 °C. The figures show estimated methane conversion, based on both FID and TCD – measurements.

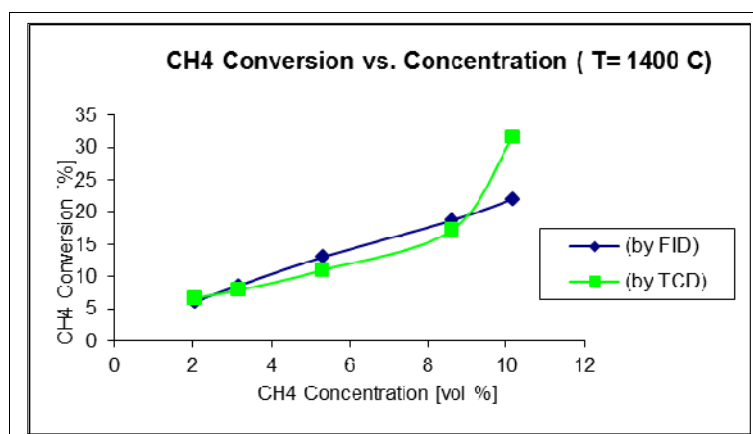


Figure 4.1.1 Methane conversions given by FID and TCD, T = 1400 °C, Set iii).

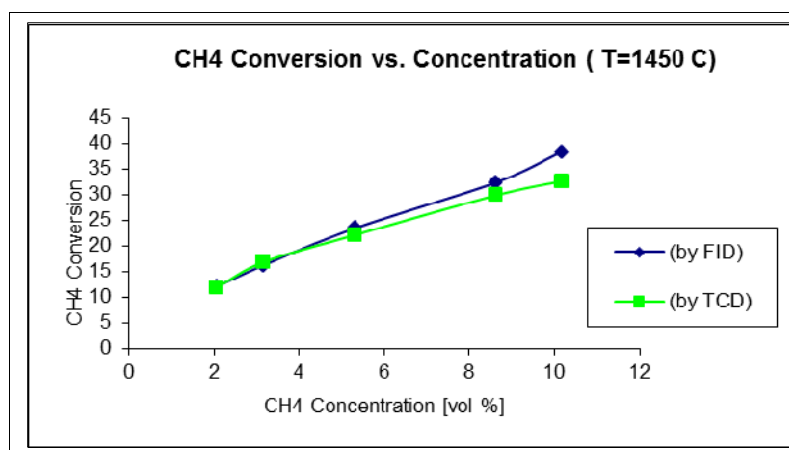


Figure 4.1.2 Methane conversions given by FID and TCD. T = 1450 °C, Set ii)

In the Figure 4.1.3 the methane conversion (given by FID) is plotted against methane concentration for different *Sets*: i) ii) iii). In addition a set from initial tests [23] and *Reference Set* is plotted in the figure. The *Reference Set* shows conversions of methane that were achieved at Pyrolyserigg by [21]. The reported experimental conditions for the *Reference Set* are $T = 1450\text{ }^{\circ}\text{C}$, $d_i = 3\text{ mm}$, $\tau = 41\text{ ms}$.

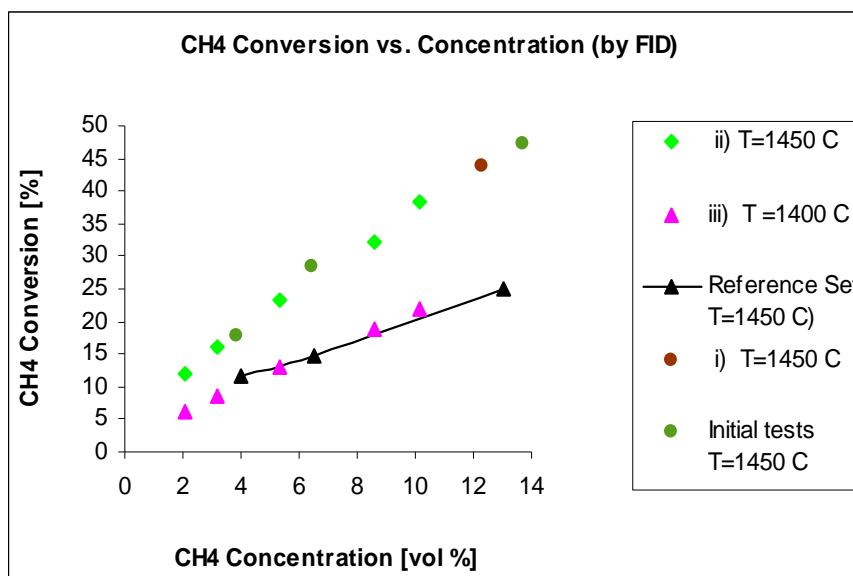


Figure 4.1.3 Methane conversion as a function of methane concentration for different experimental Sets

Ethylene and acetylene are main products of methane pyrolysis at applied experimental conditions. However, C_3 C_4 C_5 –hydrocarbons, benzene and coke were formed in some experiments. The selectivities and yields of products were calculated based on FID measurements. It is also assumed that coke is not produced. This should be acceptable assumption since low methane concentrations and short residence time are applied.

In the Figure 4.1.4 the selectivities to ethylene and acetylene are plotted as a function of methane conversion for temperatures 1400 and 1450 $^{\circ}\text{C}$.

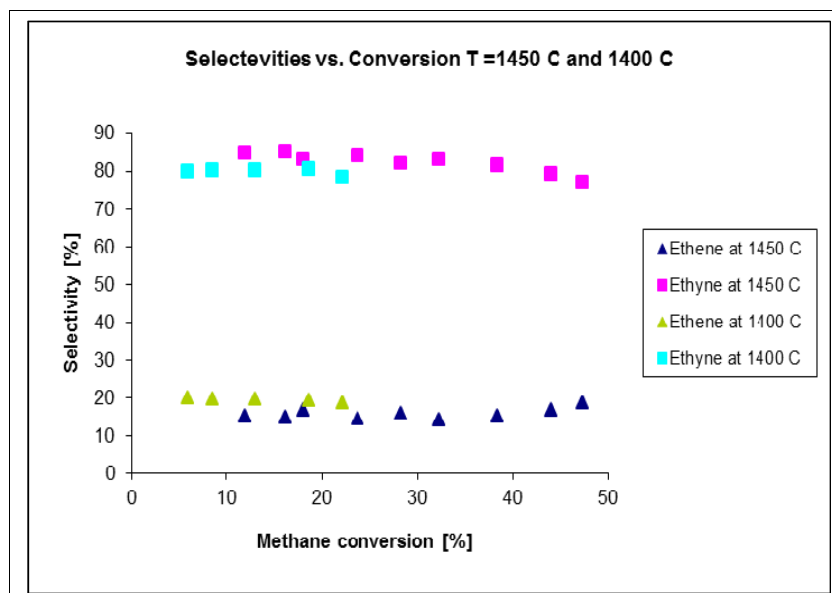


Figure 4.1.4 Selectivity to ethylene and acetylene as function of methane conversion

At temperature 1400 °C and applied experimental conditions very small amounts of hydrocarbons containing more than two carbon atoms were formed. The data from experiments at 1450 °C are more representative, and selectivities for C₃-C₅ hydrocarbons and benzene are plotted in the Figure 4.1.5, as a function of methane conversion.

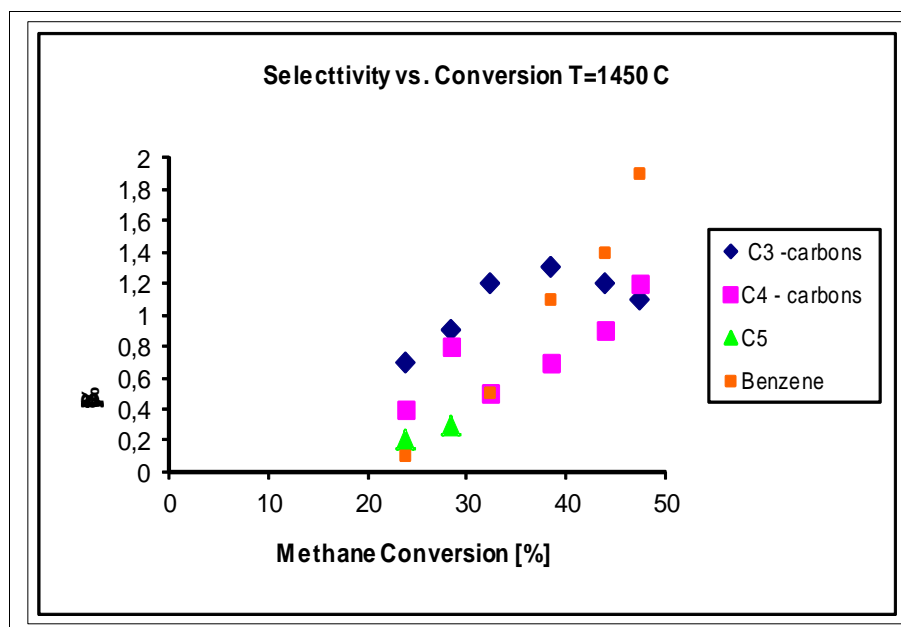


Figure 4.1.5 Selectivity to C₃-C₅ hydrocarbons and benzene

The selectivities to ethene and ethyne at 1450 °C is plotted as a function of methane concentration in the Figure 4.1.6

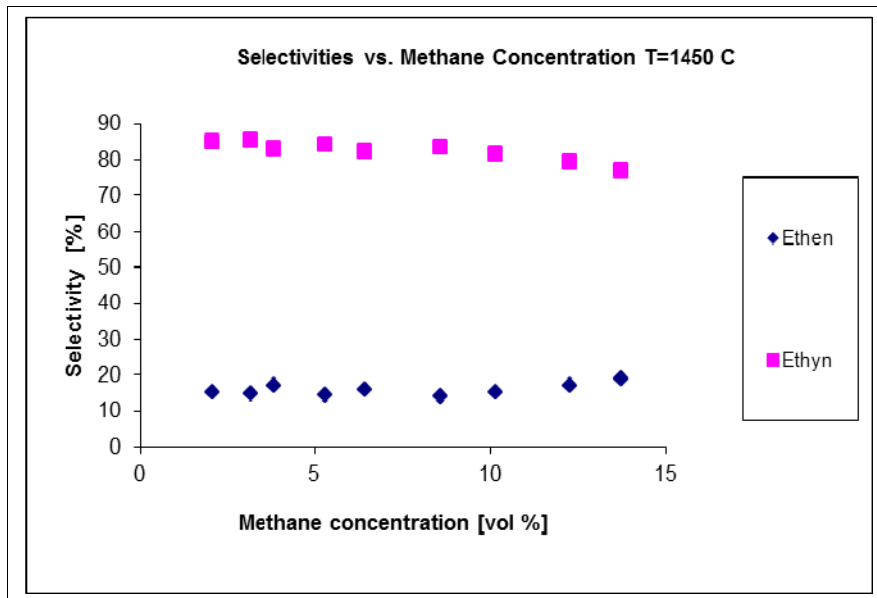


Figure 4.1.6 Selectivity to ethene and ethyne against methane concentration

The Figure 4.1.7 represents yields of ethene and ethyne that were achieved in experiments. The yields are plotted against methane conversion for the temperatures 1400 and 1450 °C.

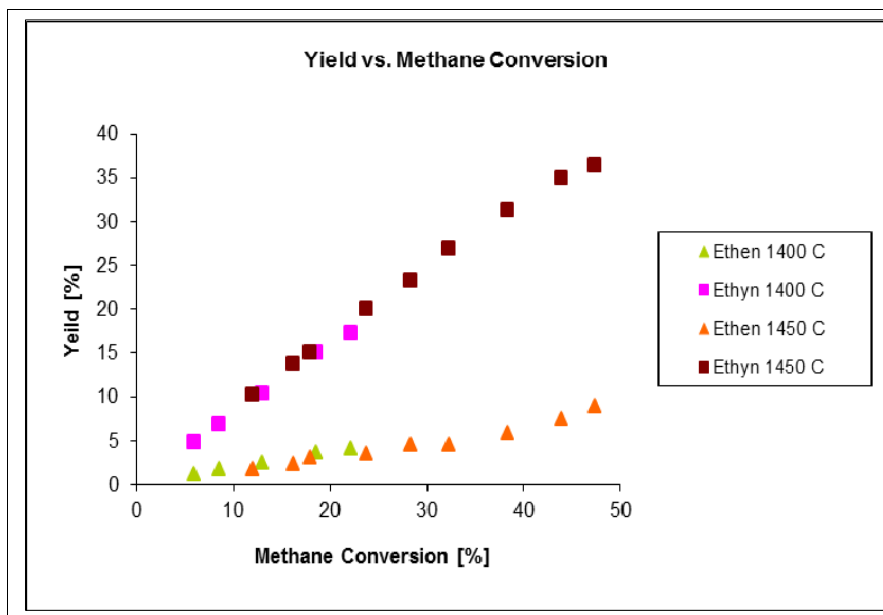


Figure 4.1.7 Yields of ethene and ethyne as a function of methane conversion

4.2 Experiments with hot inert – nitrogen. Practical knowledge about quenching system. Problems.

After the modified quenching/cooling system was installed, a set of experiments with a hot nitrogen gas was performed. The intention of these experiments was to study quenching system's behaviour: heat losses, which temperatures could be obtained inside the quencher, which gas flows could be applied, pressure variations and other practical knowledge.

Before experiments were started, it was assumed that temperature about 1300 – 1400 °C could be obtained inside the quencher. The measurement of such high temperature could be performed by S – type thermocouples which are very expensive and breakable. The first problems have occurred during leakage testing of the system. The gas leakage was identified at inlet, where thermocouple was placed, as shown in Figure 4.2.1. During the leakage was making tight, thermocouple was broken. Other S – type thermocouple was broken later, after an unlucky event. Then, it was decided to use K – type thermocouples for the temperature measurements. These are more durable, but temperature limitation for K – type thermocouples is around 1200 °C.

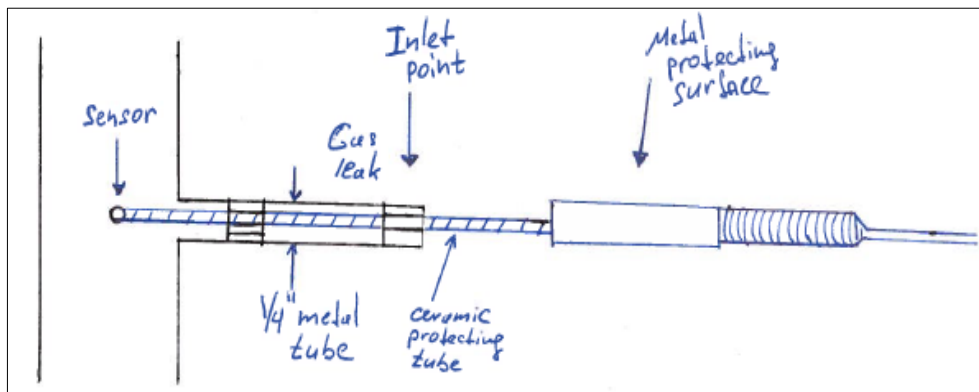


Figure 4.2.1 A sketch shows how S – type thermocouple was placed at inlet of quencher

A teflon sealing was used in junction thermocouple/tube inlet. When high temperatures are applied, it is a risk that sealing can be destroyed and gas leakage can occur. Experiments have shown that a 20 cm long $\frac{1}{4}$ - tube connected to the quencher results in sufficient cooling of junction at upper measurement point. At lower measurement point the temperature was much lower and 10 – 15 cm tube was enough to prevent destruction of the sealing.

In the first experiment with only nitrogen, the furnace was heated up to 1450 °C, in the same manner as it was done in methane pyrolysis experiments. The N_2 flow was 580 [Nml/min] and *quencher was not isolated*. The maximum temperature that was obtained in the upper measurement point $T_1 = 513$ °C, the temperature measurement in lower point failed (problem with K – thermocouple).

The experiment was repeated but quencher was isolated with quartz wool. The maximum temperature was $T_1 = 775\text{ }^\circ\text{C}$ at this time. The experiments showed that the heat losses are very high. Suggestion was to apply higher flows of nitrogen. For this purpose, nitrogen storage cylinder was connected to «hydrogen-line-2» that has high-flow MFC.

The last experiment was repeated with higher nitrogen flows. Pressure increase in the system was observed when high gas flows were applied, P_{in} 3,6 barg and P_{out} 3,4 barg at 6250 Nml/min. The sources of pressure increase were identified: a metal sinter and a needle valve. These were removed from the gas lines to avoid build-up of pressure. The maximum obtained temperatures were $T_1 = 1160\text{ }^\circ\text{C}$ and $T_2 = 667\text{ }^\circ\text{C}$ at 6250 Nml/min nitrogen flow and setpoint $T = 1450\text{ }^\circ\text{C}$.

Table 4.2.1 represent *approximately* «steady state» temperatures that were measured inside the quencher for different nitrogen flows and setpoint temperatures at the furnace. Temperatures T_1 and T_2 are dependent on heat losses and thus on isolation around quencher. The amount of isolation was different in some experiments.

Table 4.2.1: Measured “steady state” temperatures at upper and lower points for different setpoint temperatures and nitrogen flows

Flow N ₂ [Nml/min]	580	2500	3760	6250	6250	6250
Setpoint T [°C]	1450	1450	1450	1450	1300	1200
T_1 [°C] upper point	775	1062	1130	1195	977	909
T_2 [°C] lower point	-	536	630	764	671	610

Before experiments with hot nitrogen were performed, it was assumed that quencher would operate adiabatic (minimal heat losses to the surroundings). At least, it was expected that the heat loss between upper and lower measurement points would be minimal. As shown in the Table 4.2.1 a temperature gradient is very high between measurement points, around 30-50 °C/cm. The high temperature gradient between measurement points may be explained by flow pattern of gas inside the quencher and temperature gradient in radial direction. Later, it was suggested to investigate temperature gradient in radial direction but experiment was not done because the furnace was destroyed. Another explanation may be that the thermocouples showed wrong temperature. However, thermocouples were tested in temperature calibrator device and showed *write* temperature up to 500 °C that is a limit temperature for calibrator. ΔT for thermocouples were 15 °C at this temperature.

4.2.1 Limitation of maximum obtainable temperature in the quencher

As a consequence of heat losses and temperature gradients, the maximum registered temperatures were 1195 °C at upper point and 764 °C at lower point. So, the achieved temperatures were much lower than it was supposed and high heat loss was a problem. An extra layer of insulation around the quencher has been used, without significant temperature increase was marked. An increase of gas flow to around 7500 Nml/min did not give subsequent temperature increase. Vice versa, the temperature started to drop at upper point, as shown in the Figure 4.2.2.

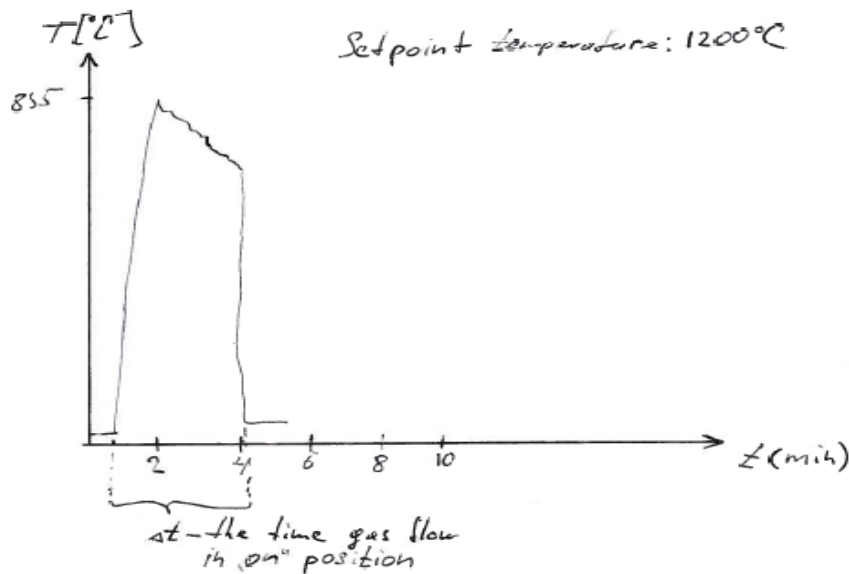


Figure 4.2.2 Sketch of how temperature drop with time at *upper* measurement point when high gas flow is applied, 7500 [Nml/min]. Setpoint temperature, 1200 °C.

The reason for the temperature drop may be that the heat transport from the ceramic tube to the passing gas begins to be a limitation. As amount of gas passing the tube increases to some level, the tube begins to cool down to some extent and wall temperature becomes lower. This results in reduction of gas temperature. The effect of temperature decrease can be compensated by increase of setpoint temperature on the furnace, but furnace has operating temperature limitation 1500 °C. It seems that the reduction of heat loss is an only way to go up in temperature if necessary.

4.2.2 Connection Quencher – Ceram Tube

Conax fitting with grafoil sealing was used to connect ceram tube and modified quencher. In methane pyrolysis experiments ceram tube was connected directly to the cold finger. This gave a relative good cooling of the connection to the ceram tube, and it was possible to disconnect fitting after experiments in usual way by using spanners. For modified quencher, the cooling of the

connection is less effective, and fittings are exposed to much higher temperatures. This results in welding of the connection. A metal sawback was used to cut the connection, and then a new Conax fitting could be welded to the quencher. This procedure is somewhat cumbersome and time consuming. The Conax fitting was replaced two times because of identified gas leakage in the connection.

The gas leakage in Conax fitting was detected during leakage tests, *after* experiments with setpoint temperature 1450 °C were performed. Presumably, grafoil sealing was destructed as a consequence of very high temperature conditions. Other problem was that the ceramic tube was *easy broken* (in connection) while the quencher was disconnected from the tube. This indicates that the tube material and fitting are exposed to both mechanical and thermal stresses, which cause the weakness of the tube material and deformation of the carbon sealing. The leakages were not detected at lower setpoint temperatures. A deformed sealing and a piece of ceramic tube that remains in the fitting are shown in the Figure 4.2.3



Figure 4.2.3 Picture of connection quencher to ceramic tube after use. Red arrow points to a cavity/hole in grafoil sealing.

4.2.3 Coke formation and plugging of the quencher

It was mentioned in section 3.4 that a simple quencher design was chosen, because it was expected that the coke formation and plugging of the quencher can be a serious problem during quenching experiments. Experiments, where propane was used as a quenching medium, showed that the coke formation is not a big problem. Coke was produced, but it was produced in small quantities. In experiment with a setpoint temperature 1450 °C and propane flow 140 Nml/min, a temperature increase was registered at some time. At the same moment a control box for MFC showed that the

propane flow decreases by itself. This could be an indication of plugging of hydrocarbon inlet. The experiment was stopped and inlet was tested for plugging with a metal rod. The plugging was not observed. The experiment was continued but higher propane flow was used. No more propane flow decrease was observed. Presumably, the problem lay in used MFC.

4.3 Experiments with hot nitrogen quenched by propane

The main objective of experiments, where propane at room temperature was introduced to the hot nitrogen, was to study a quenching effect of propane introduction by measure temperature drop. On the basis of conversion obtained experimental, the heat consumed in endothermic reactions and expected temperature drop were calculated.

4.3.1 Conversions, selectivities and yields

Conversion of propane, selectivities and yields to typical products were calculated from GC – analyses (by FID) . The calculations do not take into account the coke formation and formation of hydrocarbons with carbon content higher than six atoms. The main identified hydrocarbon products are methane, ethylene and propylene. Ethane, acetylene and C₄ – hydrocarbons are produced in lower quantities. C₅ – hydrocarbons, benzene, coke and tarlike substances were indicated at higher conversions of propane.

Figure 4.3.1 shows conversions of propane when it was used as a quenching medium at different setpoint temperatures. Setpoint temperature is used as reference. The actual temperature conditions are given in Table 3.3. The nitrogen flow was held constant and propane flow was varied.

Volumetric ratio calculated from gas flows given by MFC.

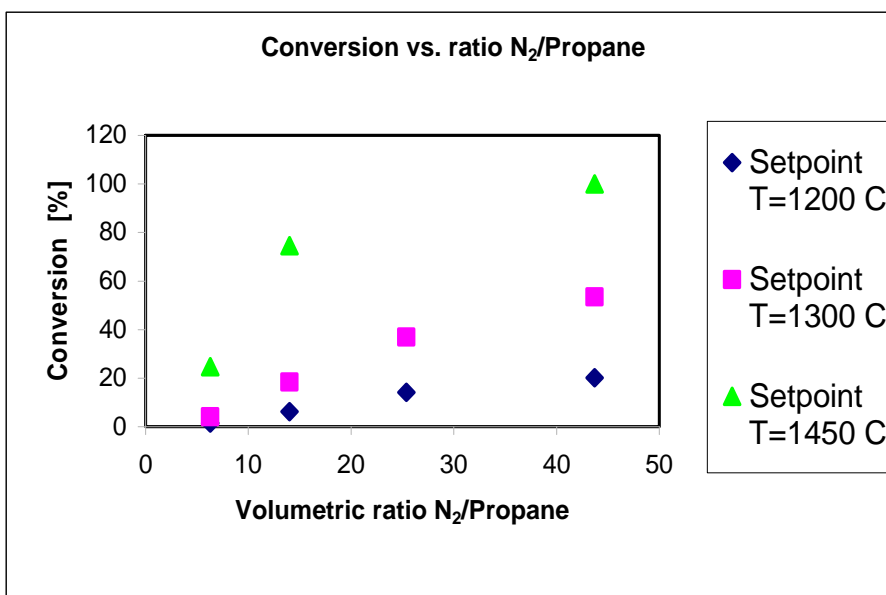


Figure 4.3.1 Total conversion of propane as a function of volumetric ratio N₂/Propane. Flow N₂ 6250 [Nml/min].

Figure 4.3.2 shows calculated selectivities to typical products as a function of propane conversion. The selectivities are influenced of that the conversion is obtained at different temperatures, residence times and N₂/Propane ratios.

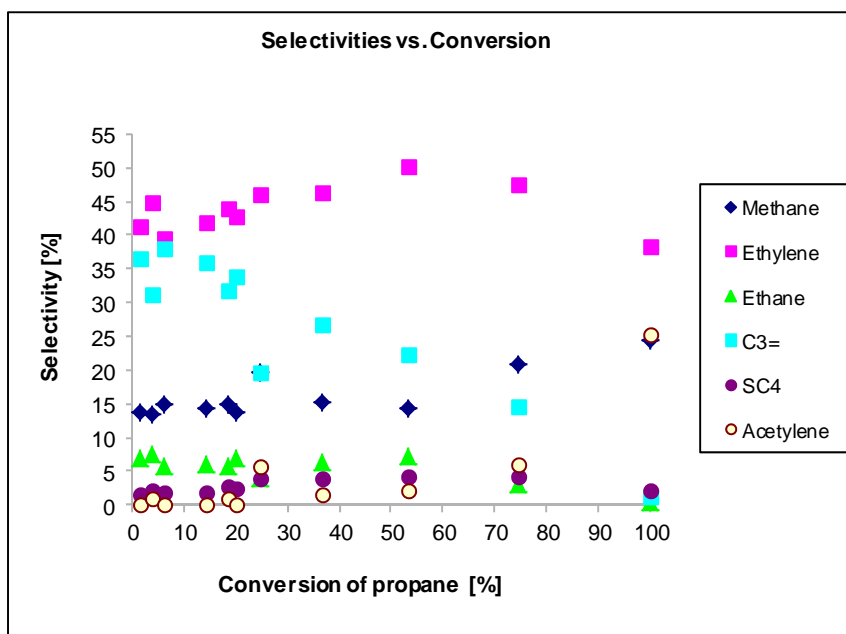


Figure 4.3.2 Selectivity to typical products as function of propane conversion. Temperature range 620-1180 °C.

In the Figure 4.3.3 yields of typical products are plotted as a function of propane conversion.

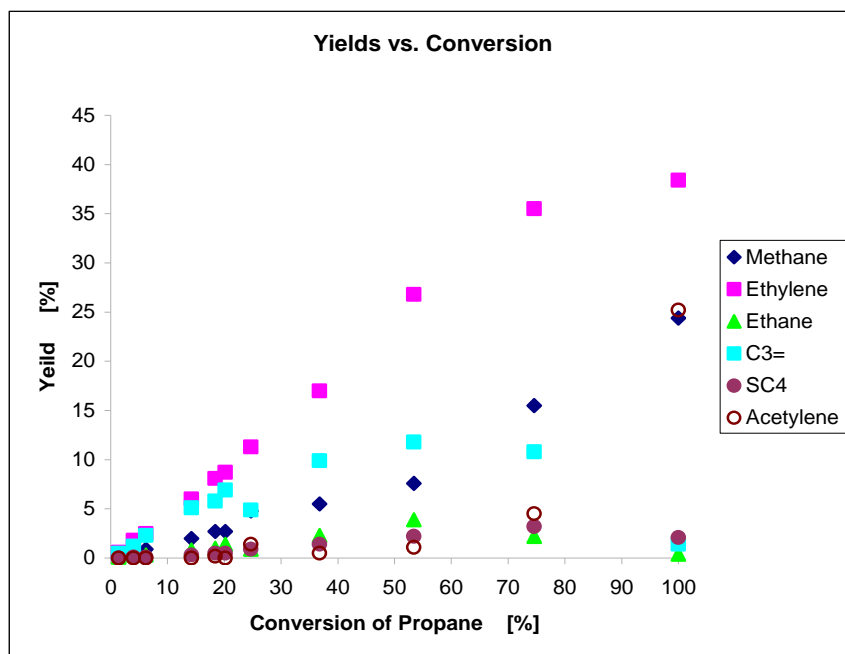


Figure 4.3.3 Yields of typical products as a function of conversion. Experimental conditions are given in Table 3.3

4.3.2 Quenching effect: measured and expected temperature drop

In the Figure 4.3.4 a measured temperature drop at upper measurement point is plotted against volumetric ratio ($N_2/Propane$) for applied setpoint temperatures. Actual measured temperatures are given in *Table 3.3*. Temperature drop calculated as a difference between temperature at «steady state» (before propane is introduced) and temperature registered during the last GC – analysis for the run, after propane introduction.

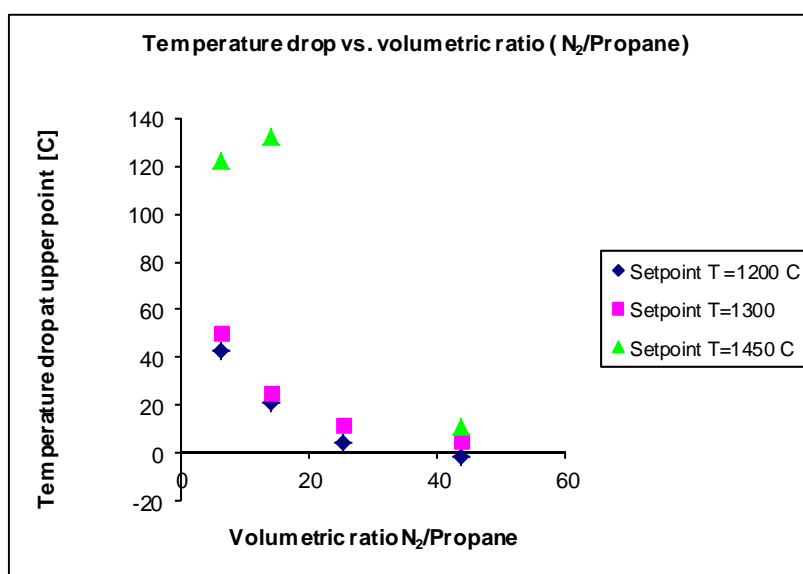


Figure 4.3.4 Temperature drop at upper measurement point as a function of volumetric ratio $N_2/Propane$ gas flows. Nitrogen flow 6250 Nml/min is constant.

In the Figure 4.3.5 a measured temperature drop at lower measurement point is plotted against volumetric ratio (N_2 /Propane) for applied setpoint temperatures. Temperature drop given in the same manner as for upper point.

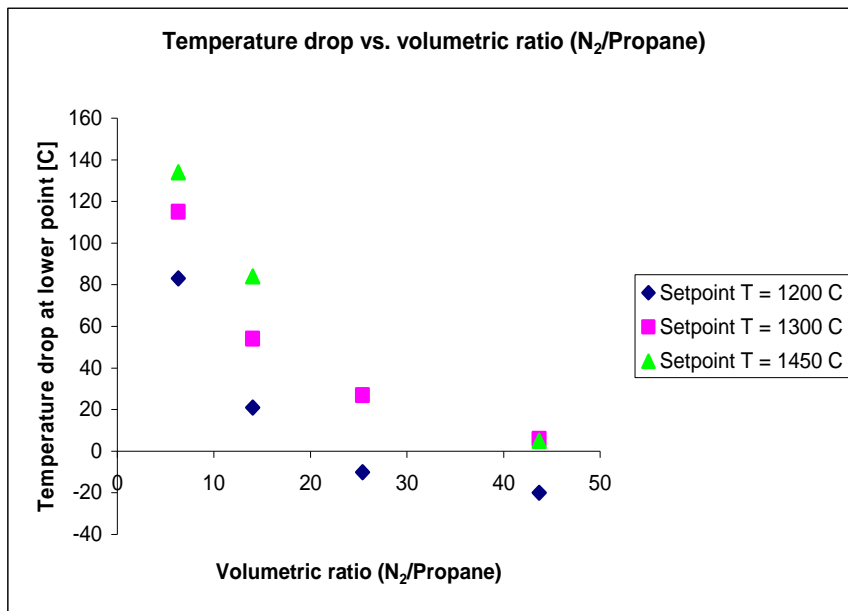


Figure 4.3.5 Temperature drop at lower measurement point as a function of volumetric ratio N_2 /Propane gas flows. Nitrogen flow 6250 Nml/min.

Quenching effect or expected temperature drop is based on calculations from combined energy and mass balance, calculated heat loss and experimental conversions of propane. Calculations are in Appendix C *Combined_Energy_Mass_Balance.xls* and in chapter 2.2.4

Figure 4.3.6 shows expected temperature drop at lower measurement point if propane would act as inert (quenching only by dilution with a cold gas) vs. volumetric ratio N_2 /Propane. Calculation of expected temperature drop based on assumptions: constant heat loss over CV for given temperature regime and constant heat capacities of gases.

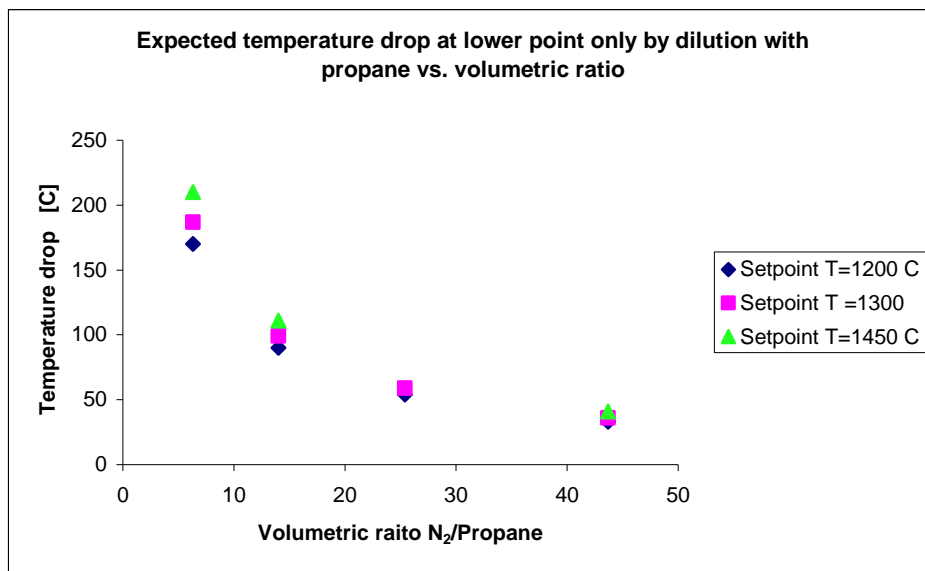


Figure 4.3.6 Expected temperature drop at lower measurement point assumed that quenching occurs only by dilution with propane vs. volumetric ratio N₂/Propane

Figure 4.3.7 shows expected temperature drop at lower measurement point in the case quenching happens both by dilution with cold propane and by endothermic reactions of propane: dehydrogenation and cracking to methane/ethylene. Calculated heat removal by endothermic reactions is based on conversions obtained experimentally. It is assumed that conversion in each reaction is a half of the total experimental conversion and heat of reactions is constant.

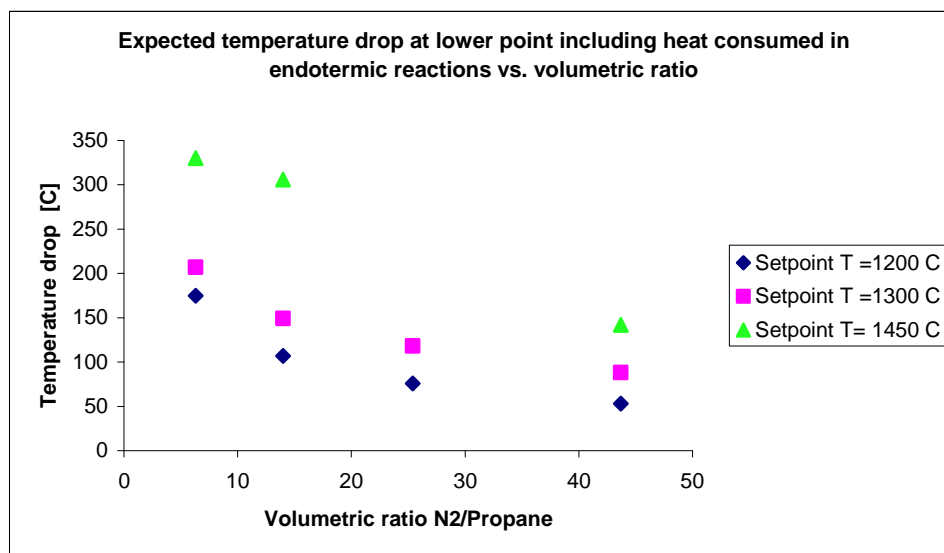


Figure 4.3.7 Expected temperature drop at lower measurement point assumed that quenching occurs both by dilution with propane and by heat consumed in endothermic reactions vs. volumetric ratio N₂/Propane.

5. DISCUSSION

5.1 Pyrolysis of Methane: verification of previous experiments

The conversion was chosen as a useful parameter in order to compare and verify the results from the earlier methane pyrolysis experiments. During *initial tests* of apparatus [23] the obtained conversion was higher than expected. For that reason, it was necessary to repeat experiments. The Set i) was performed. The Runs 1 and 2 were unlikely. Measurements through these runs were accompanied with pressure increase at the reactor inlet. Pressure increase indicates plugging of reactor and extensive coke formation inside the reactor tube. No good reason were found to describe the phenomenon. In later methane pyrolysis experiments plugging of reactor and coke formation were not observed.

Run 3 has shown an unexpected high conversion again. Then, it was suggested to perform a series of experiments at lower setpoint temperature, $T = 1400$ °C. At this temperature the methane conversion is in accordance with the results used from the *Reference Set* that was performed at 1450 °C, as shown in Figure 4.1.3.

The following explanations may be given for the deviation of obtained methane conversion from the conversion used as reference: the temperature measurements can be taken at the furnace wall at two different points. The measured temperature at the bottom path of furnace was around 1500 °C, while it was 1450 °C (set point) at the upper path. The temperature gradient between two measurement points can explain why conversion in *initial test* and in experimental sets i)-ii) was higher than in the *Reference Set*. In addition, at high temperatures there are probably a high temperature gradients in radial direction inside the furnace and measured temperature may be very sensitive to thermocouple's position. A small deviations from the reference position (5 mm from the inside wall) may result in different temperatures "reading" by "regulation box", and as a consequence, different *effective temperature* in the reactor tube. It can be concluded that the temperature control and measurement are essential to interpret the results from the pyrolysis experiments.

As shown in Figures 4.1.1 - 4.1.3, the methane conversion increases almost linearly with an increase in methane concentration. This indicates that the overall consumption rate of methane is the 1. order reaction, that is in agreement with [16] and [22]. Figure 4.1.3 shows that the higher temperatures give higher conversion that is a consequence of increasing reaction rate. The same

conclusion may be drawn looking on the Figure 2.3.2

In Figures 4.1.1 and 4.1.2 the conversions obtained by TCD and by FID are compared. Ideally, the measurements by TCD and FID would give the same conversion, if coke is not formed in the experiment. If coke is formed, the conversion given by TCD would be higher than conversion given by FID. Some points in the figures show that the conversion calculated by TCD is lower than conversion calculated by FID. This indicates that it is an inaccuracy between two measurement methods. An explanation of inaccuracy can be a bad or wrong calibration of TCD.

The Figure 4.1.3 shows that the methane conversions from sets i) ii) and *initial test*, plotted against methane concentration with a reference temperature 1450 °C, follow the same “line”. This is an indication of reproducibility of pyrolysis experiments.

In the Figure 4.1.4 the selectivities to ethylene and acetylene is plotted as function of methane conversion for the temperatures 1400 °C and 1450 °C. The results show that the selectivity to acetylene increases and selectivity to ethylene decreases with an increase in temperature from 1400 to 1450 °C. This is in agreement with results obtained by [16].

However, both experimental and simulated results from [16] show that the selectivity to ethylene decreases with increase in methane conversion at temperatures 1400 and 1500 °C, and selectivity to acetylene has a maximum at 20 – 40 % conversion. As shown in the figure 4.1.4, ethylene selectivity increases slightly with methane conversion, and selectivity to acetylene decreases without identifiable maximum. Deviation of the selectivity curves can be explained by the choice of experimental parameters which were varied to obtain a given conversion. In the first case, the $H_2/CH_4 = 2$ was held constant and residence time was varied. In the second case, the residence time was held constant and methane concentration was varied, and high hydrogen dilutions were applied. As mentioned in chapter 2.3.1, hydrogen dilution has an important effect on kinetics of methane pyrolysis.

Figure 4.1.5 represent selectivities to C_3 - C_5 hydrocarbons and benzene that were obtained in experiments (gas phase products/ coke is not considered). As shown in the figure, the selectivities are lower than 1,5 % in most cases. Low selectivity to benzene and other higher hydrocarbons can be explained by short residence times and high hydrogen dilution that prevents the condensation reactions. The accuracy of these results is not very good. Some problems with identification of

compounds happened and integration curves from GC – analyses were long from perfect for some cases.

In the figure 4.1.6 selectivities to ethene and ethyne are plotted as function of methane concentration. The shapes of the selectivity curves are similar to that for the case where these are plotted as function of conversion. This is probably because conversion varies linearly with methane concentration.

The Figure 4.1.7 shows yields of ethylene and acetylene. The yields for acetylene are higher than for ethylene, and ratio acetylene to ethylene increases with methane conversion. Yields of both ethylene and acetylene increase linearly, and temperature difference about 50 °C have low influence on Yield – Conversion relation.

5.2 Experiments with hot nitrogen quenched by propane

5.2.1 Conversions, selectivities and yields

Conversion

As shown in the Figure 4.3.1, conversion of propane decreases with decreasing N₂/Propane ratio and conversion increases with increasing temperature. At lower N₂/Propane ratios (high propane flows) conversion is low that means that quenching of hot gas occurs mainly by dilution and heat removal by endothermic reactions is low. As temperature of hot gas increases, the propane conversion increases and heat removal by endothermic reactions also increases. At setpoint temperature 1450 °C, measured temperature at «steady state» inside quencher was 1193 – 745 °C (high gradient and high heat loss). If heat loss could be eliminated, a higher conversion could be obtained although at low N₂/Propane ratios.

From Figures 2.3.1 and 2.3.6 can be concluded that high propane conversion can be obtained at temperatures higher than 800 °C at atmospheric pressure. This means that the hot gas could be quenched effective by propane from, let say, 1200 °C to 800 °C. These conditions were not realized experimentally because of presence of temperature gradient and heat loss.

The equilibrium conversion of propane is a function of total pressure in the system, Figure 2.3.1 As a consequence, the quenching efficiency will also be dependent on the pressure of the system. Heat consumption by endothermic reactions will decrease with increasing pressure. Experiments were

performed at $P_{\text{tot}} = 0,6$ barg or 1,6 bara that give something lower conversion than at atmospheric pressure. It can also be mentioned, because synthesis gas is produced often at elevated pressures, the opportunity for the quenching with alkanes may be reduced.

Selectivities

Figure 4.3.2 shows selectivities to typical products as a function of propane conversion. The results are in accordance with a Figure 2.3.5 in that the selectivity to propylene decreases with increasing conversion, selectivity to methane and ethylene increase with increasing conversion and selectivity to ethane is low, $< 9\%$. However, obtained selectivities of methane is much lower than presented in Figure 2.3.5, and selectivity to ethylene and propylene is also sufficiently lower. These deviations can be explained by the differences in experimental conditions. Deviations at higher conversion can also be explained by the fact that the hydrocarbons with more than 6 carbon atoms and coke are not included in calculations. The results at higher propane conversion are more uncertain. The indirect quenching at lower path of cooling system was less effective after removal of cold finger. This can also affect the results.

Yields

Yields of typical products as a function of conversion are presented in the Figure 4.3.3. Yield of ethylene increases almost linearly with propane conversion. Yield of propylene goes through a maximum at 55 % conversion and approach a zero at 100 % conversion. Yield of acetylene is low, $< 5\%$ for the most runs but reaches 25 % at run that gave 100 % conversion. This run is very uncertain because of problems with propane flow.

The idea of chemical quenching experiments was to investigate the opportunity of heat utilization of high energy streams in a desirable way. Effective *chemical quenching* means that the temperature reduction of the hot gas would occur by heat consumption in endothermic reactions to highest possible extent. Thus conversion of quenching medium needs to be highest possible. An other important aspect is which *valuable products* could be obtained at these high conversions. In the case when propane is used as quenching medium, ethylene and propylene are considered to be the most valuable products. It seems that the yield of propylene is very low at high conversions. Ethylene yield is much higher. [17] reports ethylene to propylene ratio is 6 at 95 % conversion. Hydrogen and other hydrocarbons are also produced during propane cracking. It can be mentioned that if the synthesis gas would be quenched by propane the selectivities and yields of products can be

different. As in the case with methane pyrolysis, hydrogen present in synthesis gas will probably inhibit propane cracking. The experiments with synthesis gas were not performed because the furnace has been out of stand.

5.2.2 Quenching effect: measured and expected temperature drop

Temperature was measured at upper and lower points inside the quencher. Figures 4.3.4 and 4.3.5 shows temperature drop at these points after propane was introduced. Temperature drop is plotted as a function of volumetric N₂/Propane ratio for three setpoint temperatures, used as reference temperatures. Actual measured temperatures are given in Table 3.3.

Initially, the temperature drop at *upper point* was not expected at all, because thermocouple was placed above inlet to hydrocarbon and temperature of hot gas alone should be measured. However, the temperature drop increased with decreasing N₂/Propane ratio (increasing propane flow). Assumed that the propane do not reach the sensor at upper point, the temperature drop may be explained by reduction of wall temperature. At higher propane flows, cold gas reaches probably the sensor that result in lower temperature measurement. As seen in Figure 4.3.4 a setpoint temperature has low effect on temperature drop, except for the case $T_{\text{setpoint}} = 1450 \text{ }^{\circ}\text{C}$ and low N₂/Propane ratio.

At *lower point*, setpoint temperature 1200 °C and high N₂/Propane ratio the temperature increase (negative temperature drop on the figure) was observed after propane was introduced. This is probably because the «steady state» was not reached previous to propane introduction. As seen in the Figure 4.3.5, temperature drop increases both with decreasing N₂/Propane ratio and with increasing temperature of hot gas. A higher temperature drop at higher hot gas temperatures for the same N₂/Propane ratio indicates that the quenching is more effective at higher temperatures.

Nevertheless, the obtained quenching effect and measured temperature drop are long from what can be expected. In the figure 4.3.6 expected temperature drop was calculated for the case when quenching occurs only by dilution with a cold gas, propane acts as inert. It was assumed that the heat loss from CV is constant for a given setpoint temperature and do not vary with N₂/Propane ratio. Heat loss calculation is based on measured temperatures at upper and lower points. When results from Figures 4.3.6 and 4.3.5 are compared, one can conclude that, even if quenching would occur only by dilution, the expected temperature drop would be higher than measured. The explanation of deviation is a poor mixing of hot and cold gases inside the quencher.

In Figure 4.3.7 heat consumption by endothermic reactions of propane (dehydrogenation and cracking to methane/ethylene) is included in calculation of expected temperature drop at lower point. Calculated heat consumption is based on propane conversions obtained in experiments. The calculated temperature drop are much higher than measured.

Temperature drop for the two cases, including endothermic reactions and not including, was calculated to give a sense of importance of heat consumption in endothermic reactions in quenching process. At setpoint temperature 1450 °C and N₂/Propane ratio 6,3 expected temperature drop 1,6 times higher in the case when endothermic reactions are included. As N₂/Propane ratio increases to 44, the temperature drop is 3,5 times higher for the same case.

5.3 Quencher Design

As was mentioned in chapter 3.4, a quencher with a simple design was constructed and used to test the concept of chemical quenching. After the experimental work was performed the following can be said about quencher design:

- Very high temperature gradients between measurement points registered. The temperature gradient increases with increasing gas temperature and decreases with increasing gas flow.
- Heat losses are high and maximum obtainable temperatures inside the quencher are low, 1195 – 795 °C.
- Heat transfer from the ceramic tube to the hot gas limits obtainable temperature in quencher when gas flows higher than approximately 7000 Nml/min are applied
- Low measured temperature drop in quenching experiments indicates poor mixing of hot and cold gases.
- At setpoint temperature 1450 °C problems with connection quencher – ceramic tube occurs: welding of the fitting and destruction of the gasket sealing that cause the gas leakage.
- K – type thermocouples are more durable and easy-to-handle than S – type thermocouples with respect to make connections tightly. K – type thermocouples have a temperature limit around 1200 °C. If experiments at higher temperature will be performed, the S – type should be used.

- Removal of cold finger reduces efficiency of *cold wall* quenching in lower part of cooling system. This can influence the results of experiments with propane. Temperature of outgoing gases from the cooling system was not measured but it was much higher than room temperature when high setpoint temperatures were applied.
- As shown in the Figure 3.4.2 it is a quencher section between lower temperature measurement point and «cold finger». The volume of this section is higher than the control volume, CV. The presence of the section affects the conversion, selectivities and yields in the quenching experiments because of increasing residence time. The section should be reduced or extra thermocouple inlet should be installed right above «cold finger».

5.3.1 High temperature gradients and high heat losses

In chapter 4.2 was mentioned that high temperature gradients between measurement points can be explained by high heat losses or by high temperature gradient in radial direction. If high temperature gradient in radial direction is a really case, especially at lower point, the calculations of the heat loss may be wrong, thus calculated expected temperature drop may also be wrong. The fact, that the use of extra insulation layer around quencher has not resulted in significant temperature increase, can indicate that the «cold finger» is an important source of heat loss and temperature gradient for the quencher-part.

Heat transfer by conduction through the metal material downwards the cooling system, from the point with a high temperature (connection to the ceramic tube) to the point with a low temperature («cold finger»), will occur. Figure 5.3.1 shows how heat is transferred through the quencher wall.

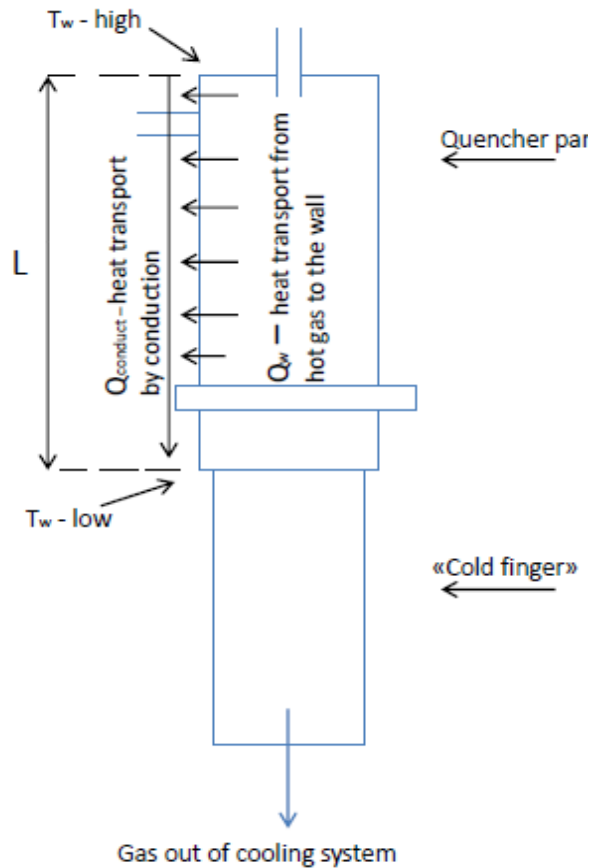


Figure 5.3.1 Heat transfer through the wall of quencher part

If this conductive heat transfer is high compared to heat transfer from the gas phase to the tube wall, the consequence may be the high temperature gradient through the wall of the quencher. Thus the wall temperature at lower measurement point may be much lower than the wall temperature at upper measurement point. Low wall temperature may result in that the measured temperature is much lower than the *true gas* temperature.

Neither wall temperature nor true gas temperature are known. Equation (20) from chapter 2.5 was used to calculate how true gas temperature T_g may vary as a function of wall temperature T_w , for the same measured temperatures T_p , 610 °C and 909 °C, taken from Table 4.2.1. The results are shown in figures 5.3.2 and 5.3.3 below.

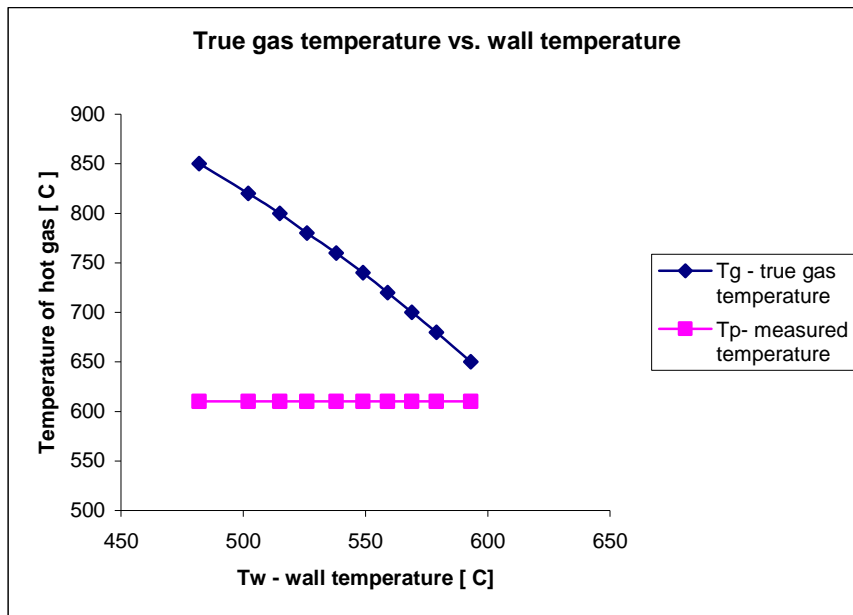


Figure 5.3.2 True gas temperature vs. wall temperature. $T_p = 610$ °C
Parameters used in calculations: $h_c = 40$ W/m²·K; $\varepsilon = 0,6$; $\sigma = 5,676 \cdot 10^{-8}$ [W/m²·K⁴] [14]

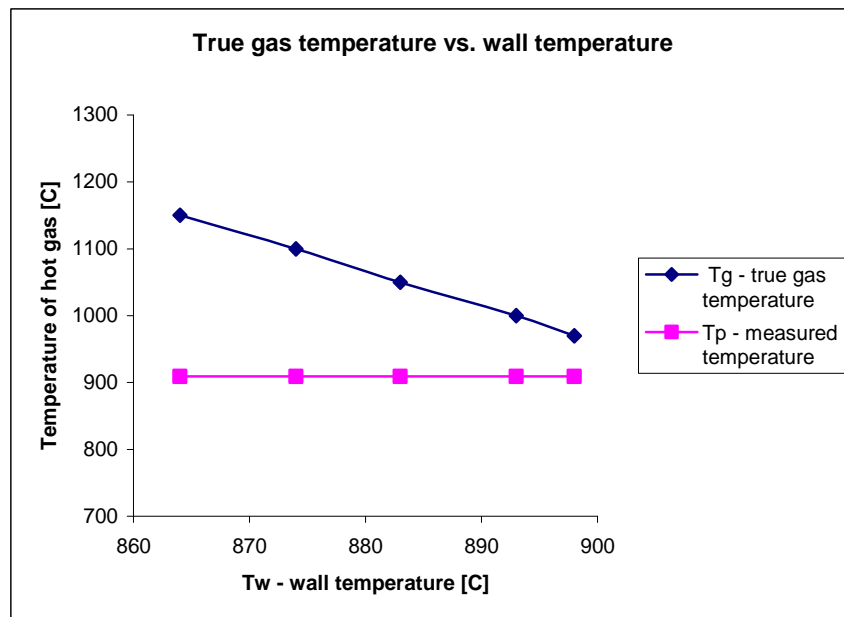


Figure 5.3.3 True gas temperature vs. wall temperature. $T_p = 909$ °C
Parameters used in calculations: $h_c = 40$ W/m²·K; $\varepsilon = 0,6$; $\sigma = 5,676 \cdot 10^{-8}$ [W/m²·K⁴] [14]

The calculations show that the difference between true gas temperature and measured temperature increases with decreasing wall temperature.

As shown in the Figure 5.3.1, heat is transferred through the wall both in axial and radial directions. Assuming that the heat transfer in radial direction is negligible, the one dimensional model for the heat transfer at steady state can be used to describe the temperature distribution through the wall.

Assume also that $T_w = 1000\text{ }^\circ\text{C}$ in connection to ceram tube and $T_w = 70\text{ }^\circ\text{C}$ in connection to «cold finger» and $L = 27,2\text{ cm}$ is a distance in between. Then, the temperature distribution will be as presented in the Figure 5.3.4.

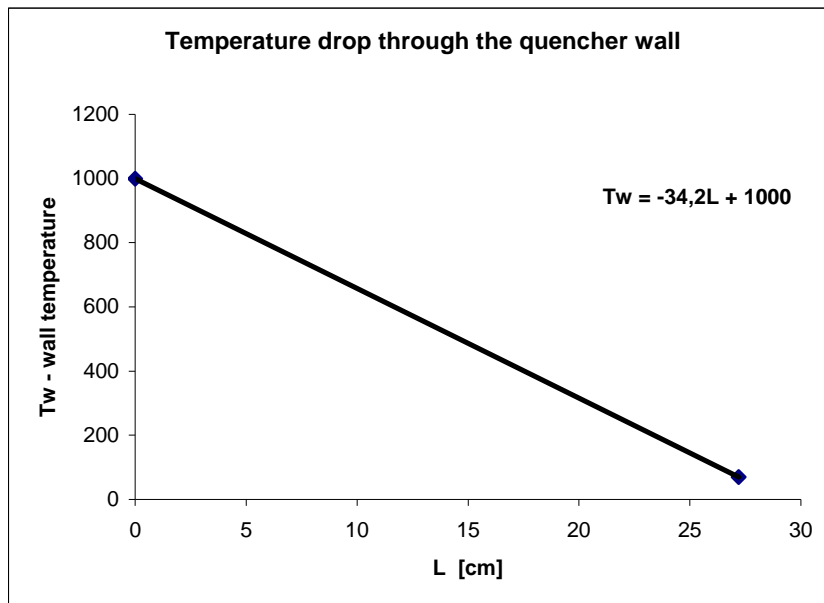


Figure 5.3.4 Temperature distribution through the quencher wall.
Boundary conditions: $T_w(0)=1000\text{ }^\circ\text{C}$ $T_w(L)=70\text{ }^\circ\text{C}$. $L = 27,2\text{ cm}$
Heat transport in radial direction is not taken into account.

A lower measurement point is at $L=13,5\text{ cm}$ that give $T_w = 538\text{ }^\circ\text{C}$ according to model above. From the Figure 5.3.2, true gas temperature is $T_g = 760\text{ }^\circ\text{C}$ and the difference $T_g - T_p = 150\text{ }^\circ\text{C}$.

Due to numerous assumptions, it is likely that the temperature difference is overestimated. However, the example above shows that the conductive heat transfer through the quencher wall may have a significant impact on temperature measurements, and «cold finger» may be a source of heat losses for the quencher – part. If this is a really case, the material with a lower thermal conductivity should be chosen for the quencher.

5.3.2 Bad mixing of hot and cold gases

Quenching experiments with propane have shown an unexpected low temperature drop that indicates a poor mixing of hot and cold gases inside the quencher. As was discussed in chapter 2.2.1, a gas mixing occurs usually by diffusion or by convective transport or by both transport types, depending on flow conditions. In turbulent flow regime gas mixing is mainly by convective transport and mixing is much better than in laminar flow.

The Reynolds number for the typical hot gas flow in experiments was calculated as $N_{Re} = 457$ for

the quencher – part and $N_{Re} = 1085$ for the ceram tube, calculation is in Appendix A. The low Reynolds number indicates that the hot gas flows in laminar regime and there is no effective turbulent mixing. According to equation (4) in chapter 2.2.3 an entry length L_e is calculated to be 34 cm that means the fully developed velocity profile was not established.

The cold propane flow is introduced perpendicular to the hot nitrogen flow and the gas flow pattern is not really known. Since temperature drop at lower point is low and it is assumed that the reason for that is a bad gas mixing, one can think of situation when cold propane flow push hot nitrogen to the quencher wall. Then, both gases flow in some kind laminar flow with a boundary layer in between. The Figure 5.3.5 shows how the gas flow pattern may look out. The consequence may be that the mixing of gases is dominated by the diffusion transport that is relative slow.

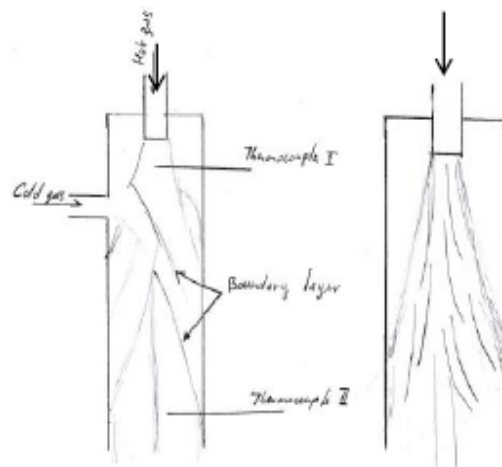


Figure 5.3.5 Gas flow pattern. To the left: cold gas is introduced. To the right: only hot gas entering quencher.

The gas flow pattern inside quencher was discussed with Hugo A. Jakobsen, Professor at Reactor Technology Group, NTNU [24]. He has mentioned that the gas flow is probably much higher in the middle of the quencher than the gas flow at the quencher wall. He meant also that the temperature difference between upper and lower measurement points is to high, when isolation around quencher is applied. The temperature gradient in radial direction and positions of thermocouples are most likely the explanation of the high measured temperature difference between upper and lower points.

On the basis of estimated Reynolds number and measured temperature drop, it can be concluded that the mixing of gases is poor. Thus, the used quencher design do not realize the conditions of completely mixing of hot and cold gases that makes testing of quenching concept difficult.

In chapter 2.1.1 was mentioned that in the case of coaxial mixing of hot and cold gases the diameter

of the hot jet and the ratio of coaxial to jet velocity are important factors for cooling rate. A smaller hot jet diameter and higher velocity ratios reduce the time necessary to establish turbulent mixing processes. In quenching experiments with N_2 and propane the turbulent mixing was not established, and gas flows are perpendicular to each other. However, conclusions from chapter 2.1.1 may probably be used to improve the gas mixing. Ceram tube used to heat up nitrogen had inner diameter 6 mm. If ceram tube with a smaller diameter will be used, the hot jet will be smaller and gas velocity out of tube will be higher.

A nozzle should be installed at cold gas inlet or diameter of the inlet should be reduced to increase the cold gas velocity. The cold gas inlet may also be placed at an angle to hot gas flow as shown in Figure 5.3.6. When hot and cold gas flows will meet together at higher velocities a forced convective mixing would occur to an larger extent. These small changes in quencher design may hopefully improve gas mixing sufficiently.

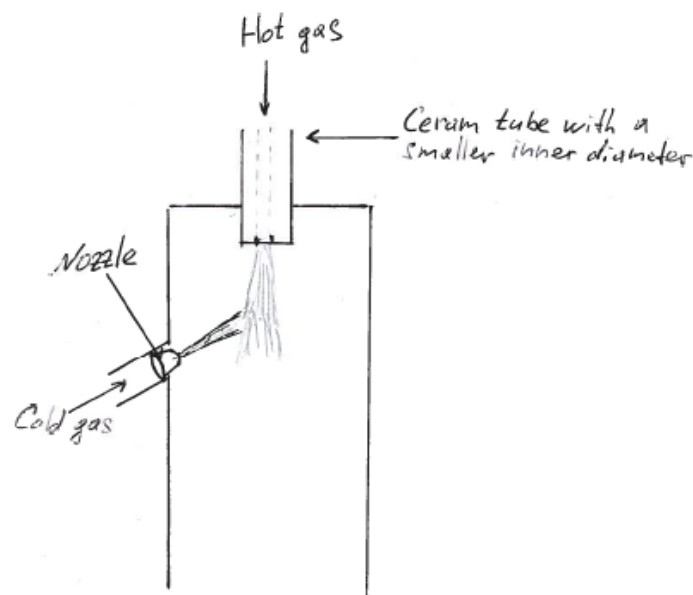


Figure 5.3.6 Sketch of proposed changes in quencher design to improve gas mixing

6. CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

- Concept of chemical quenching was demonstrated by experiments with a hot nitrogen gas quenched by propane: temperature drop was indicated and propane was converted to the products. However, the observed quenching effect was low that can be explained by poor mixing of gases.
- Quenching effect increases with a hot gas temperature that can be explained by increasing propane conversion.
- A high conversion of quenching medium is a requirement because thermal energy should be recovered in the form of valuable products to an largest extent. At high conversion of propane the ethylene is a product that was obtained in the highest yield.

If synthesis gas will be quenched by propane, the conversion, yields and selctivities will be different. The synthesis gas produces often at elevated pressures and high partial hydrogen pressure. This may result in lower conversion of propane and as a consequence, the quenching effect may be reduced.

- Conversion of hydrocarbon (propane) decreases with decreasing N_2 /Propane ratio. As the N_2 /Propane ratio decreases (propane flow increases), the importance of endothermic heat consumption decreases and quenching occurs by dilution to a higher degree.
- Quencher design is poor and do not realize expected experimental conditions: completely gas mixing and adiabatic quench that makes the proof-of-concept study difficult. The obtained results (conversions,yields and selectivities) are not very useful.
- The quenching of syngas by light hydrocarbons may result in production of different amounts of products that will be necessary to separate later. Even if, quenching will be effective and high yields of valuable products will be obtained, the separation costs of the products will reduce the total efficiency of the process.

A hypothetical situation may be that the quenching process is optimized in such a way that the quenching hydrocarbon reacts to CO and H₂ in the presence of O₂ or water. Thus, the

final product is synthesis gas, and problem with a products separation may be avoided.

- A better quencher design is necessary in order to investigate the concept.

6.2 Recommendations

1. A nozzle should be designed and incorporated into hydrocarbon inlet, to increase gas velocity. Gases at higher velocity will have higher kinetic energy and as result – better mixing. If coke will plug the nozzle, the inlet can be disconnected and the needle or metal rod can be used to remove the plug.
2. A hydrocarbon inlet should be placed at an angle as shown in the Figure 5.3.6.
3. The stainless tube with a lower diameter should be used for heating up the hot gas, $d_i = 3$ mm or smaller if possible, to improve mixing. The gas velocity out of tube will increase. Different tube diameters may affect the heat transfer from the tube to the gas. If it will be possible to apply higher gas flows, the higher temperature inside the quencher can be obtained and temperature gradient between measurement points can be reduced.
4. 2. section of the quencher, defined in chapter 3.2, should be reduced/cut. 1. section may retain its dimensions. If high gas velocities will be applied, it will be enough space to mix gases.
5. First of all, it is recommended to investigate if temperature gradients in radial direction exist. This may be an explanation of measured temperature gradient between upper and lower points. If radial temperature gradient is not significant, the gradient in axial direction may be explained by conductive heat transport through the quencher wall.

If gradient in axial direction and/or heat losses can not be eliminated, it is proposed to make a model describing heat transport and temperature distribution through the quencher.

6. The *cold finger* should be moved back into the outer shell of water quencher. It will be necessary to lift up the furnace.
7. If higher temperatures in the quencher will not be reached (problems with *Conax* fitting at

8. It is not recommended to go higher than $T = 1300\text{ }^{\circ}\text{C}$ for the setpoint temperature on the furnace, for given quencher configuration because problems with connection to the ceramic tube.

9. It is proposed to make a mathematical model, if possible, that will describe the quenching of synthesis gas by alkanes. The model should include reactions kinetic, thermodynamics, mass and heat transfer phenomena. To make such model may be a difficult task in itself, so it is recommended to cooperate with Reactor Technology Group at NTNU. In combination with experimental work a more useful results may be obtained.

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APPENDIX A

Appendix A 1

Example of calculation of Reynolds number N_{Re} for the quencher and for the ceram tube

A gas flow given by MFC (volume flow at standard conditions)

$$V_{N_2} = 7 \frac{Nl}{\min} = \frac{0,007 Nm^3}{60s} = 1,16667 \cdot 10^{-4} \left[\frac{Nm^3}{s} \right]$$

By ideal gas law $\frac{P_1 V_1}{T_1} = Rn = \frac{P_2 V_2}{T_2}$

+ assume constant pressure $\Rightarrow V_2 = \frac{T_2}{T_1} \cdot V_1$

For the approximately temperature inside the quencher $T_2 = 900 \text{ }^\circ\text{C} = 1173 \text{ K}$

$$V(T = 900^\circ\text{C}) \approx 5 \cdot 10^{-4} \left[\frac{m^3}{s} \right]$$

The cross sectional area of the quencher calculated as

$$A_{cross} = \frac{\pi D_i^2}{4} = \frac{\pi \cdot (0.02m)^2}{4} = 3,142 \cdot 10^{-4} m^2 \Rightarrow v_{av} = \frac{V}{A} \approx 2,3 [m/s] \quad \text{- average gas velocity}$$

Reynolds number is calculated as $N_{Re} = \frac{D_i v_{av} \rho}{\mu}$

D_i – inner diameter of the tube/quencher [m]

ρ – gas density [kg/m^3]

μ – gas viscosity [$\text{Pa}\cdot\text{s}$]

$$\rho_{900^\circ\text{C}} = 0,45914 \quad [\text{kg}/\text{m}^3]^*$$

$$\mu_{900^\circ\text{C}} = 46,191 \cdot 10^{-6} \quad [\text{Pa}\cdot\text{s}]^*$$

($P = 1,6 \text{ bara}$)

$$\Rightarrow N_{Re} = 457 \text{ (Reynolds number for the quencher)}$$

For the ceram tube

Assume an average gas temperature for the ceram tube $T_{av} = 1100 \text{ }^\circ\text{C}$,

then the volume flow of nitrogen

$$V(T = 1100^\circ\text{C}) \approx 5,87 \cdot 10^{-4} \left[\frac{m^3}{s} \right]$$

$$A_{cross} = \frac{\pi D_i^2}{4} = \frac{\pi \cdot (0.006m)^2}{4} = 2,827 \cdot 10^{-5} m^2 \Rightarrow v_{av} = \frac{V}{A} \approx 20,8 [m/s]$$

Use viscosity and density data at 999 °C

$$\begin{aligned} \rho_{999\text{ °C}} &= 0,4234 && [\text{kg/m}^3]^* \\ \mu_{999\text{ °C}} &= 48,7 \cdot 10^{-6} && [\text{Pa}\cdot\text{s}]^* \end{aligned} \quad \Rightarrow N_{\text{Re}} = 1085 \text{ (Reynolds number for the ceram tube)}$$

* http://www.peacesoftware.de/einigewerte/stickstoff_e.html

25.Juni 2012

Appendix A 2

Pyrolyse experiments. The method of analysis.

The analysis of the product gas mixture is done by gas chromatograph (GC) equipped with Thermal Conductivity Detector (TCD) and Flame Ionization Detector (FID). The sample of the product gas is introduced to the GC where separation of mixture's components occurs inside a two columns: Carbosieve S-2) and GS-Q. Each component separates according to its retention time. The detectors register the output signals in a chromatogram. Areas corresponding to each component are obtained after integration. These areas are used to calculate the relative amount of components in the sample and product gas mixture composition.

Calculations for the product gases

In the following it assumed that integrated areas from chromatogram are proportional to the amounts of components in the analysed sample. In addition the areas given by FID are proportional to the number of carbon atoms corresponding to the hydrocarbon presented in the sample. The nitrogen gas is used as internal standard since nitrogen is not consumed during the reactions.

The gas mixture containing hydrogen, nitrogen, methane, ethane, propane and n-butane are used to calibrate the GC and to identify retention times for the listed components. Calibration gas used from the bottle No 10181806.

The combination of outputs from TCD and FID is used in calculation of mass balances for the species.

Mass balance by TCD

Using the calibration gas mixture correction/response factors f_i are estimated for H_2 , N_2 and CH_4 by

$$f_i = \frac{X_i^c P}{100A_i^c}$$

where X_i^c – mole fraction of component i in calibration gas
 A_i^c – measured area corresponding to component i in calibration gas
 P – the atmospheric pressure
 i - H_2 , N_2 or CH_4

The calculated response factors for nitrogen and methane are assumed to be constant, but response factor for hydrogen will vary since helium is used as carrier gas for GC. The variation in response factor for hydrogen will not affect the calculations of methane conversion because nitrogen used as

internal standard. The methane flow in product gas is related to nitrogen gas flow. However, the estimated flow of hydrogen in product gas can be something uncertain.

The ratio

$$K_i = \frac{f_i}{f_{N_2}}$$

shows how response factor for specie i is related to response factor for nitrogen.

Molar ratio of species (hydrogen or methane) to nitrogen is estimated as

$$r_i = K_i \frac{A_i}{A_{N_2}} = \frac{X_i}{X_{N_2}}$$

Then, molar flow of component i can be calculated as

$$F_i = F_{N_2} r_i$$

$F_{N_2} = F_{N_2}^0$ – nitrogen gas flow is given by mass flow controller

Conversion of CH₄ given by TCD measurements:

Methane conversion estimated as

$$X_{CH_4} = \frac{F_{CH_4}^0 - F_{CH_4}}{F_{CH_4}}$$

where $F_{CH_4}^0$ - average methane flow given by two measurements of feed gas mixture
 F_{CH_4} – the flow given by measurement at experimental conditions

The final calculated methane conversion is an average conversion of three measurements at experimental conditions.

Mass balance by FID

Molar ratios of carbon species present in product gas mixture registered by FID calculated as

$$r_j = \frac{X_j}{X_{N_2}} = \frac{A_j}{jA_{CH_4}} \cdot r_{CH_4}$$

Where r_j – molar ratio of hydrocarbon specie to nitrogen
 X_j – mole fraction of carbon specie in product gas
 X_{N_2} – mole fraction of nitrogen in product gas
 A_j – measured area corresponding to identified carbon specie in product gas
 A_{CH_4} – area of methane (given by FID)
 r_{CH_4} – molar ratio of methane to nitrogen (given by TCD - measurement)
 j – number of carbon atoms in specie j

Then, molar flow of hydrocarbon specie estimated as

$$F_j = F_{N_2} r_j$$

And coke flow rate can be estimated as C_1

$$F_{coke} = F_{CH_4} - \sum_j jF_j$$

Conversion of CH_4 (gas phase/ by FID):

Conversion of CH_4 estimated only by FID measurements. Conversion given as a difference between total carbon atoms registered by FID and C – atoms present as methane, divided by total carbon atoms present in the product mixture. This estimation method does not take into consideration the coke formation.

$$X_{CH_4} = \frac{mol\%(total_C_atoms) - mol\%(CH_4)}{mol\%(total_C_atoms)}$$

The mole % of carbon compound present in the product gas mixture is calculated as

$$mol\%C_n = \frac{A_n}{n} \cdot \frac{1}{\sum_n \frac{A_n}{n}}$$

Where n – number of carbon atoms in the compound
 A_n – area measured by FID for specie with n carbon atoms

When mole % of carbons species is known, the carbon distribution in gas phase is calculated as

$$(\% C - atoms as C_n) = \frac{\%C_n \cdot n}{\sum_n \frac{\%C_n}{n}}$$

Selectivity

The selectivity to hydrocarbons is estimated as percent of carbon atoms presented as hydrocarbon relative to the total amount of carbon atoms, divided by the percent of converted methane:

$$S_n \% = \frac{(\% C_atoms_as_C_n)}{100\% - (\% C_atoms_as_C_1)}$$

Yields

The Yield of hydrocarbons calculated as conversion of methane multiplied by selectivity to hydrocarbon:

$$Y_n \% = X_{CH_4} S_n$$

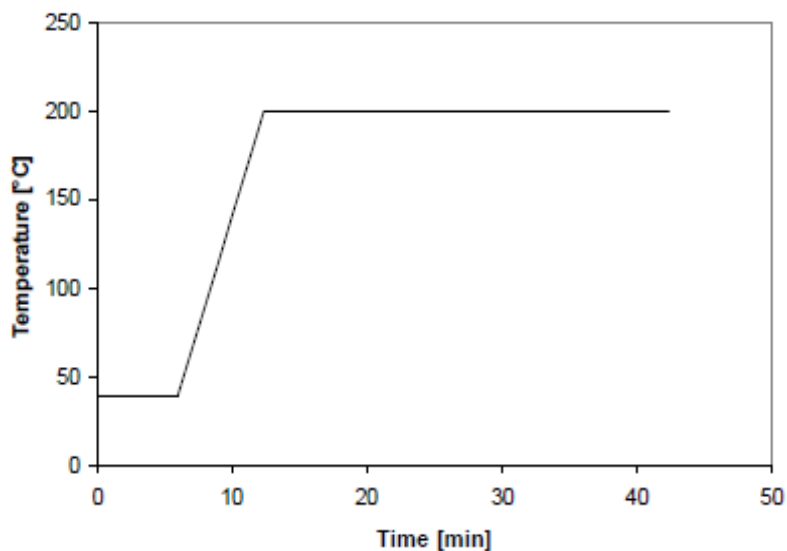
NB! The same formulas were used for calculation of results from quenching experiments with propane. Propane is considered to be reactant. Analyses were taken only by FID.

Appendix B

GC - method

The GC – method used for the experimental analysis is a method that was used in earlier methane pyrolysis experiments. The name of the method is ODDL1.M.

Oven temperature versus time



Initial temperature: 40 °C
Initial time: 6 min
Heating rate: 25 °C/min
Final temperature: 200 °C

Valve on: 0,1 min
Valve off: 3,0 min

Calibration of GC:

FID:

Carrying gas (He):	4,5 [ml/min]
H ₂ gas:	30 [ml/min]
<u>Air</u>	<u>248 [ml/min]</u>
Total:	313 [ml/min]

TCD:

Carrying gas (He)	27 [ml/min]
<u>Refer. flow</u>	<u>46 [ml/min]</u>
Total flow	73 [ml/min]

Retention times for the *calibration gas* (average of three analysis):

FID:

CH ₄	Rt = 2,179 min
Ethane	Rt = 4,417 min
Propane	Rt = 9,818 min
n-Butane	Rt = 12,364 min

TCD:

H ₂	Rt = 1,210
N ₂	Rt = 5,884
CH ₄	Rt = 11,427

Example of retention times from the quenching experiments with propane:

$T_{\text{set}} = 1300 \text{ }^{\circ}\text{C}$, $V_{\text{propan}} = 143 \text{ [Nml/min]}$ $V_{\text{N}_2} = 6250 \text{ [Nml/min]}$

FID:

Methane	Rt = 2,210
Ethylene	Rt = 3,647
Acetylene	Rt = 4,349
Ethane	Rt = 4,478
Propylene	Rt = 9,643
Propane	Rt = 9,838
C4	Rt = 12,259; 12,420
Benzene	Rt = 17,607

Comment: Retention times for Acetylene and Ethane, and for Propylene and Propane are very close to each other. The separation of components in the column is not very good. The areas on chromatogram overlap that result in some uncertainty in calculations. The GC-method should be changed to get a better separation of components.

Appendix D



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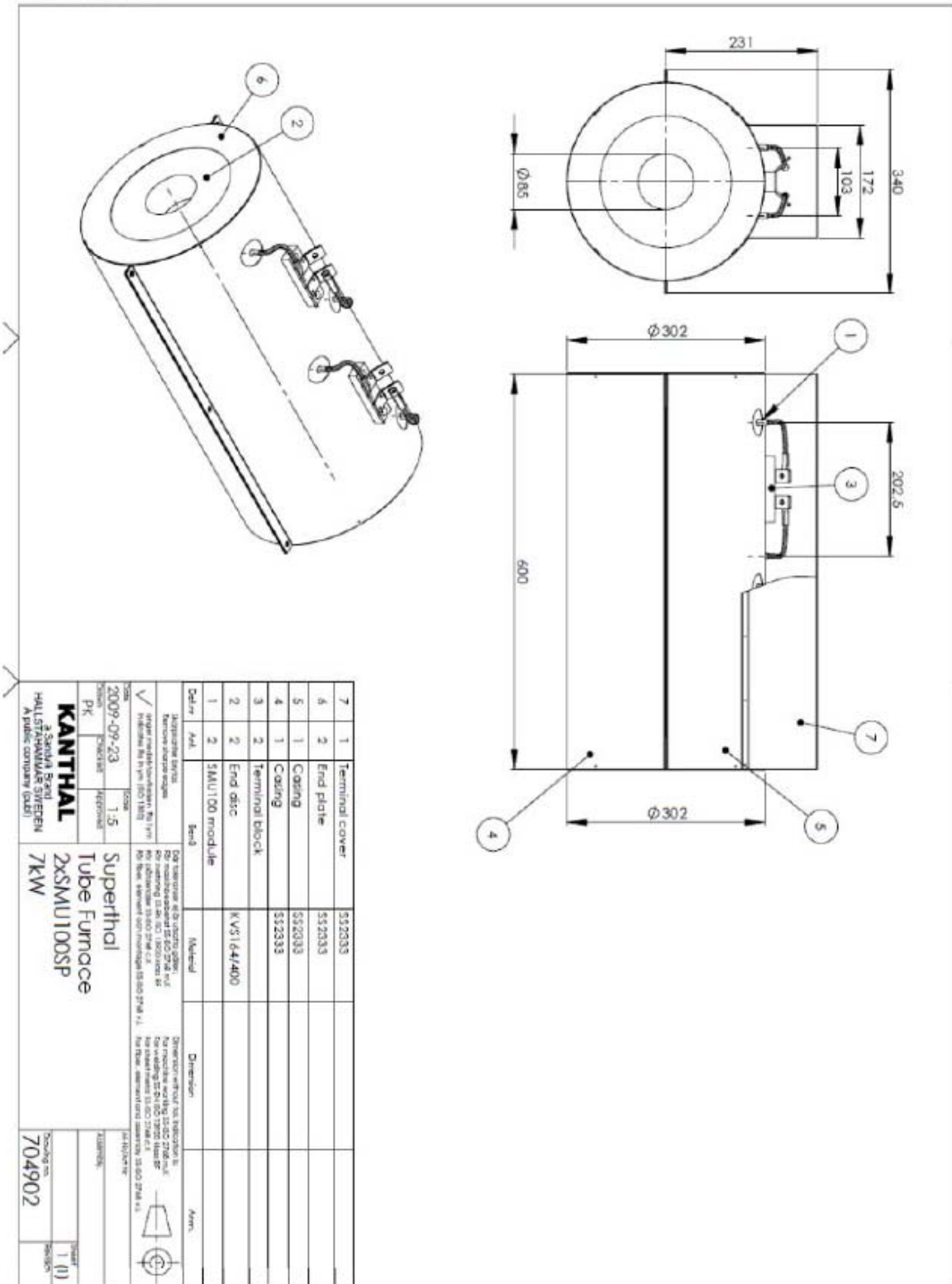


Figure A.2: Technical drawing of the new furnace. 2 times SMU 100 heating elements à 3,5 kW.

