TAMPEREEN TEKNILLINEN YLIOPISTO

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THERMOCATALYTIC DECOMPOSITION OF METHANE
Master of Science Thesis

ABSTRACT

Concerns about the rising carbon dioxide concentration in the atmosphere and its possible negative effects on life on Earth have forced governments to take actions. Many new technologies are being investigated in order to find more economically and environmentally friendly and energy-efficient methods, which could replace the conventional technologies. The power-generation industry, in particular, has shown interest, as currently the majority of electricity is produced from fossil fuels.

In the thesis, one potential way to reduce emissions is examined. Combustion of natural gas produces flue gases containing a low proportion of CO_2. Conventional methods for removing carbon dioxide from the flue gases are either expensive or inefficient. This provides the motivation for the current work - a way of removing the carbon from the fuel feedstock before combustion in order to avoid the emissions completely.

The methane decomposition reaction is evaluated based on equilibrium calculations, a review of patents related to the subject is undertaken and possible ways of scaling up the process are considered. In addition, laboratory experiments were conducted to gain information from the catalytic reaction and also from the catalyst.

Several areas concerning the topic were noted as "needing further research". Plans for the future research have been made in the thesis, mainly based on the promising results in the literature, but partly also on the encouraging results obtained from the laboratory experiments.

The conclusion of the thesis is that the technology examined has obvious potential, but more research is needed both into the reaction itself, and into possible implementation on an industrial scale.

TIIVISTELMÄ

Huoli kasvavasta hiilidioksidikonsentraatiosta ilmakehässä ja sen mahdollisista haittavaikutuksista maapallolle on pakottanut valtiot tarttumaan toimiin. Lukemattomia uusia tekniikoita tutkitaan tavoitteena löytää ympäristöystävällisempiä ja energiatehokkaampia tapoja vanhojen tilalle. Erityisesti energiantuottajat ovat olleet kiinnostuneita, sillä suurin osa sähköstä tuotetaan nykyään fossiilisilla polttoaineilla.

Diplomityössä tarkastellaan erästä lupaavaa tapaa vähentää päästöjä. Kun maakaasua poltetaan, muodostuu CO_2-pitoisuudeltaan laihaa savukaasua. Perinteiset hiilidioksidin erottelumenetelmät ovatkin maakaasun polton yhteydessä joko kalliita tai tehottomia. Edellämainitusta syystä kannattaa kehittää menetelmiä, joissa polttoaineen hiili erotettaisiin ennen polttoa.

Metaanin hajoamisreaktiota tutkittiin tasapainolaskennan avulla. Lisäksi tehtiin patenttikatsaus, jossa arvioitiin aihetta käsitteleviä patentteja. Lisäksi suoritettiin mittauksia, jotta saatiin tietoa metaanin katalysoidusta hajoamisreaktiosta ja katalyytistä itsestään.

Lukuisten menetelmän osa-alueiden havaittiin vaativan lisätutkimuksia. Tulevia tutkimuskohteita määritettiinkin rinnakkain diplomityön kanssa. Suurimpaan osaan saatiin ideoita uusista tutkimustuloksista, mutta myös kohtuulliset tulokset laboratoriossa tehdyistä kokeista vaikuttivat tulevaisuuden suuntalinjoihin.

Diplomityön loppupäätelmänä voidaan sanoa, että tarkastellulla teknologialla on selvästi mahdollisuuksia, mutta lisätutkimuksia kaivataan sekä reaktiosta itsestään, että prosessin kasvattamisesta teolliseen kokoluokkaan.

PREFACE

This thesis has been done as a part of Cleen Ltd's carbon capture and storage research program (CCSP). The work began in May 2010 and was finished in February 2012. I would like to express my gratitude to Professor Risto Raiko for offering me this opportunity and aiding me during the thesis.

The coordinating company behind the subtask, Gasum Oy, deserves acknowledgement as does the company representative Sari Siitonen. Furthermore, I would like to thank Risto Sormunen from Fortum Oyj, Timo Arponen from Helsingin Energia and Markku Raiko from ÅF Consult for encouraging words and attitude towards the author during the thesis work.

Without the help of mr. Jarmo Ruusila the experimental part of this work could not have been done, thus he deserves to be mentioned.

I want to thank PhD Antti Aronen for helping and tutoring me with many practical issues during the work. In addition Eerik Mäkitalo, a colleague and a friend, earns to be thanked for being an example, both in school and otherwise.

Finally, my gratitude and thoughts go to my family and friends for their love, support and understanding during this project. Without the Father and them I would never be writing the last words to this thesis.

Tampere, February 2012

Markus Fager-Pintilä

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ABBREVIATIONS AND NOTATION

Symbol	Units	Definition
a	-	chemical activity
FL	-	flammability limit
q	J kg^{-1}	lower heating value (LHV)
ΔH_0	J mol^{-1}	molar reaction enthalpy
K		chemical equilibrium constant
K_p		chemical equilibrium constant in terms of pressure
M	g mol^{-1}	molar mass
$\dot{n}$	mol s^{-1}	molar flow rate
p	Pa	pressure
T	K	temperature
$VHSV$	1/h	volume hourly space velocity, see p. 15
$\dot{V}$	m^3 s^{-1}	volumetric flow rate
x	-	volumetric fraction

Greek symbols	Units	Definition
ρ	kg m^{-3}	density
τ	s	residence time
χ	-	conversion

Constants	Units	Definition
R_u	J mol^{-1} K^{-1}	universal gas constant, 8.314 J mol^{-1} K^{-1}

Subscripts		Definition
ads		specie adsorbed on the active site
b		boiling
cat		catalyst
$cryst$		crystalline
i		species i
i		ignition
p		pressure

ref	reference
tot	total
0	initial

Abbreviations

ATP	Autothermal pyrolysis
BAT	Best available technology
BN	Billion (10^9)
CCS	Carbon capture and storage
CNT	Carbon nanotube
EU	European union
FBR	Fluidized bed reactor
FWR	Fluid wall reactor
GHG	Green house gas
NG	Natural gas
OECD	Organisation for economic co-operation and development
PSA	Pressure swing adsorption
SBR	Spouted bed reactor
SRM	Steam reforming of methane
TCD	Thermocatalytic decomposition
TDM	Thermocatalytical decomposition of methane
TR	Tubular reactor

1   INTRODUCTION

On a global scale, energy-related carbon emissions rose by about 26 percent between 1990 and 2005. The International Energy Agency (IEA) has made estimates, which indicate that the overall emissions will rise by approximately a further 57 percent between 2005 and 2030 unless action is taken to prevent this. According to IEA's world energy outlook 2010, the current global CO_2 concentration in the atmosphere is, on average, about 390 ppm. The concentration of carbon dioxide in the atmosphere has increased by 32% since the pre-industrial era. The upper limit for the CO_2 concentration should be set at 450 ppm if the target is to limit the atmospheric temperature rise to a maximum of 2°C. With the current trend, we are heading towards a 6°C temperature rise.

The majority of current energy needs are supplied by combustion of non-renewable energy sources, namely fossil fuels, and this is associated with the release into the atmosphere of large quantities of greenhouse gases (GHGs), especially carbon dioxide (CO_2), as well as other harmful emissions. There is no doubt about the non-sustainability of our current energy system because of problems with the future supply of fossil fuels. The gradual depletion of these fossil fuel reserves together with efforts to reduce pollution and greenhouse gas emissions, have generated considerable interest in the use of alternative sources of energy.

The aim of this thesis is to examine the thermocatalytic decomposition of methane (TDM) where the only reaction products are gaseous hydrogen and solid carbon. This has the potential to be part of the actions required to reduce carbon dioxide emissions in Finland. Methane is the main component of natural gas, which is used in Finland mainly for the production of energy. As natural gas is mostly used in small units, the post-combustion sequestration and storage of CO_2 is both impractical and expensive. An alternative approach is to separate and capture the carbon before combustion. The main objective of carbon sequestration is to prevent anthropogenic CO_2 emissions from reaching the atmosphere. Similar processes are used in industry in, for example production of carbon black. A comparison between steam-methane reformation and thermocatalytic decomposition of methane is also made. Steam reformation is the main source of today's hydrogen. To become economically attractive, TDM must have both lower costs and lower emissions than steam.

Research in the area of catalytic conversion of methane to carbon and hydrogen is somewhat limited and relatively new. It was not until the seventies, when the idea of a hydrogen economy saw daylight that interest in new ways of producing hydrogen arose. The only motivation then was to develop an economically more efficient process

compared to the existing steam reformation of natural gas. Only since the Kyoto protocol, has climate change and mitigation of global warming attracted worldwide attention. As a result, there is nowadays an increasing interest in greenhouse emissions. As emission trading becomes widespread, and the permitted emission quantities are periodically reduced, formerly expensive and uneconomic technologies have suddenly become attractive areas to develop and implement.

The majority of the journal articles, research reports and patent applications are from the past twenty years, particularly in the last decade. The main focus in today's research is on harnessing solar energy as the heat provider for the reaction and development of long-sustainability catalysts. Adjacently, novel methods for exploiting the generated carbon are under research.

The main idea of TDM can be expressed as follows: "Why should we produce tens of millions of tons of CO_2 and then spend hundreds of millions of dollars trying to dispose of it at a great environmental risk, when the production of this pollutant should be avoided in the first place."

2   NATURAL GAS

The focus for this thesis is the study of methane cracking to produce hydrogen and solid carbon. It has to be remembered that natural gas also contains other components including heavier hydrocarbons, nitrogen, carbon dioxide and sulphur. Depending on the natural gas field, the total amount of hydrocarbons varies roughly between 90 and 98% with methane being the dominating component. The impurities have to be taken into consideration when planning the natural gas decomposition process. Studies into the effect of heavier hydrocarbons on the reaction show that the heavier feedstock decomposes more easily, and also that the formed carbon is more catalytically active than the one formed in the methane decomposition [1].

2.1   Properties

Natural gas is a colorless and almost odorless hydrocarbon, and one of the primary fossil fuels. Natural gas composition varies according to the source (see Table 2.2), thus some of its properties also vary. The values shown in Table 2.1 are the most common for Russian natural gas.

Table 2.1. Properties for natural gas [2], [3].

molar mass	M	16.181	kg/kmol
density (NTP)	ρ	0.723	kg/m^3
relative density	ρ_{NG} / ρ_{air}	0.56	-
lower heating value	q_{volume}	35.6	MJ/m$_n^3$
	q_{mass}	49.2393	MJ/kg
boiling point	T_b	-161.5	°C
ignition temperature	T_i	600..650	°C
flammability limits	LFL..UFL	5..15	vol %

2.2   Global reserves

Natural gas reserves are not spread evenly over Earth. The three countries having the largest proven reserves of natural gas are the Russian federation (23.7 %), Iran (15.8 %) and Qatar (13.5 %), which together have over 50 % of the total reserves. At the end of 2009, the proven global reserves of natural gas were 187,490 bn m^3 and the reserves to production (R/P) ratio was 62.80. The R/P ratio indicates the number of years that

proven reserves will last at current production rates. Thus, at the present rate of consumption, natural gas will be available for a little over sixty further years. [4]
Figure 2.1 illustrates how the amount of proven reserves of natural gas has changed in the last twenty years due to new discoveries.
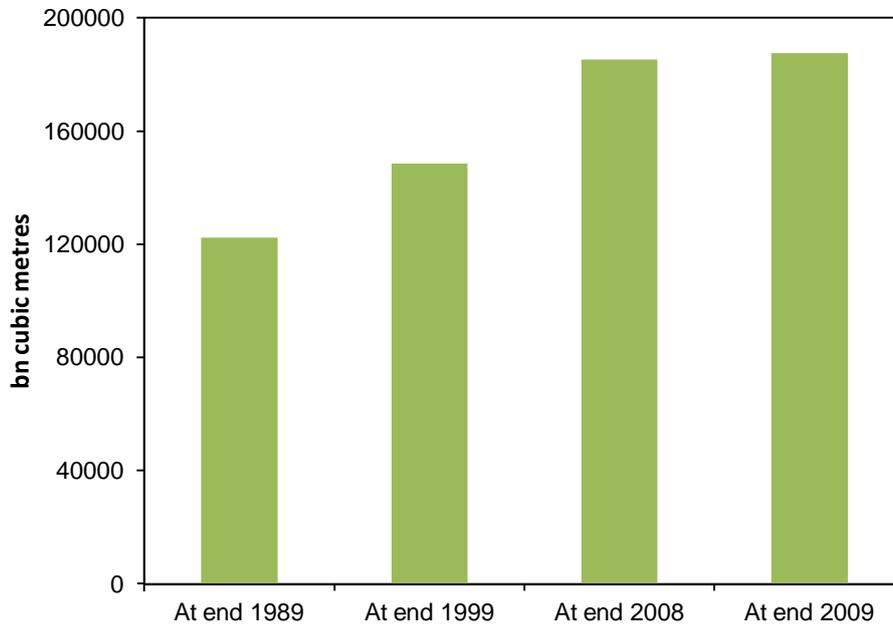
Figure 2.1. *Proven global reserves of natural gas, adapted from [4].*

Despite advances in conventional technology and corresponding reductions in consumption as well as the discovery new natural gas fields, the inescapable fact is that the reserves are limited. An alternative approach is taken in [5], where biogas produced by fermentation of biodegradable waste is proposed as the raw material for the thermocatalytic decomposition reaction. However, even the theoretical maximum production of biogas is only a minute fraction of the total demand of NG, so biogas alone will not be the answer to replacing fossil, non-renewable, natural gas.

As reserves become scarce, formerly uneconomic NG reserves will be reconsidered. Offshore drilling is one of the alternatives likely to become more important in the coming years. In addition, both Poland and especially the U.S. have vast reserves of shale. Shale can be refined to form shale oil or gas by hydraulic fracturing, in which fluid is injected straight into the shale deposits in the ground. There is no common agreement on the environmental impact of this method, and this currently restricts the increase in shale gas production. One thing the scientific community has come to agree on is that in the near to medium future fossil fuels are likely to continue to play a major role in the global energy supply.

2.3   Use

In 2009, the worldwide consumption of natural gas was 2940 bn m^3 [4]. The information in the following charts is from the International Energy Agency database [6]:

a)   b)
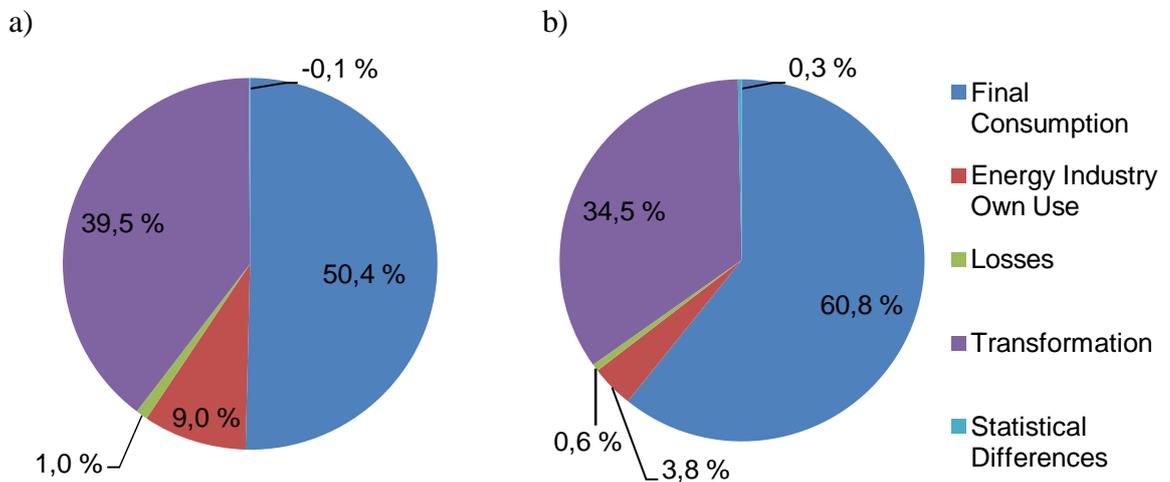
Figure 2.2. Use of natural gas in a) the world, and b) in OECD countries in 2008.

The OECD countries share of world consumption is roughly 18 % [6]. The categories represented in Figure 2.2 are as follows: Final consumption covers both industrial and residential use, petrochemical feedstock and transportation. Energy industry's own use includes the primary and secondary energy consumed by transformation industries for heating and pumping purposes, etc. Losses include losses in gas distribution, electricity transmission, and coal transport. Finally, transformation mainly consists of both separate and combined heat and power production.

The two biggest producers, the Russian federation and the United States, together accounted for roughly 40% of world's total production in 2008. They were also the biggest consumers, with 14% and 22% respectively of total consumption in 2008. [7]

2.4   Natural gas in Finland

Since 1974, natural gas has been used in Finland mainly for production of heat or electricity. The amount of natural gas used in 2010 equals 10% of Finland's total primary energy consumption. NG sales in 2010 were 4.5 bn m^3 in volume. [8]
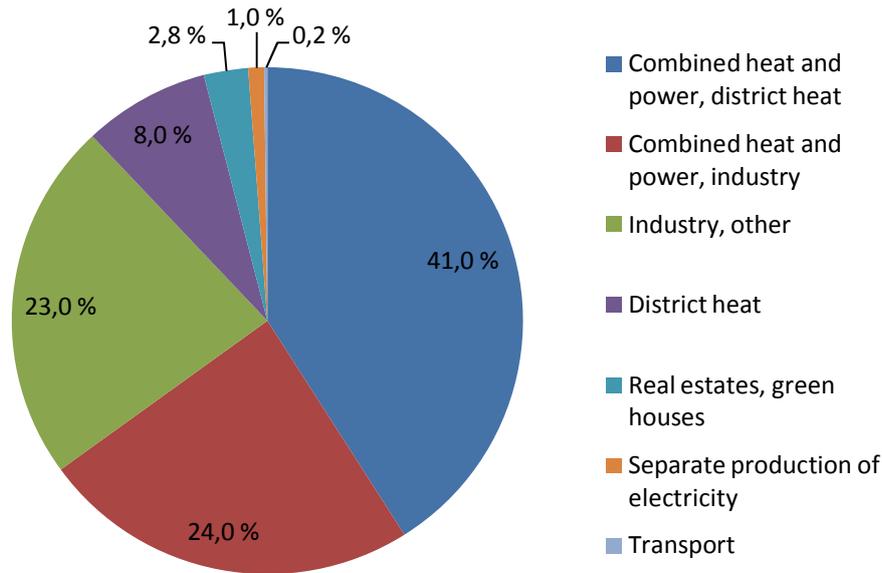
Figure 2.3. *Use of natural gas in Finland in 2009, adapted from [7].*

As shown in Figure 2.3, combined heat and power production from natural gas is 65% of the total use. Significantly, almost 75% is used in energy transformation. In the future, the share of transport is expected to increase.

All the natural gas used in Finland originates in the Urengoi gas field in Western Siberia, Russia. Its distribution inside the borders of Finland is exclusively the responsibility of Gasum Oy, owned by Fortum Heat and Gas Oy (31%), OAO Gazprom (25%), Government of Finland (24%) and E.ON Ruhrgas International Gmbh (21%).

Table 2.2. *Examples of the composition of NG from different fields [3].*

		Russian Fed., Urengoi	Germany, Goldenstedt	USA, Kansas	The Netherlands, Groningen	Norway, Troll
Methane	CH_4	98.0 %	88.0 %	84.1 %	81.3 %	93.2 %
Ethane	C_2H_6	0.8 %	1.0 %	6.7 %	2.8 %	3.7 %
Propane	C_3H_8	0.2 %	0.2 %	0.3 %	0.4 %	0.4 %
Butane	C_4H_{10}	0.0 %	-	-	0.4 %	0.5 %
Nitrogen	N_2	0.9 %	10.0 %	8.4 %	14.3 %	1.6 %
Carbon dioxide	CO_2	0.1 %	0.8 %	0.8 %	0.9 %	0.6 %

As can be seen from Table 2.2, the Russian natural gas used in Finland is almost pure methane. Such a natural gas is excellent for burning. In addition, the necessary purification steps for removing harmful sulphur compounds are carried out at the well-head and thus no further purification at the power plant is needed.

The use of natural gas in Finland is heavily concentrated in the southern part of the country. The total length of the main transfer pipeline is about 1100 km, and the local distribution pipeline consists of a further 1750 km of pipes. The plans for expanding the gas infrastructure to West Finland, particularly to Turku, are still under consideration. [7]

Figure 2.4 illustrates the pipeline network in Finland. The end-users are scattered, but all rely on the same distribution system.

Figure 2.4. *The natural gas pipeline network in Finland [8].*

This network is the driving force for the current thesis. It would be neither economically feasible nor practical to install post-combustion sequestration of carbon dioxide at every separate place of use. It should also be mentioned that typically the fraction of CO_2 in flue gas from natural gas combustion is relatively small (less than 10%). Thus the separation of CO_2 from the stream is difficult with conventional methods. These factors have generated interest in the centralized pre-combustion capture of carbon at an early point along the distribution network. A possible option is to carry out the sequestration near the NG control and measuring point on the Russian border.

3 METHODS FOR REDUCING CO$_2$ EMISSIONS

There are basically two methods of preventing CO$_2$ from entering the atmosphere due to the utilization of fossil fuels as an energy source. Carbon is either removed before or after combustion. Removal of carbon from fossil fuels prior to combustion requires removal and sequestration of the carbon either as CO$_2$ or as elemental carbon. Removal of carbon post-combustion requires sequestration of carbon specifically as CO$_2$. All the options are said to be decarbonisation methods. [9]

In the future, legislation and the charges for emissions from the different sources will play a major role in determining the direction of development of the emission reduction methods. The transition period is primarily set in motion by subsidies, but in the future fees and penalties will be applied. Emission trading also plays a role, as the emission quotas are periodically reduced. It will encourage the sources of release to apply new technologies and, in particular, to select the best available technology (BAT). To protect the environment the best commercially available technology should be used in preventing emissions. This benefits both the developer and the user of the technology. The developer sets the limits and, if other competitors cannot match them with their technology, then the market potential is vast. At the same time the user is able to increase the margin between the real emissions and the legislative emission limit.

3.1 Carbon capture and storage (CCS)

The carbon capture and storage research program (CCSP), which started in 2011 and is coordinated by Cleen Oy, aims to provide detailed information on carbon capture and storage, particularly under Finnish conditions. It is not within the scope of this thesis to offer a thorough investigation of CCS, and it is suggested that readers interested in post-combustion sequestration use other reports produced during work related to the subject.

The CCS process is based on capturing carbon dioxides after combustion. CO$_2$ is separated from effluent gas, pressurized (liquefied), transported and injected at a suitable location.

The process is expensive and energy intensive and no consensus has been reached on the long term storage of liquid carbon dioxide. Potential sites for sequestration could be deep (> 3000 m) locations in the oceans or gas impermeable geological formations deep underground [10]. Even though saline aquifer disposal is in use by Statoil in the Sleipner West field in the North Sea [11], these options involve considerable uncertainties and may cause severe harm both to the natural world and to people.

There is a reason why CCS attached to a gas turbine process is not an attractive option in Finland - the natural gas utilizing power generation plants are relatively small, starting from only a few megawatts. It would be economically very expensive to attach CCS facilities to every one of them and thus alternative approaches need to be examined. CCS could be feasible attached to a large power production unit, such as a coal combustion plant.

The crucial factors when considering CCS are the two major challenges which remain for CO_2 sequestration - (i) reducing its costs and (ii) understanding the reservoir options. These cannot be adequately predicted given current levels of understanding, and more research and field demonstrations are needed to confirm practical considerations, such as economics, safety, and permanence as well as public acceptance. [10]

3.2   Reducing natural gas generated CO_2 emissions

For natural-gas based power-generation plants, the three most promising types of concepts for reducing CO_2 emissions are: (i)separation of CO_2 from exhaust gas coming from a standard gas turbine combined cycle, using chemical absorption by amine solutions; (ii)oxy-fuel combined cycle with a close to stoichiometric fuel/oxygen ratio with oxygen from an air separation plant as the oxidizing agent, producing CO_2 and water vapor as the combustion products; (iii)decarbonisation, where the carbon of the fuel is removed prior to combustion, and the fuel heating value is transferred to hydrogen [12]. This present work concerns (iii). Decarbonisation prior to combustion is discussed in greater detail in Chapter 4.

Flue gases generated by burning natural gas usually contain carbon dioxide in amounts of less than 10%, usually closer to 5%. This is challenging for the conventional washers and scrubbers, which are designed to act with higher CO_2 concentrations in flue gas. One option is to use different chemicals to wash the exhaust gases but these chemicals, being very harmful both to man and to nature, are unattractive alternatives.

4 THERMOCATALYTIC DECOMPOSITION OF METHANE

Thermocatalytic decomposition of methane can be considered as a combination of two decomposition processes: thermal decomposition, often called thermal cracking, and direct catalytic decomposition. The combined process optimizes the best characteristics of both processes.

Due to a very strong C-H bond, 440 kJ/mol, methane is one of the most stable organic molecules: thermal dissociation of methane in reasonable amounts would require temperatures in excess of 1000 °C [10].

4.1 Theoretical reaction study

The overall total reaction taking place in thermocatalytic decomposition is

$$CH_4(g) = C(s) + 2H_2(g). \tag{4.1}$$

The reaction is moderately endothermic, requiring 75.6 kJ/mol of CH_4. As can be seen from the Equation 4.1, only solid carbon and hydrogen is produced. This makes TCD an attractive method for reducing harmful emissions, mainly consisting of carbon dioxide.

No definite conclusion has been reached on the decomposition mechanism, but Muradov et al. [13] propose the following reaction steps. Numerous experimental studies corroborate these steps:

(a) Methane adsorption and dissociation on the active sites

$$CH_4(g) \rightarrow CH_3(ads) + H(ads) \tag{4.2}$$
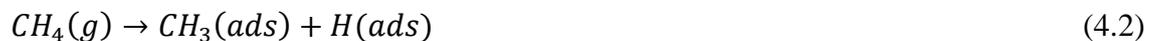
(b) Progressive dissociation releasing hydrogen-rich adsorbed species

$$CH_3(g) \rightarrow CH_2(ads) + H(ads) \tag{4.3}$$

$$CH_2(g) \rightarrow CH(ads) + H(ads) \tag{4.4}$$

(c) Crystallization and growth of the carbon deposits

$$CH\,(ads) \rightarrow C\,(ads) + H(ads) \tag{4.5}$$

$$C\,(ads) \rightarrow 1/n\,C_n\,(cryst) \tag{4.6}$$

(d)   Formation and desorption of H_2 gas

$$2 \cdot H\,(ads) \rightarrow H_2(g) \tag{4.7}$$

Notations *ads* and *cryst* denote a species adsorbed on the active site and crystalline, respectively. The stepwise reaction model above is also acknowledged by Serrano et al. [14].

4.2   Equilibrium constant

4.2.1   In general

In general a chemical reaction can be expressed as follows

$$jA + kB \leftrightarrow lC + mD, \tag{4.8}$$

where upper case letters A and B represent the reactants and C and D the products of reaction. Lower case letters denote the stoichiometric reaction coefficients.

The equilibrium constant, K, for reaction 4.8, is calculated with the following formula

$$K = \frac{(a_C)^l (a_D)^m}{(a_A)^j (a_B)^k}, \tag{4.9}$$

where a_i denotes the chemical activity of a substance. The exponents for the substance activities are the corresponding stoichiometric coefficients.

The activity can be expressed in terms of pressure, when it becomes

$$a_i = \frac{p_i}{p_{ref}}, \tag{4.10}$$

where p_i represents the partial pressure of a gas, and p_{ref} the reference pressure, the value of which is usually 1 atmosphere (1 atm). In addition, it has to be remembered that in heterogeneous reactions the activity of non-gaseous substances is unity. [15]

4.2.2   For methane decomposition

With the method described in the section above, the equilibrium constant for methane decomposition reaction (4.1) becomes

$$K = \frac{(a_C)^1 (a_{H_2})^2}{(a_{CH_4})^1} \tag{4.11}$$

When the activities are replaced with the pressure ratio from Equation 4.10 (and remembering that $a_C=1$), the value of the equilibrium constant K_p, is normally given by

$$K_p = \frac{1 \cdot \left(\dfrac{p_{H_2}}{p_{ref}}\right)^2}{\left(\dfrac{p_{CH_4}}{p_{ref}}\right)^1} \tag{4.12}$$

Equation 4.12 can be further modified to show the effect of the operating pressure, by expanding the equation to include the total operating pressure:

$$K_p = \frac{\left(\dfrac{p_{H_2}}{p_{tot}} \cdot \dfrac{p_{tot}}{p_{ref}}\right)^2}{\left(\dfrac{p_{CH_4}}{p_{tot}} \cdot \dfrac{p_{tot}}{p_{ref}}\right)} \tag{4.13}$$

From the ideal gas law it can be shown, that the pressure fraction equals the mole fraction of a substance. Although the equilibrium constant relates to non-ideal gases, at close to atmospheric pressures the difference is negligible. It must be remembered, that the equilibrium calculations do not take into account in any way the contribution of the catalyst to the reaction. Furthermore, the reaction kinetics, i.e. the rate at which the reactions take place, has to be determined experimentally. It is not within the scope of the thesis to research the kinetic parameters. They vary considerably depending on the catalyst used so that fresh experiments have to be undertaken every time a new catalyst is to be used.

In the literature, the equilibrium constant for the reaction is usually expressed in terms of methane formation, thus after obtaining the constant for the formation reaction, the complementary values are used for decomposition. The logarithmic value of the equilibrium constant versus temperature is plotted in Figure 4.1.
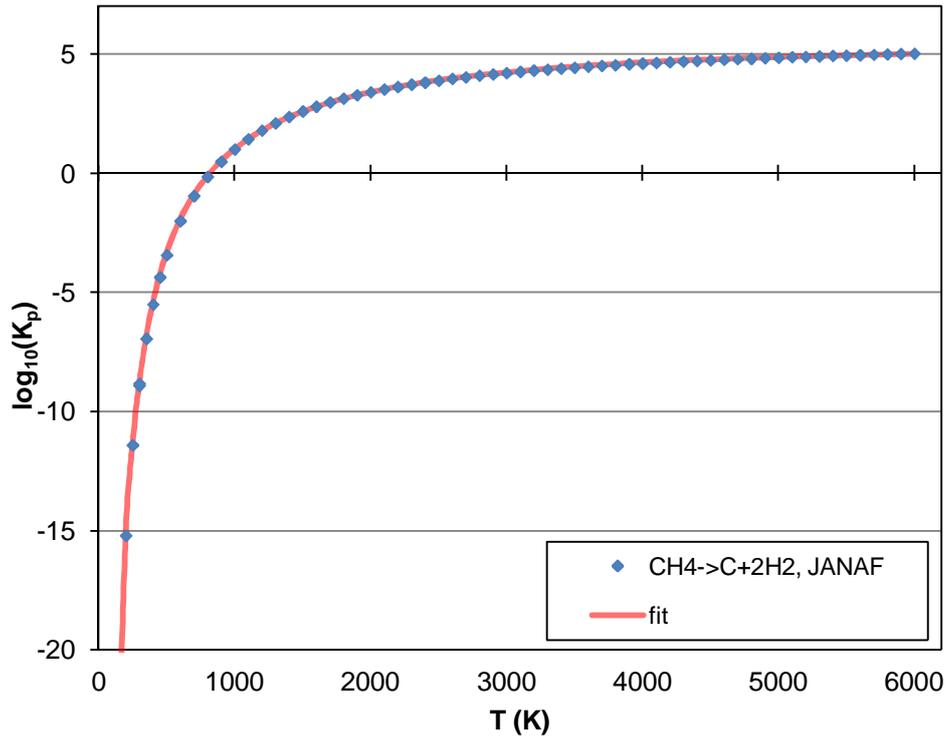
Figure 4.1. *The logarithmic value of the equilibrium constant for methane thermal decomposition reaction versus the temperature, data obtained from [16].*

The fit shown in Figure 4.1 was constructed using the equilibrium constant tables, with the help of mathematical software, MatLab. The fit correlation is of the form

$$log_{10}[K_p(T)] = A \cdot \frac{\ln(B \cdot T)}{T} + B \cdot \ln(T) + \frac{C}{T} + D \cdot T + E, \qquad (4.14)$$

where the constants are as follows:

$$
\begin{aligned}
A &= -290.2 \\
B &= 0.5561 \\
C &= -2623 \\
D &= -1.266 \cdot 10^{-4} \\
E &= 1.749.
\end{aligned}
$$

The higher the value of K_p, the more the balance of the reaction moves towards the products. The figure shows that the temperature is an essential parameter in achieving a satisfactory level of decomposition.

4.3 Process parameters

4.3.1 The effect of pressure and temperature

The equilibrium position for the methane decomposition reaction at different pressures and temperatures is calculated using chemical equilibrium software AsTher. From the resulting data, the fraction of converted methane in each case can be calculated by using the formula

$$\chi_{CH_4} = \frac{1 - x_{CH_4}}{1 + x_{CH_4}}, \qquad (4.15)$$

where χ_{CH_4} is the conversion percentage of methane, which determines the fraction of the inlet gas that has decomposed to products. x_{CH_4} is the volume percentage of methane in the outlet gas. The formula 4.15 is derived from (4.13), and it is widely used in research reports, e.g. in [17]. When nitrogen atmosphere is used it has to be taken into account in Equation 4.15. The results of the calculations are plotted on the contour map in Figure 4.2.

a)

b)
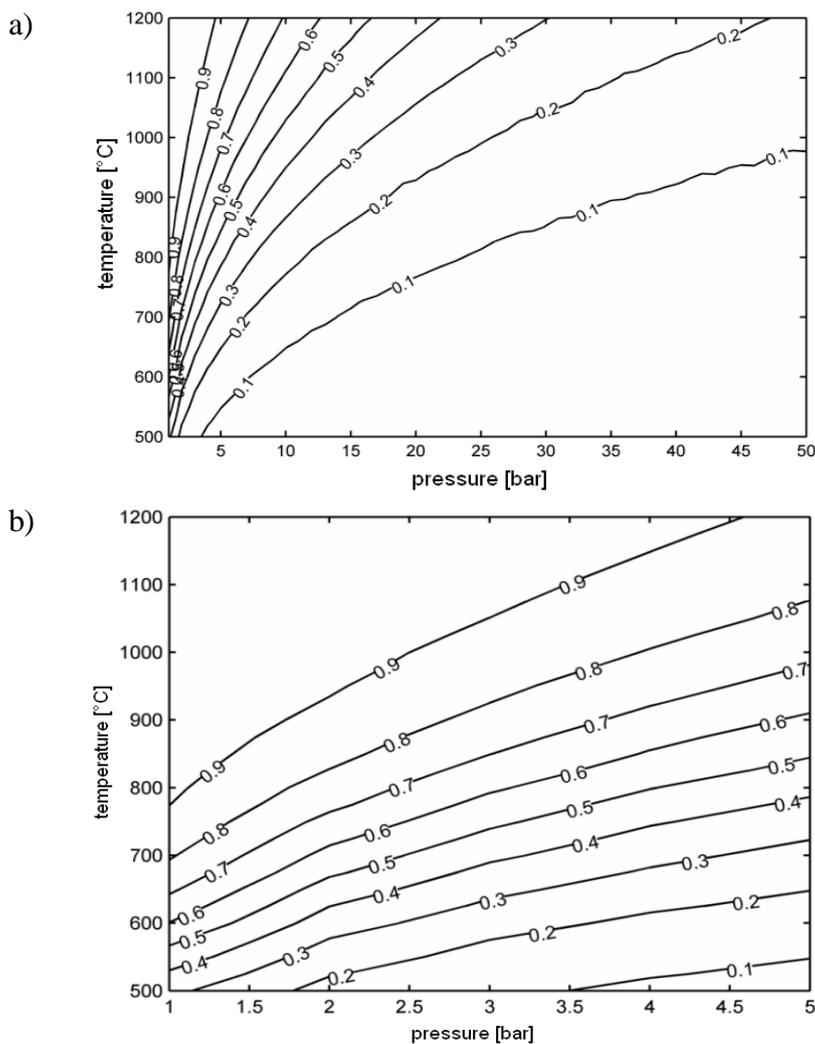
Figure 4.2. *Equilibrium conversion percentage of methane at different pressures and temperatures. a) pressure range 1-50 bar, b) pressure range 1-5 bar.*

As can be seen from the contour map, the reaction is favored by high temperatures: the higher the temperature, the higher the methane conversion percentage. The area of interest, that is the pressure range close to ambient, is shown in more detail in Figure 4.2b. Wavy behaviour of the lowest curves in Figure 4.2a is due to the calculation method and they should be smooth.

It is also evident that methane decomposition is favored by decreasing pressure. This is due to the increase in volume during the decomposition. Although most studies are carried out at atmospheric pressure, Steinberg deduces that TCD is favoured by lower pressures, but the reaction rate is favoured by higher pressure and appears to be catalyzed by the carbon particles formed by the reaction. [18]

4.3.2 Volume hourly space velocity

In chemical reactor design, space velocity indicates the relation between volumetric flow and reactor volume. When a catalyst is present, the corresponding catalyst volume is often used. The notation for the space velocity is SV and it is related to the residence time in a chemical reactor, τ, by the relationship

$$SV = \frac{\text{volumetric flow}}{reactor\ volume} = \frac{1}{\tau}. \tag{4.16}$$

The space velocity indicates how many reactor volumes of feed can be treated in a unit time. Usually the reference time is one hour, and the values presented hereafter refer to the volume hourly space velocity (VHSV). Furthermore, if we consider the reactor dimensions to be unchanged and the catalyst density to be constant, we can deduce that the catalyst mass increase is linearly proportional to the catalyst volume:

$$VHSV = \frac{\text{volume of gas feed/ hour}}{volume\ of\ catalyst} = \frac{1}{\tau}. \tag{4.17}$$

Abbas and Daud concluded after their measurements in [17], that the initial methane decomposition rate was enhanced by the increase of the VHSV. In order to increase the VHSV, either the gas feed rate is increased or the catalyst volume (mass) is decreased. This is obvious from Equation 4.17, and is also consistent with the results published in the literature. The rate of decomposition seemed to be more sensitive to the change in the gas feed rate than to the mass change, but only at a relatively large VHSV. It can be presumed that with different catalyst materials we might end up with different absolute values, but the trends would remain the same.

4.3.3 Effect of the catalyst particle size

There is some controversy as to whether particle size affects the rate of decomposition or not. Abbas and Daud reported in [17], that particle size was insignificant in methane

conversion. Sizes used in the test varied between 135 µm and 1095 µm. However, they also mention that their previous experiments gave different results, (in [19]), showing that particle size was a critical variable. It is suggested that the difference might be due to the thermogravimetric analysis method that had previously been used. Kim et al. [20] also report that particle size plays an important part in catalytic activity in TDM. Abbas and Daud suggest that the different results might also be a consequence of the greatly differing amounts of catalyst used. Whereas in their earlier experiments, and in Kim et al., they used only a few grams of carbon, in the later test 20-120 g of catalyst was used. This amount has not previously been reported in the literature so further testing is needed for confirmation.

4.4   Used catalysts

The catalysts being used in research can be divided into two categories; metal based and carbon based catalysts. Catalysts are critical to the process and are used to accelerate an otherwise slow reaction rate and to lower the reaction temperature, thus reducing costs. Furthermore, catalyst acts as a platform for the forming product carbon.

The last mentioned factor is a drawback yet to be overcome since metal catalysts, in particular, are reported to rapidly lose their activity due to carbon deposits. It should be noted that the catalyst itself does not disappear during deactivation, but the formation of carbon deposits separate the catalyst particles from the surroundings. By removing this formed layer of carbon, the catalyst can be recycled.

Muradov, in [10], collected the available data on catalysts to make a graphical representation (Figure 4.3) of the reported relations between temperature ranges, carbon products and the catalysts used.
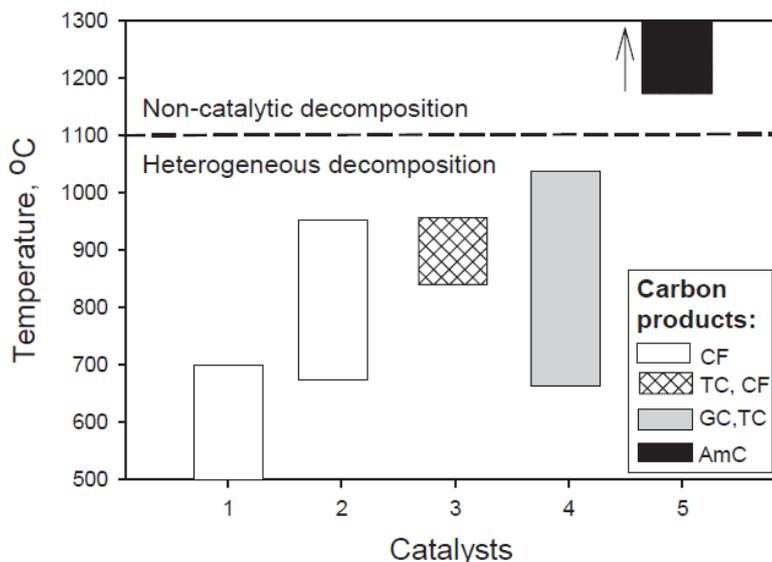
Figure 4.3. *Graphical representation of the bulk of the reported methane TCD data. Catalysts: 1)Ni-based, 2)Fe-based, 3)carbon-based, 4)summary of data related to Co, Ni, Fe, Pd, Pt, Cr, Ru, Mo, W catalysts, 5)non-catalytic decomposition Carbon products: CF-carbon filaments, TC-turbostratic carbon, GC-graphitic carbon, AmC-amorphous carbon [10].*

4.4.1   Metals

Different transition metal catalysts have been used to reduce the maximum temperature of methane thermal decomposition but there is no general agreement among researchers regarding the relative catalytic activities of metals in methane TCD. It has been reported that the rate of methane decomposition activity by the transition metals follows the order: Co, Ru, Ni, Rh > Pt, Re, Ir > Pd, Cu, W, Fe, Mo [21]. However, other researchers have found that Ni or Ni/alumina exhibited the highest activities [22].

The most important factors influencing carbon deposition during metal catalyzed methane decomposition are the particle size, dispersion and stabilization of the metallic catalyst particles, which are controlled by selecting an appropriate support. Various supports for one of the most promising catalyst, nickel, have been tested including TiO_2, SiO_2, MgO, ZrO_2 and Al_2O_3, of which SiO_2 provided the best carbon yield. [23],[24]

Although metal catalysts have higher activity in accelerating the methane TCD reaction and thus reduce the required temperature compared to carbonaceous catalysts, the catalyst activity is eventually lost due to the covering of active sites with carbon deposits. Even though catalyst regeneration is possible and simple to carry out by burning off the deposited carbon with steam, this would lead to CO_2 emission in amounts similar to those in a conventional SRM process [25]. By contrast, mechanical separation of carbon and metal particles is difficult.

Abbas and Daud have made a comprehensive summary of the recent studies on metal catalysts in [26], where catalyst compositions, preparation techniques and major findings can be easily compared. A method for developing a catalyst for the thermo-catalytic decomposition is also reported [27].

In order to scale up and industrialize the process, cheap bulk catalysts will be required in great amounts. This probably excludes metal-based catalysts hence only carbon based catalyst was used in the experimental part in this thesis.

4.4.2   Carbonaceous materials

According to the literature, carbon-based catalysts offer several advantages over metal catalysts: (i) high temperature resistance, (ii) tolerance to sulfur and other potentially harmful impurities in the feedstock allowing higher fuel flexibility, (iii) no metal carbides formed (formation of carbides may complicate the regeneration of metal catalysts), (iv) production of a marketable by-product, carbon, (v) no contamination of hydrogen with carbon oxides, (vi) lower price and (vii) carbon formed can be used as catalyst precursor. Furthermore, some research indicates that there is no need for regenerating of catalysts by burning off the deposited carbon which can be seen to mitigate overall CO_2 emissions from the process. However, this contradicts the findings of other publications, and the current best position is that the deposited carbon is less active than the original catalyst, thus requiring replacement, recycling or refreshment after a certain amount of use. [28],[29],[13]

In the case of methane TCD, further advantages of using carbonaceous catalysts include the following: (viii) it can be catalyzed by carbon produced in the process, so external catalyst is required only at start-up. However, additional treatment is most likely to be required. Catalyst activation is discussed in 4.5.4. If the intention is to reduce the net emissions then it is necessary to utilize the generated carbon, thus minimizing the need for a separate emission creating catalyst making process. Finally, (ix) the separation of the carbon product from the carbon catalyst is not necessary [10].

Various carbon materials have been used for methane TCD including a wide range of activated carbons (AC), carbon blacks (CB), graphite, glassy carbon, acetylene black, graphite, diamond powder, carbon nanotubes (CNT) and fullerenes. According to Muradov, carbons can be arranged in decreasing order of catalytic activity as follows: amorphous > turbostratic > graphite. [13]

The most widely studied carbon materials are activated carbons and carbon blacks because of their activity and their good stability. Operating parameters that have been studied for the activity and long-term stability of these catalysts are temperature range (700-1000 °C), pressure (usually atmospheric) and methane flow rate.

Both Han et al. [28] and Lázaro et al. [29] show that although activated carbons exhibit higher initial activity, this decreases markedly with time. Carbon blacks, however, exhibit lower initial activity compared to the activated carbon catalysts, but their activity tends to reach a quasi-steady state and is sustained over time.

Recently, Serrano et al. [14] reported that, depending on the catalyst's nature and on its pore structure, the carbon deposited may remain within the pores, causing their blockage and catalyst deactivation. Alternatively, it may leave pores growing on the outer part of the catalyst particles. It is said that the latter is expected to occur mainly with catalysts having a high proportion of external surface area (e.g. carbon blacks), which explains their higher resistance to deactivation shown by these carbon catalysts. The same study also indicates that the major property governing carbon activity is the defect concentration present in the graphene layers rather than the surface area.

Both Muradov et al. [13] and Serrano et al. [14] claim that the metal impurities in catalysts play only a small or negligible role in carbon-catalyzed methane decomposition.

4.5   Adapting to large-scale production

Although numerous experiments have been carried out to study the thermocatalytic decomposition of methane, there is little information in the literature on the commercial or large scale production of hydrogen by catalytic decomposition of methane. One of the first patents to include the catalytic decomposition of methane was applied for by Universal Oil Products, and this is discussed in Chapter 6. Modelling and scaling-up studies of the fluidized bed reactor for TCD of NG are presented in [25].

4.5.1 Reactor types

Fixed (or packed) bed reactors have been used in studies to screen the catalytic activity of carbon samples. However, in continuous and large scale action, the addition or withdrawal of carbon generated from a fixed bed reactor would present technical problems.

Tubular reactors (TR) are simple and versatile, and have been widely used for hydrocarbon pyrolysis in refineries. The main problem with the use of TR relates to the difficulty of preventing carbon deposition inside the reaction zone. Reactor clogging is avoided only by using material with minimal catalytic activity with respect to TCD. From this angle, the use of ceramic (e.g. alumina) or quartz tubes is preferred to metallic tubes made of catalytically active iron and its alloys (e.g. stainless steel) This suggests that special surface treated tubes should be employed to prevent carbon deposition inside the commercial tubular reactor. [30]

A fluid wall reactor (FWR) is a modification of a tubular reactor where TCD reaction takes place in a thin layer of a carrier gas heated to the required temperature, thus preventing carbon from depositing on the reactor wall [31]. Due to very high operational temperatures (comparable to those required for methane thermal dissociation) and reduced methane decomposition rates, FWR is unlikely to be used for the large scale production of hydrogen from NG. [30]

In a spouted bed reactor (SBR), hydrocarbon feedstock enters from a small nozzle at the base of the catalytic bed at high velocity, creating a centrally dilute core. The carbon particulates rise inside the core forming a fountain. Very short residence times in the operational area of SBRs are likely to yield relatively low methane conversion rates. Another potential problem arises when the minimum particle diameter for which spouting appears to be practical is about 1 mm, whilst the expected range of carbon particle in the TCD process is about 10-100 µm. Taking these arguments into consideration, SBR is not an option for TCD of NG in large scale units. [30]

Fluidized bed reactor (FBR) technology is well known, especially in Finland. FBR provides a constant flow of solids through the reaction zone, which makes it particularly suitable for the continuous addition and withdrawal of carbon particles from the reactor. According to Muradov, carbon withdrawal could be easily accomplished in large scale units, similar to the existing industrial processes of fluid coking or fluid catalytic cracking. The residence time of carbon particles in the reaction zone could be easily controlled by adjusting the ratio between the feed rate and the weight of the bed. The bed also acts as a buffer for any instability which may arise during continuous operation. [30]

Further advantages of fluidized bed reactors over fixed bed ones are said to be the ease of temperature control, ease of maintaining a constant temperature, enhanced heat and mass transfer, and low cost of catalyst handling. [32]

4.5.2 Heat input methods

Several ways of producing the heat necessary to drive the reaction are reported in the literature. These can be divided roughly into two categories: heat sources that are based on the material streams essentially attached to TCD reaction, and sources that are independent of TCD. A division could also be made according to whether the heat input is direct or indirect. This becomes an option when the catalyst particles are circulated to a separate regeneration reactor, where they could be heated and carrying the energy necessary to drive the decomposition reaction in the decomposition reactor.

The attached heat sources include using a portion of methane (approximately 10-15% of methane LHV), hydrogen previously generated (approximately 15-20%) or carbon as formed in the process, as a fuel [33]. However, using methane or carbon would mean additional CO_2 emissions, although significantly less than in SRM.

Independent sources of energy include concentrated solar energy, nuclear energy, plasma or electrical furnace heating [26]. An electrical furnace would be feasible where case low-cost electricity is available. Research into using nuclear energy is largely based on generation IV nuclear reactors, because the methane could be forced through a molten metal bath which acts as a catalyst [34]. Solar energy has attracted attention not only because of the free 'fuel', but also because in the scenario where all the currently used methane would be converted to carbon and hydrogen, the only adequate source of energy would be the sun [26] (according to [35]).

Muradov et al. introduce internal, external and thermo-neutral heat input options in [36]. Schematics of these are displayed in Figure 4.4.
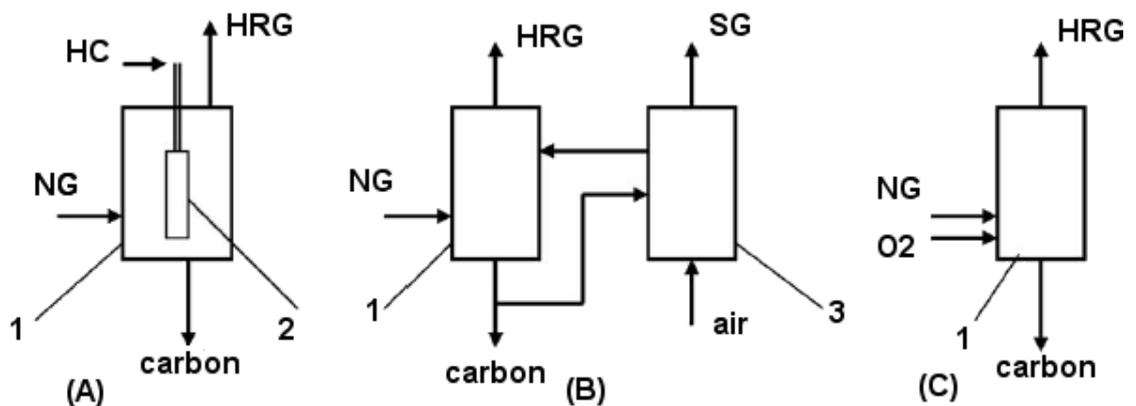
Figure 4.4. *Heat input options: internal (A), external (B) and thermo-neutral (C). Three process heat input options for thermocatalytic decomposition of methane.*
NG, natural gas; HRG, hydrogen rich gas; SG, stack gases; HC, heat carrier.
1, methane decomposition reactor; 2, reactor heater; 3, catalyst particles heater, [37].

The thermo-neutral option (C) is also known as autothermal pyrolysis (ATP) since it involves the combination of endothermic methane decomposition and exothermic methane combustion processes in one reactor. The ATP process is said to produce much less CO_2 emissions than partial oxidation or SMR since it uses less oxidant. Most of the

feedstock carbon ends up in the form of a value-added carbon product rather than CO_2. [36]
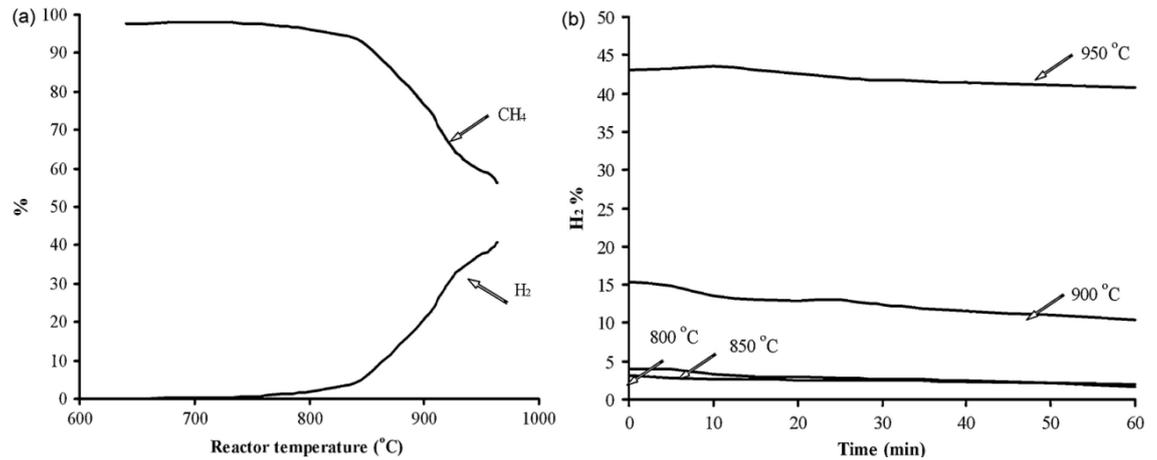
4.5.3 Reactor material

Laboratory scale tests have usually been carried out in reactors constructed of quartz. However, on a commercial scale the construction material will be stainless steel. Abbas and Daud, in [17], have studied the effect of the reactor material on the methane decomposition reaction. The reactor material they used in the tests was stainless steel (SS310S). The composition and the physical properties of the stainless steel are presented in Table 4.1.

Table 4.1. *Chemical composition and physical properties of SS310S [17].*

Chemical composition (%)		
Carbon	C	0.08 max
Manganese	Mn	2.00 max
Silicon	Si	1.50 max
Phosphorus	P	0.045 max
Sulfur	S	0.030 max
Chromium	Cr	24.00-26.00
Nickel	Ni	19.00-22.00
Iron	Fe	balance
Physical properties		
Density	(kg/m^3)	8000
Melting range	(°C)	1400-1450
Specific heat	(J/kgK)	500
Thermal conductivity at 100 °C	(W/mK)	14.2

The authors found that at temperatures higher than 850 °C, the decomposition in an empty reactor increases rapidly. The conclusion is that the reactor material has a significant effect on the decomposition rate. This becomes clear when comparison is made between the composition of the stainless steel and the metal-based catalysts described in Section 4.4.1: Nickel is found in both and is also mentioned as one of the most active metal catalysts. Figure 4.5 further clarifies the effect of the temperature on the material activity.

As austenitic steel has the highest temperature resistance, it would be the most suitable construction material for the TDM. All austenitic steels contain at least some amount of nickel and this should be taken into account.

Figure 4.5. *Effect of reactor material on the hydrogen concentration at a methane flow rate of 0,7 l/min. (a) Temperature program of the percent change of methane and hydrogen concentrations with respect to reactor temperature. (b) Change of hydrogen percentage with respect to reactor temperature and time. Adapted from [17].*

4.5.4   Catalyst activation

One of the main drawbacks for the sustainability of the process is catalyst deactivation. Various activating agents have been studied in order to regain the activity. Muradov et al., in [25], experimented with steam and found that it has a positive effect on catalyst activity. Figure 4.6 illustrates the effect of activation on the methane conversion percentage.
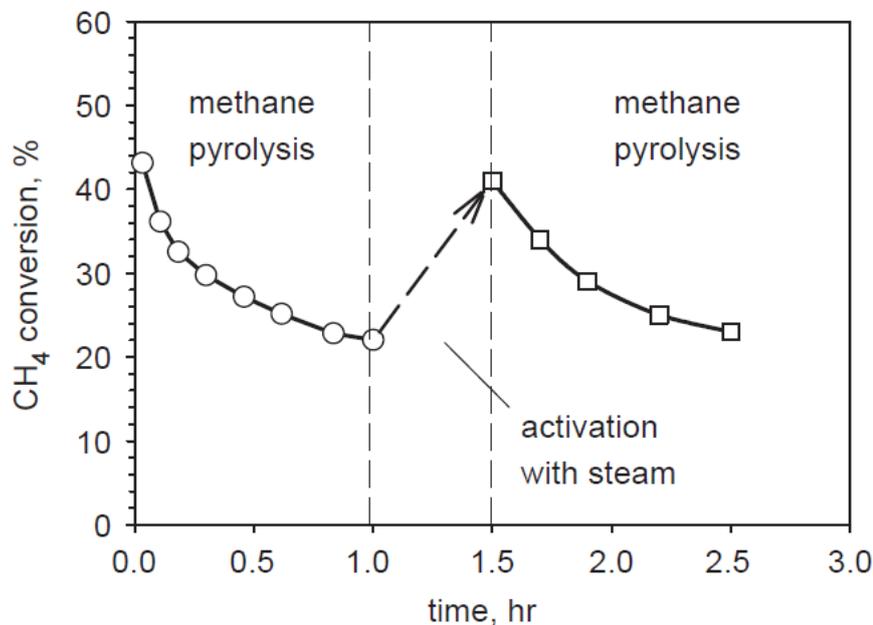
Figure 4.6. *Methane decomposition (850 °C) over AC (lignite) catalyst with intermittent activation of catalyst with steam at 950 °C. [25].*

They deduce that although the regeneration of carbon catalysts requires the gasification of a certain portion of carbon (approximately 15-20 % of the total), the amount of CO_2

emissions per unit of H_2 would be a fraction of that generated during metal catalyst regeneration. In the latter, all carbon has to be combusted or gasified. Furthermore, estimated CO_2 emissions from TDM would be significantly less than those from SRM. [25]

Pinilla et al. have studied CO_2 as an activating agent. They conclude, that the specific surface area and the oxygenated surface groups regenerated by CO_2 activation of a deactivated AC catalyst present a positive linear relationship with the degree of burn-off. In their research, the burn-off degree (BOD) expresses the ratio between the amount of carbon loss during the regeneration stage and the amount of carbon deposited during the previous stage. The regeneration conditions must allow regenerating of the initial textural properties (both oxygenated surface groups and surface area recovery) keeping BOD as low as possible. The authors show that it is possible to find a reasonable compromise between catalyst activation and CO_2-emissions caused by regeneration. [38]

4.5.5   Balance of plant

Heat exchangers should be used to enhance the process efficiency. The enthalpy of the effluent gas stream can be used to preheat the incoming feedstock to approximately 500-600 °C [25]. Further evaluation is needed for the full-scale process.

The majority of the researchers mention pressure swing adsorption (PSA) as a method for separating hydrogen from the effluent gas stream. It is commonly used in conventional steam-methane reformation plants to separate carbon dioxide from hydrogen, but it would also be suitable for TDM.

4.6   Visions for TDM as a part of a process

4.6.1   Carnol process

The Carnol (i.e., carbon dioxide-methanol) process is designed to produce methanol fuel for automotive engines. The method for producing methanol is described in [18]. It is based on TDM, and the additional step is to make the hydrogen react with carbon dioxide from a fossil source. The aforementioned step also enhances the carbon sequestration percentage for the process.

4.6.2   Plasma-assisted carbon black process

Fulcheri and Schwob patented hydrocarbon cracking using a plasma source to produce carbon black in 1980. In [39] they compare the plasma process to the older furnace process, where a substantial amount of carbon dioxide is generated. As a result, they conclude that plasma-assisted hydrocarbon decomposition is essentially CO_2 free. Carbon black is used in the rubber industry as a pigment.

The Kvaerner group started the commercial operation of its first carbon black plant in Montreal, Canada in 1999. The Karbomont plant annual capacity was said to be

20,000 t of carbon black plus 50 million standard-m^3 of H_2 [40]. Investment costs for the plant were \$65 million, and the plant was closed before 2008, apparently due to process problems. Very little information is available on the plant closure [41].

4.6.3 Catalytic decomposition of methane in the presence of in situ generated ethylene

A way of preventing the catalyst deactivation is to use ethylene in the decomposition reactor. Ethylene, being expensive, is created *in situ* in the process of oxidative coupling of methane (OCM), which is combined with the TDM reaction. The OCM-TDM process is researched and discussed in [42]. It is also stated that the combined process is less favourable than the decomposition of pure methane, although the ethylene partially prevents rapid deactivation of catalyst.

4.6.4 TDM attached to a biomass pyrolysis facility

In their report, Dufour et al say that a wood catalyst is the cheapest and the most ecological catalyst for CH_4 conversion as it is directly produced in the pyrolysis facility. The conversion of methane reaches 70% for a contact time of 120 ms at 1000 °C. As pyrolysis also produces CO_2 and steam, it is possible to regenerate the catalyst to maintain its activity. Effluent gas is said to consist of H_2, CO and unconverted C_xH_y. [43]

4.6.5 TDM with direct carbon fuel cell

A new energy production cycle, integrated plasma fuel cell (IPFC), is introduced, where first plasma-assisted decomposition of hydrocarbon takes place and the carbon black formed is then consumed in a direct carbon fuel cell (DCFC). A hydrogen-containing gas is produced in the first phase and electricity in the latter phase, of which a small portion is used in the plasma reactor. [44]

4.7   Use of the carbon formed

Continuous operation of TDM requires constant withdrawal of carbon from the reactor. A portion of the carbon formed is treated and returned to the reactor as a carbon catalyst, but the largest part is sequestered. As can already be seen in Figure 4.3, the carbon produced can have various structures depending on the reaction conditions. Some economical evaluation has been made which discusses the effect of the carbon resale value on the cost of TDM (e.g. [9],[10]). The researchers suggest selling the carbon formed to, for example, the petroleum industry. Several papers also discuss how to produce the most valuable form of carbon, namely carbon nanotubes ([45],[46]).

According to Muradov, if an assumption is made that 50 % of all NG available in the United States were to be converted into hydrogen and carbon via the TDM process, close to 40 million ton of carbon would be produced [10]. Since the annual

world production of carbon black is approximately 8.1 million ton per year [47], and that the combined market for activated and graphitic carbon does not exceed 1 million ton per year [10], there would be vast amount of surplus carbon. Thus, only acertain amount of the carbon produced could be marketed and consequently, the unit costs of the TDM are only reduced to a limited extent by carbon market.

Some innovative ways of consuming the carbon formed are proposed in the literature and it is suggested that building and construction materials could work as a carbon sink. It is also suggested that using carbon as fertilizer could have a positive effect on agricultural production. Being a biologically stable substance, carbon could also be used as a landfill.

In Finland, however, the most probable option is to transport the carbon formed to a large coal-fired power plant, burn it centrally possibly with oxyfuel combustion, and then capture and store the carbon dioxide formed in the combustion process.

5 HYDROGEN PRODUCTION METHODS: COMPARISON

5.1 Steam reforming of methane

Today, steam reforming of methane (SRM) is the most important and well-researched industrial process for the production of hydrogen, and also of carbon monoxide. The first steam reforming plant was commissioned in the early 30s [48] (according to [49]). Literally SRM refers only to the reaction where methane decomposes to carbon monoxide and hydrogen, but commonly also covers the adjacent water-gas shift reaction. The reactions that occur are as follows:

$$CH_4 + H_2O = CO + 3H_2 \qquad\qquad ; \Delta H_0 = 206 \text{ kJ/mol} \qquad\qquad (5.1)$$

$$CO + H_2O = CO_2 + H_2 \qquad\qquad ; \Delta H_0 = -41 \text{ kJ/mol} \qquad\qquad (5.2)$$
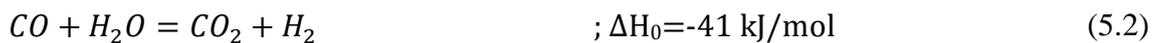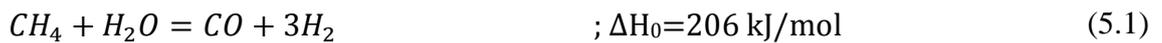
The SRM reaction (5.1) usually takes place over a nickel catalyst in a metal alloy tube at temperatures in the region of 800-1000 °C and at pressures of 30-60 bar. The reaction is equilibrium limited and is highly endothermic, requiring heat input of 251 kJ/mol$_{CH4}$ including the heat needed to produce steam from liquid water. The heat for the reaction is provided by heating the outside of the tubular reactor in a furnace fired by natural gas/air flame. Any impurity, such as sulphur, in the natural gas must be cleaned out prior to SRM. [9]

Water-gas shift reaction (5.2) also takes place in a tubular reactor at lower temperatures than the steam reformer and at approximately the same pressure. The reaction is exothermic and the reaction energy is somewhat balanced so little additional heat is required to maintain the reaction. The reaction produces a mixture of CO_2 and hydrogen with small amounts of CO. [9]

Thus, the overall hydrogen production reaction is as follows:

$$CH_4 + 2H_2O = CO_2 + 4H_2. \qquad\qquad ; \Delta H_0 = 165 \text{ kJ/mol} \qquad\qquad (5.3)$$
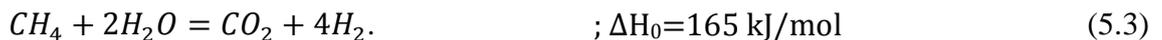
As we can see from the reaction (5.3), the product gas consists mainly of carbon dioxide and hydrogen. Minute amounts of unreacted methane or carbon monoxide can also be traced in the product gas mixture.

Currently, the last phase of SRM has been separating the desired product, namely hydrogen, from the gas mixture. Several methods are available, e.g., solvent

adsorption and stripping. However, the consensus in the literature considers pressure swing adsorption (PSA) as not only to be the most suitable for use, but also the most advanced and economical technique. Once separated, the unwanted compounds are usually vented to the atmosphere. According to [50], the net greenhouse gas (GHG) emissions are 11.9 kg CO_2 equivalent/kg of net hydrogen produced. In order to reduce the GHG emissions, the CO_2 sequestration after the gas separation is required.

5.2   SRM versus TDM

In order for the thermocatalytic decomposition of methane to become a fully viable alternative to steam methane reformation, TDM has to challenge SRM economically. With increasing costs for CO_2 emissions the methods are actually similar financially. Muradov conducted an economic comparison between the two hydrogen production methods in [33], which is summarized in the following illustration. The comparison envisaged a large-scale hydrogen production plant (60 MMscfd ≈ 1.7 M m_N^3/d). Figure 5.1 shows that if capturing CO_2 becomes obligatory in the future, TCD becomes feasible even without carbon credit.
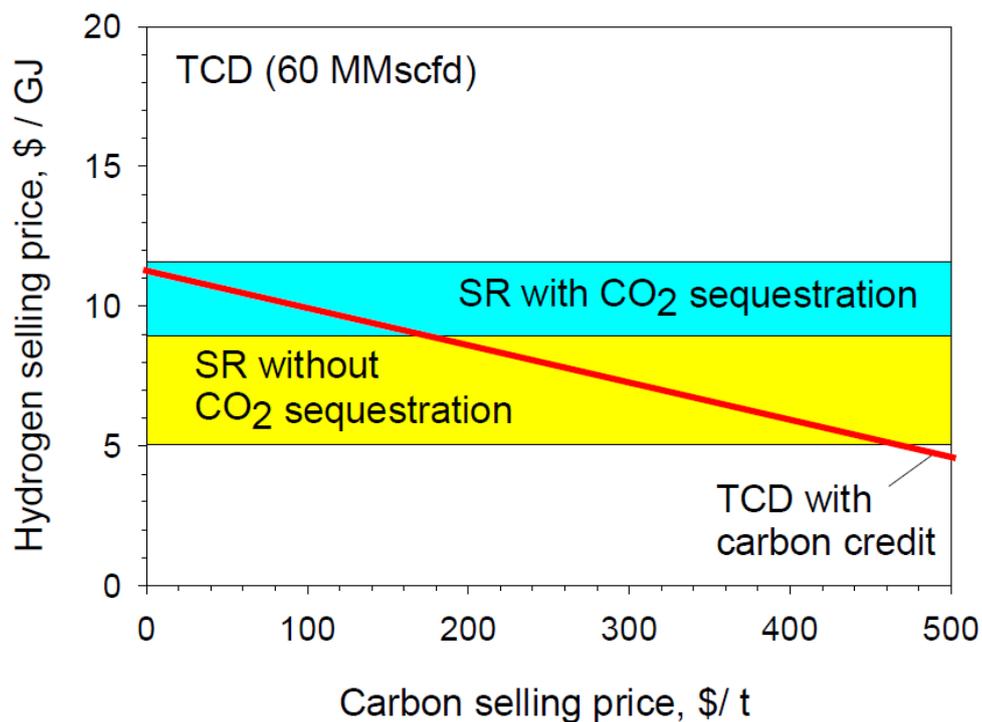
Figure 5.1. *Comparative economic assessment of TCD and SMR [33].*

However, the TDM process is yet to be developed to a commercial level. Steinberg, in [9], compares SRM with TDM and the results of the study are summarized in Table 5.1.

Table 5.1. *Comparison between reforming and pyrolysis of natural gas for hydrogen production, adapted from Steinberg,[9].*

Item		SRM-Reforming	TDM-Pyrolysis
Reaction chemistry		$CH_4 + 2H_2O = CO_2 + 4H_2$	$CH_4 = C + 2H_2$
Mols H_2 per mol CH_4		4	2
Endothermic heat of reaction	*kJ/mol CH_4*	251	75
At 80 % thermal efficiency process heat	*kJ/mol H_2*	79	47
Process thermal efficiency for H_2 production		75 %	58 %
CO_2 emission	*mols CO_2 / mol H_2*	0.43	0.05
kg CO_2 gas / MWh H_2		240	28
kg C solid / MWh H_2		0	76
Process unit operations		1. Reformer	1. Pyrolyzer
		2. Water-gas shift	2.CH_4 separation if needed
		3.CO_2 separation	
Sequestration		Liquid CO_2, in ocean, gas wells, aquifers	Solid C, in land fill, mines or market
Uncertainties		Possible hazardous environmental effects	Minimal
Net energy reduction		≈15 %	≈ 0 %
Net energy efficiency		75-15 = 60 %	58-0 = 58 %
		energy lost = 40 %	energy stored = 42 %
By-product value		Low	High materials potential
Process development		Well developed	Needs development

Recent life cycle assessments ([51],[52]) indicate that the least desirable method for CO2-free hydrogen production with carbon sequestration would be steam-methane reforming enhanced with CCS. In fact, according to [51], the total environmental impact increases slightly when using SRM with CCS due to the high electric consumption of the conventional techniques used to capture and storage the CO_2. Furthermore, the environmental impact of various low greenhouse gas emission technologies are compared in [53], including TDM.

6 INSIGHT INTO PATENTS

The current subject has inspired numerous patents and patent applications. In this chapter, certain promising patents are described and illustrated when figures are available. Table 6.1 at the end of the chapter summarizes the process parameters along with details of patents not discussed below.

6.1 Patent review

6.1.1 Universal Oil Products Company: Process for the production of hydrogen (1964)

The hydrocarbon stream is decomposed with no side reactions and at very high conversions per pass to produce hydrogen and carbon, generally in the range of 816-1093 °C.

A wide range of catalyst base materials is introduced but according to the patent the preferred materials are metals or metal oxides from group VIII of the periodic table. Nickel, iron and cobalt compounds are mentioned. [54]

In the process, catalyst regeneration is carried out by gasifying the carbon formed on the catalyst, which causes CO_2 emissions. A modification of this application would thus be necessary prior to use.

6.1.2 Jha et al.: Process for production of value-added coproducts from coal and other carbonaceous materials (1993)

The relevant part of the patent considers methane decomposition at temperatures above 1095 °C to form fine particles of pure carbon and hydrogen. This reaction can be accomplished in a 2-reactor system such as used in the thermal black process for producing carbon black from natural gas. Alternately, a continuous indirect heat exchanger may be used to accomplish the thermal decomposition of methane.

The hydrogen and carbon-rich gas from the second step is cooled and then passed through filters to separate and collect pure carbon particles. [55]

6.1.3 Steinberg et al.: Process for the conversion of carbonaceous feedstock to particulate carbon and methanol (1995)

The patent includes a methane pyrolysis sub-process as part of a methanol production chain. Only the methane pyrolysis is discussed here.

A counter-current heat exchanger is suggested as a method for producing the required heat to drive the endothermic process. Carbon black is removed from the gas stream employing a gas-solids separation facility.

The residence time, i.e., the contact time of the methane-rich gas with the moving bed of particulate refractory matter, in the reactor varies between 2 and 40 seconds, being typically of the order of about 6 seconds. A suitable exit gas temperature is said to be about 1100 °C. [56]

6.1.4 Lynum et al.: Production of carbon black (1996)

This process has been developed for Kvaerner engineering. The feedstock, i.e., natural gas, is preheated to 650-700°C and fed through a hydrogen-fueled plasma flame to cause a pyrolytic decomposition. Mixing of the feedstock and the plasma gas occurring after the plasma flame raises the temperature to circa 1600 °C. As a consequence, free hydrogen and drops of liquid of dehydrogenated carbon material are formed. Dehydrogenated material is passed to a second stage and maintained at a temperature of 1200-1600 °C to complete the decomposition of the feedstock to carbon black and hydrogen. [57]

6.1.5 Murata et al.: Process for producing hydrogen from hydrocarbon (1997)

The object of the invention is to provide a process which can convert a hydrocarbon such as natural gas into hydrogen without producing CO_2. Hydrogen is produced by thermal decomposition of a hydrocarbon using fine particles of a carbonaceous material as a catalyst, having an external surface area preferably of 4-100 m^2/g. The average particle size of the particulate carbonaceous catalyst is preferably 0.05-50 µm. The particulate carbonaceous catalyst generally contains at least 90 % by weight of carbon. For reasons of catalytic activity and ease of manufacture, the use of soot obtained during arc discharge between carbon electrodes or during thermal decomposition of organic compounds is preferred.

In order to efficiently perform the pyrolysis of the hydrocarbon, it is desirable to dilute the hydrocarbon with an inert gas such as nitrogen, argon or helium so that the feed has a hydrocarbon content, preferably of 0.8-5 % by volume. The pyrolysis is preferably performed at a temperature of 400-1200 °C and the hydrocarbon feed is contacted with the catalyst preferably for 0.1-50 seconds. It is advisable to keep the oxygen concentration in the pyrolysis zone as low as possible, generally below 0.1 volume percentage.

The pyrolysis of the hydrocarbon in the presence of the particulate carbonaceous catalyst may be carried out using any conventionally used solid-gas contacting system. A continuous gas flow mode using a packed bed system, a moving bed system or recirculating fluidized bed system is preferable.[58]

6.1.6 Nakamura: Process for simultaneously producing hydrogen and carbon black (1999)

In this process, ethylene is decomposed in an inert atmosphere at a temperature of 400-600 °C and a pressure of 5-10 bar in the presence of nickel. The flow rate of ethylene in the reaction is 5-50 ml/min. Ethylene could be generated in situ by methane oxidation coupling. [59]

6.1.7 Lynum et al.: Decomposition of hydrocarbon to carbon black (2000)

A decomposition reactor for installation in connection with a thermal decomposition chamber for hydrocarbon gases, especially a plasma torch, is designed in the form of an insulated chamber, with an inlet for admixtures and gases in the walls of the reactor space. The main feedstock is introduced at a temperature of 1000-2000 °C, in the upper part of the reactor. [60]

Figure 6.1 illustrates the decomposition chamber, in which the numbers from 1 to 4 refer to the reactor itself, plasma torches, reaction products and additional feedstock or heating gases, respectively.
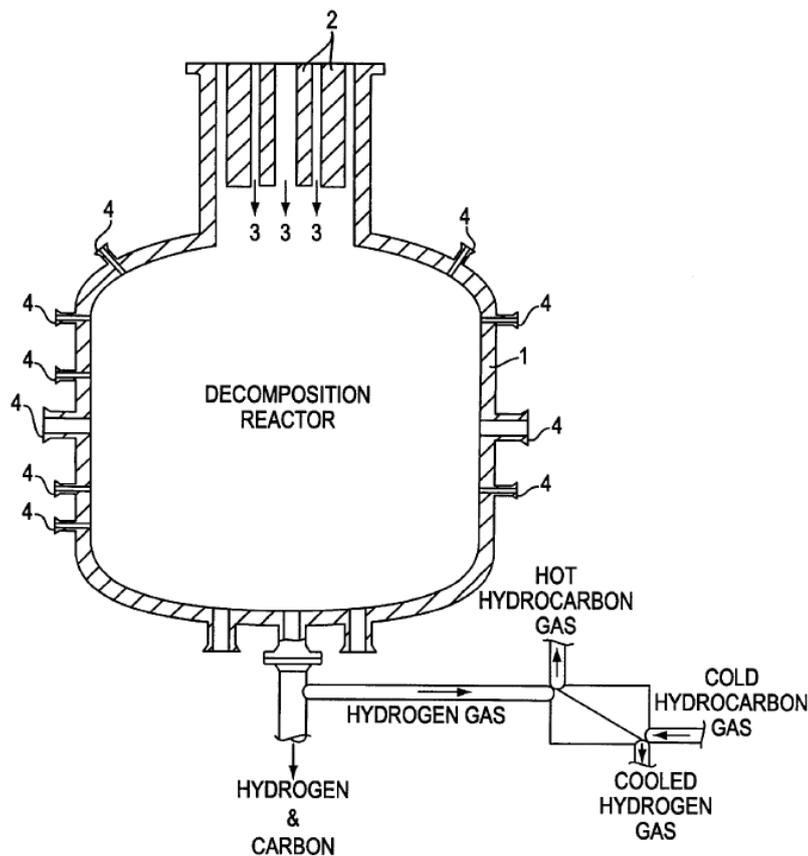
Figure 6.1. *The basic concept of a reactor chamber[60].*

6.1.8 Wang et al.: CO free hydrogen from decomposition of methane (2006)

The method proposed in this patent is to decompose methane to hydrogen and carbon with substantially no carbon oxides. The temperature range is 425-625 °C and the presence of a catalyst is required, for which the patent has also been applied. The catalyst is of the form $Ni_xMg_yO_z$ or $Ni_xMg_yCu_zO$ but the molar ratios presented are rather inaccurate. [61]

The same inventors have also applied for a patent covering only the catalyst. A more detailed description of the molar ratios and examples can be found in [62].

6.1.9 Tada et al.: Method for producing functional nanocarbon and hydrogen by direct decomposition of lower hydrocarbon (2010)

The process parameters for carrying out the direct decomposition of methane are said to be 650-850 °C for the temperature and 1.0 MPa or less for the pressure. The following catalysts are proposed: Ni/Al_2O_3 and Fe/Al_2O_3, depending on the process parameters. Figure 6.2 presents the basics of the method.
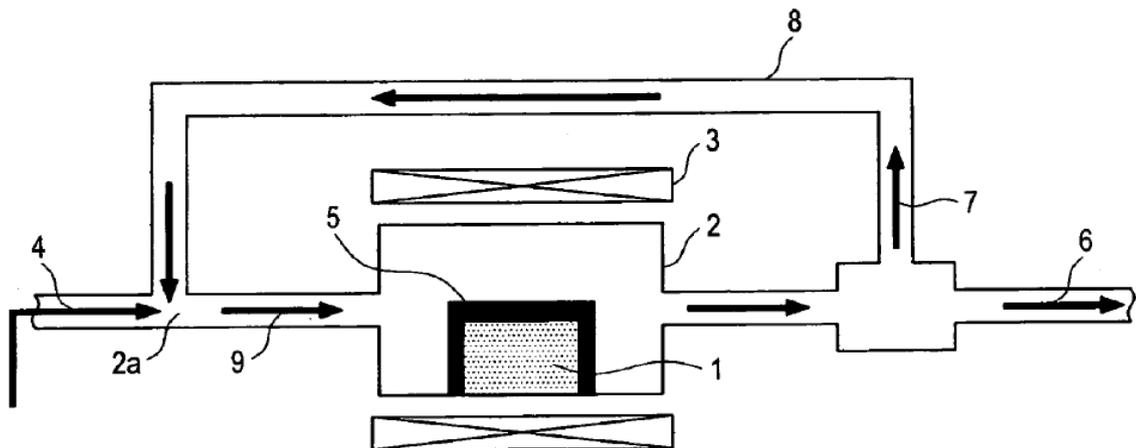
Figure 6.2. Conceptual diagram illustrating an apparatus for hydrocarbon decomposition [63].

Catalyst (1) is placed in a reactor (2), which is heated by the heater (3). Gaseous hydrocarbon (4) is then decomposed into carbon (5) and hydrogen (6) by the action of the catalyst. Hydrogen and the unreacted hydrocarbon (7) are discharged from the reactor, separated and then the unreacted stream is led back to the inlet (2a) of the reactor through a return pipe (8). A low concentration of oxidizing gas, reducing gas or a mixture thereof (9) is fed into the reactor as an admixture to the hydrocarbon. [63]

6.1.10 Chu: System and method for hydrocarbon processing (2004)

In this process, small carbon catalyst particles (300-850 µm) are introduced into the reactor as a catalyst to provide surface catalytic sites for hydrocarbon decomposition and carbon deposition. Large solid carbon particles are continuously withdrawn from the reactor to balance the total surface areas within the reactor chamber and ensure

proper carbon structure. The large carbon particles can be ground to smaller particles to be used as feed material. The sample runs described in the patent application were conducted at 1350 °C. The flow chart for the process contained in the patent application is shown in the Figure 6.3. [64]
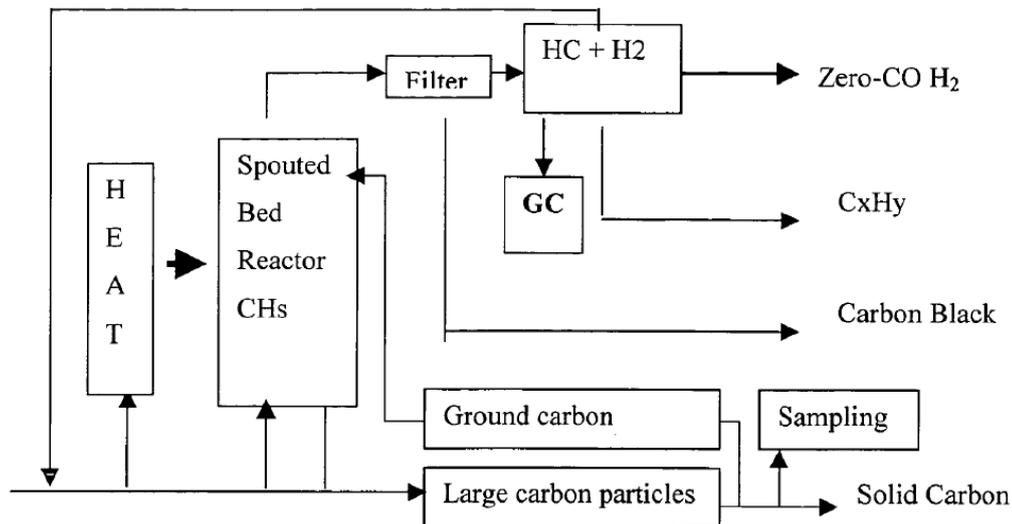
Figure 6.3*. Process flow of the spouted bed reactor for the continuous thermal decomposition of hydrocarbons [64].*

6.1.11 Muradov: Thermocatalytic process for CO₂ free production of hydrogen and carbon from hydrocarbons (2007)

The process is applicable to any hydrocarbon fuel, including sulfurous fuels. A combination of a catalytic reactor with a gas separation unit allows production of high purity hydrogen, completely free of carbon oxides. Sustainable continuous production of hydrogen and carbon is achieved by both internal and external activation of carbon catalysts. Internal activation of carbon catalyst is accomplished by recycling of hydrogen-depleted gas containing unsaturated and aromatic hydrocarbons back to the reactor. External activation can be achieved via surface gasification of carbon catalysts by hot combustion gases during catalyst heating. The process can conveniently be integrated with any type of fuel cell.

A preheated stream of a hydrocarbon feedstock enters the thermocatalytic reactor (1), as seen in Figure 6.4, where it is thermocatalytically decomposed at fluidized bed temperatures, preferably between 850-1000 °C and a pressure preferably of 1-25 atm over a fluidized bed of the catalytically active carbon particles. The residence time within the reaction zone is preferably 1-60 seconds.

The hydrogen-containing gas (HCG) after the reactor (1), a cyclone (2) and a heat exchanger (3) is directed to a gas separation unit (GSU) (4). The concentration of hydrogen in the HCG after the reactor (1) depends on the residence time and varies in the range of 30-90 volume percentage. A hydrogen-depleted gas (HDG) after the GSU is recycled to the catalytic reactor (1). The product carbon (coke) is withdrawn from the

bottom of the fluidized bed reactor (1) in the form of carbon particulates. A fraction (20-30%) of the carbon is ground into fine powder in a grinder (5) and is directed to a heater (6) where it is heated, preferably to 950-1200 °C, activated, and recycled to the reactor.

The heat input necessary to drive the endothermic process can be provided by several methods. According to the patent application, it is possible to use one of the following streams as a fuel: a portion of the carbon formed with air, part (approximately 10 %) of the hydrocarbon feedstock, a portion (approximately 10 %) of the HDG, portion (approximately 10-15 %) of the HCG or a portion (approximately 15 %) of the hydrogen. The combustion takes place in a heater (6). [37]
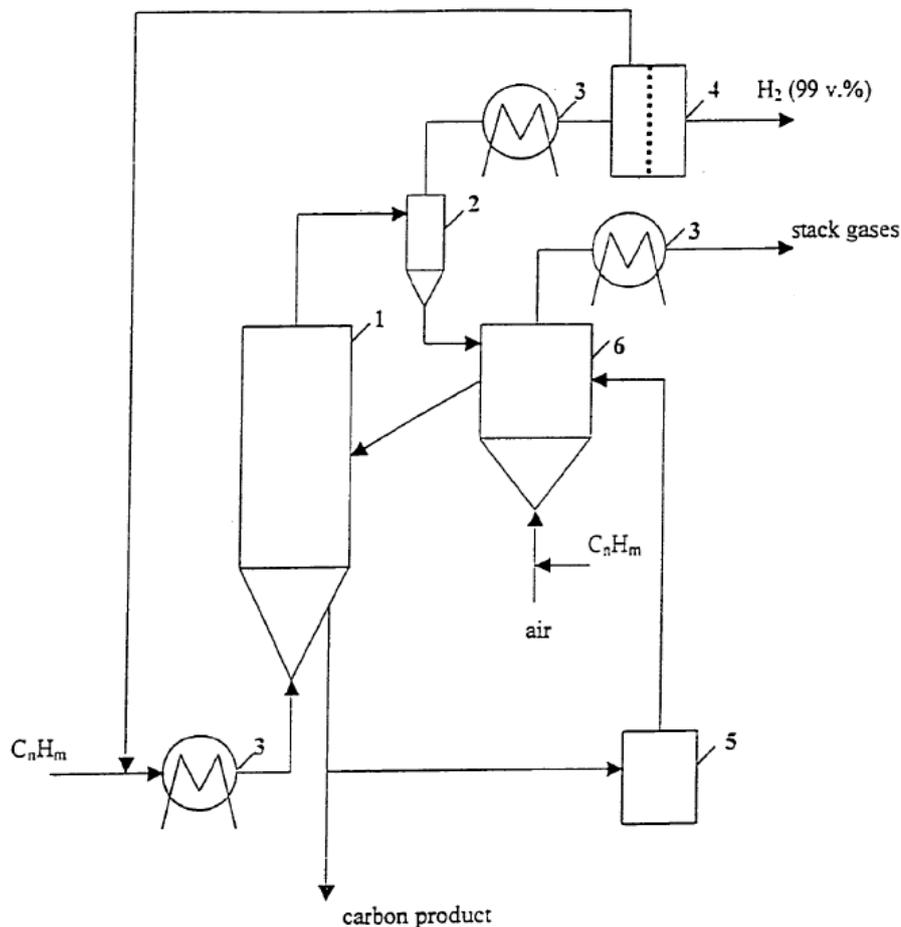
Figure 6.4. *Schematic diagram of an apparatus for carrying out the process of the invention [37].*

6.2   Patent evaluation

Of the patents described above, Nazim Muradov's patent (2007) seems to be the most promising. It involves circulating fluidized bed technology, which offers the opportunity to extract the carbon formed, thus making it possible to have a continuously running process. In addition, the fluidization technology is an area of Finnish expertise, which may give a head start in developing and designing large-scale plants in the future.

The carbon-based catalyst used is activated on-site using different activating agents, which could be obtained from the adjacent power generation process. Furthermore, the excess process heat is integrated and used in other parts of the process, thus increasing efficiency.

6.3   Patent summary

Table 6.1 contains the process data obtained from the patents described above and also information on some additional patents. Where parameters are missing, no details were included in the application. Where pressure information is missing, an assumption of atmospheric pressure for the process can be made.

***Table 6.1***. *Summary of the process parameters described in patents.*

Year	Tempera-ture	Pressure	Catalyst	Products	Heating method	Patent
	[°C]	[bar]				[ref.]
1964	816-1093	-	group VIII metals/metal oxides	H_2	-	[54]
1967	704-927	min.	alumina with nickel, alumina-silica with nickel	H_2, carbon	-	[65]
1993	>1095	-	-	pure carbon, H_2	combustion gases	[55]
1995	~1100	50	-	carbon, H_2	effluent gases	[56]
1996	1200-1600	-	-	carbon black	plasma torch	[57]
1997	400-1200	-	soot	H_2, solid carbon	-	[58]
1999	400-600	5-10	nickel	H_2, carbon black	electric heater	[59]
2000	1000-2000	-	-	carbon black	plasma torch	[60]
2001	500-1000	5-20	nickel	H_2	-	[66]
2004	1000-1800	-	carbon	nanocarbon, H_2	various options	[64]
2004	600-1000	>1	group VIII metal	H_2	-	[67]
2005	500-800	-	binary metal	H_2, high-value carbon	-	[68]
2006	500-900	-	CoO-based	multiwalled CNTs	-	[69]
2006	500-575 /750-760	-	$Ni_xMg_yO_z$ / $Ni_xMg_yCu_zO$	H_2, carbon	electric furnace	[61]
2007	850-1000	1-25	carbon	H_2, carbon	portion of feedstock	[37]
2008	900-1000	-	Fe-based & carbon mix.	H_2, CNTs	microwave irradiation	[70]
2008	~500	-	nickel oxide	H_2	-	[71]
2010	650-850	<10	Ni-based, Fe-based	nanocarbon, H_2	electric heater	[63]

7   EXPERIMENTAL STUDY

7.1   The experimental setup

The experimental apparatus used is based on the designs found in the research reports. Stainless steel tube (I.D. 42.3 mm) was used as the reactor core material. Porous quartz frits are used as a bed material in order to avoid possible catalytic effects on the reaction. The top of the reactor is filled with quartz wool to capture possible airborne carbon particles. The inlet gas flow, consisting of methane diluted with nitrogen, is controlled with commercial Bronkhorst mass flow controllers. The effluent gas is fed to Fourier transform infrared (FTIR) gas analyzer. The analyzer is unable to directly measure diatomic gases – hydrogen, for example - thus the amount of hydrogen formed has to be calculated from the difference between the methane in the inlet and outlet flows.

Temperature control of the heaters is conducted with two independent thermocouples, and the catalyst bed temperature is used as the reaction temperature. The reacting gas is only fed into the reactor after the bed has reached the desired temperature. Once the temperature level is reached, there is little change and the temperature stays within ±1 K of the preset value.
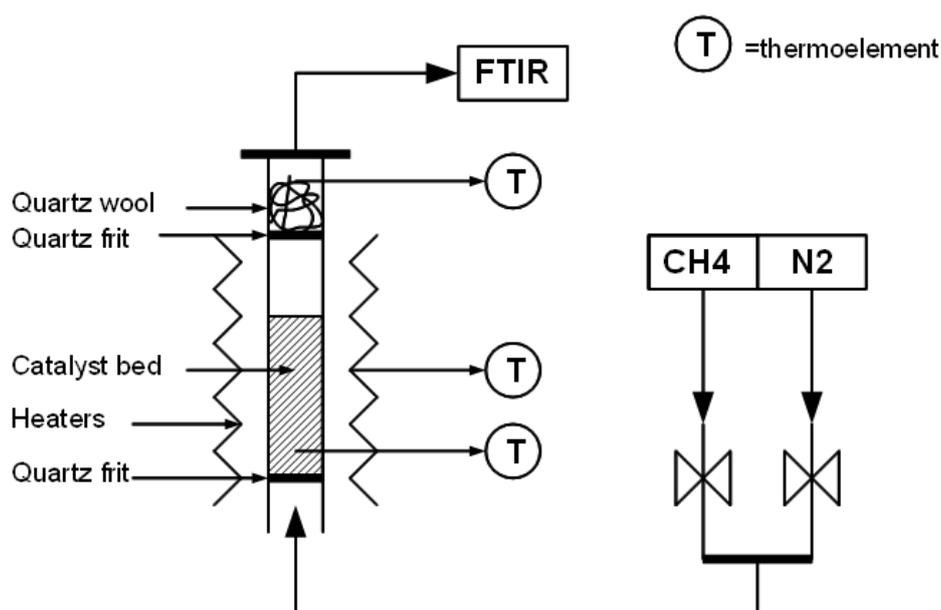

Figure 7.1. *Schematic diagram of the decomposition reactor.*

7.2 The catalyst used in experiments

Commercial carbon black from Cabot Carbon Black Pearls 2000 (BP2000) was selected as the carbon catalyst to be used in the experiments. It is a carbon black with a high surface area and high pore volume [72]. In addition, it is commonly used in the laboratory-scale experiments (e.g. [73], [30], [32]) due to its reactivity with respect to methane decomposition and it provides a representative reference material for the current tests. The carbon black is in fine powder form and has very low moisture content.

In order to have comparable results, the catalyst was always used without further processing. It was expected, that the sphere shaped carbon particles would be ground while the gas flows through the catalyst bed. However, this didn't happen and thus the available surface area for the reactions has been smaller than predicted. In the future more effort is put into catalyst preparation and more information will be gathered from the density, weight increase and particle size. In large scale use, fine powder form catalyst can cause both health and environmental risks which have to be carefully evaluated.

Microscopic images of the BP2000 carbon catalyst are seen in Figure 7.2. The 'shiny' spots in the Figure 7.2b tell that the particle surfaces have been colliding and polishing which has lead to loss of the active sites.

a)

b)
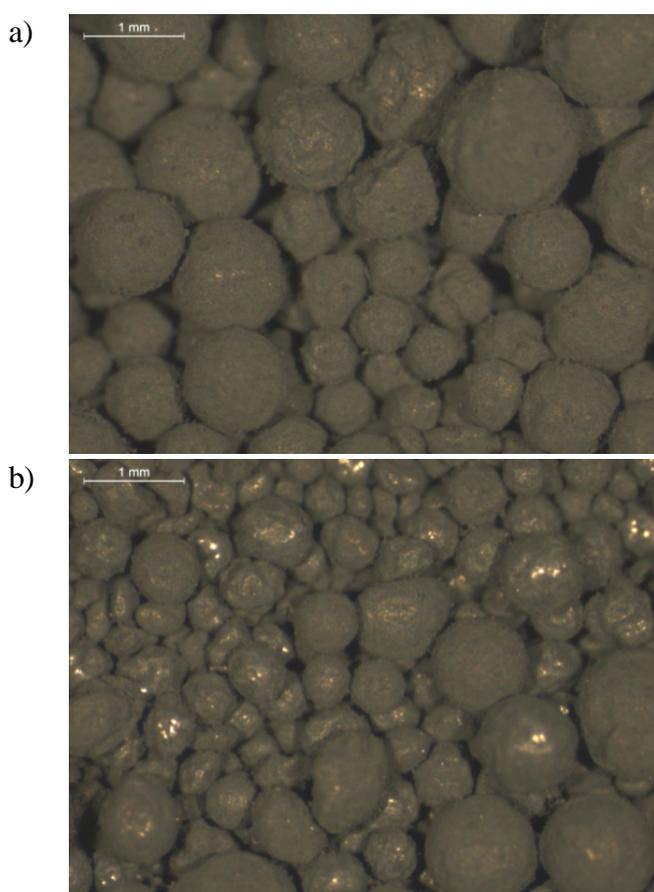
Figure 7.2. *Microscopic images of the BP2000 carbon catalyst.*
a) fresh catalyst b) used catalyst.

8 RESULTS

8.1 The runs

8.1.1 Experiment without catalyst

Experiments without the presence of the catalyst were conducted during the preliminary runs. The aim was to measure the effect of the reactor material on the decomposition reaction. The reactor walls are stainless steel X15CrNiS 20/12 (AISI 309), and the additional components in the alloy may catalyze the reaction, as is discussed in Section 4.4.1. Negligible rate of methane decomposition was detected within the temperature range used, 500-950 °C. This is in contrast to the results referred in the literature (see 4.5.3), and indicates that no generalizations can be made about which materials catalyze and which do not. The catalytic effect has to be checked in preliminary test runs, until the reaction chemistry has been thoroughly examined. One substantial difference in the materials used in the current tests and those cited is the amount of nickel. As Abbas and Daud used stainless steel with 20 wt-% of nickel, there is only 12 wt-% of Ni in the steel used here. This the difference could contribute to the results observed.

8.1.2 Experiments in the presence of catalyst

Before the actual experiments, the catalyst bed is treated with nitrogen flow to remove moisture and any oxygen absorbed on the carbon surface. A run was only started after the temperature of the catalyst bed had stabilized and the gas analyzer showed no signs of oxygen or any other unexpected gases.

An interesting phenomenon was observed after the first few experiments. In the conversion curves, a clear step change can be seen in the fraction of methane converted. There seems to be no consistency as to when this drop occurs. As far as the author is aware, similar phenomena have not been reported in the literature. The step might indicate the catalyst's ability to absorb a certain amount of methane in itself, and the saturation point of the catalyst can be seen as the drop in conversion. Its contribution to the overall process could be analyzed further in the future. Other suggestion is that the gap in conversion percentage is due to an unpredicted behaviour of the methane flow control valve, which will be replaced in the future.

In runs with the catalyst, the ppm-levels of higher hydrocarbons were observed. The hydrocarbons measured, apart from methane, were ethane (C_2H_6), propane (C_3H_8), ethylene C_2H_4) and acetylene (C_2H_2). Of these only ethane and propane were detected in measurable amounts. The step drop discussed in previous paragraph is observable also

in the amounts of these compounds. Figure 8.1 is an example of the behaviour of the higher hydrocarbon concentrations in one of the experiments.
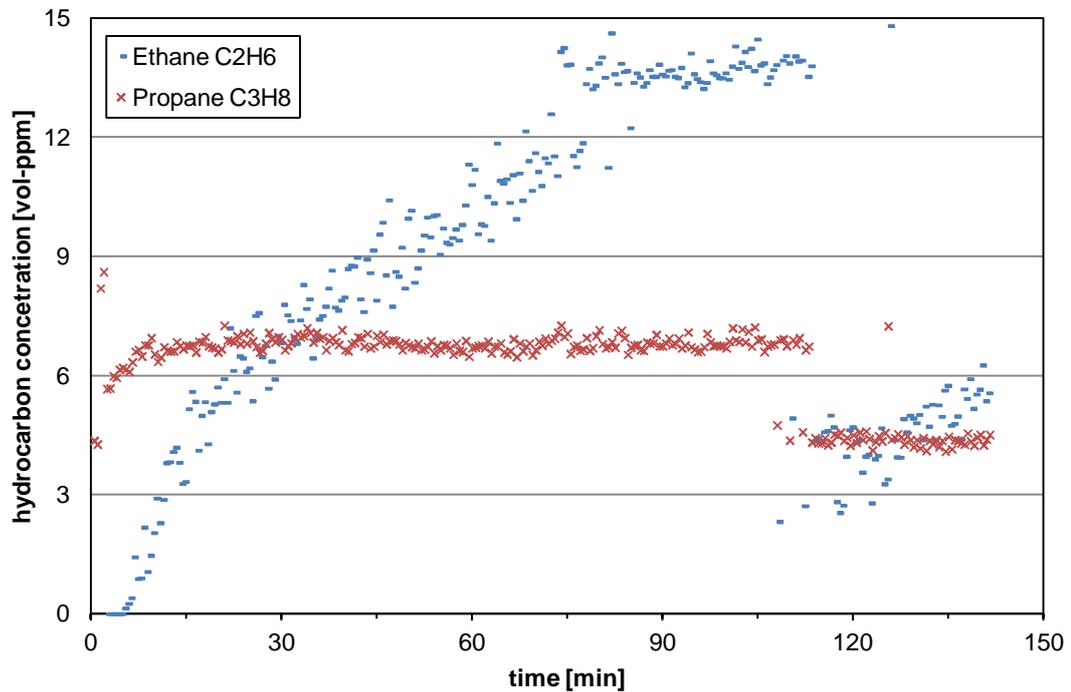
Figure 8.1. *Higher hydrocarbons measured in the effluent gas.*

8.1.3 Effect of temperature

Based on the equilibrium calculations, temperature seems to be an essential parameter affecting the reaction. Its effect on the conversion percentage became evident after the test runs, which were conducted under the following conditions (Table 8.1):

Table 8.1. *Parameters used in runs to determine the effect of temperature.*

pressure	p	1	atm (amb.)
methane flow rate	$\dot{V}_{CH4}$	0.206	l/min
nitrogen flow rate	$\dot{V}_{N2}$	3.925	l/min
methane mole fraction	x_{CH4}	5	%
catalyst mass	m_{cat}	50	g
space velocity		1190	1/h

	run 1	**run 2**	**run 3**
temperature	850 °C	900 °C	950 °C

Figure 8.2 illustrates the three runs in terms of the % of methane converted.
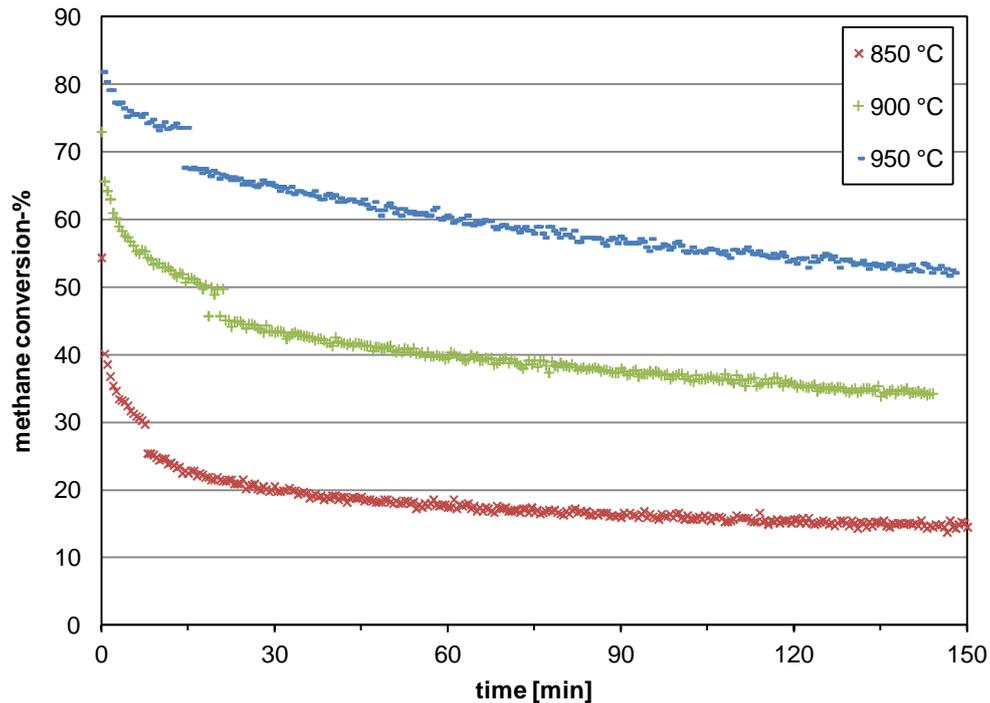
Figure 8.2. *The effect of temperature on the % of methane converted.*

8.1.4   Effect of the space velocity

Space velocity was discussed in Section 4.3.2. In the experiments, the space velocity can in theory be changed either by changing the gas flow or by changing the amount of carbon catalyst. As problems arose with the methane flow control valve, lowering of the space velocity had to be conducted by increasing the volume of the catalyst bed in the reactor. After the first test runs it became evident, that the lower the space velocity, the higher the methane conversion percentage is. It could be deduced, that the reactions taking place in the catalyst bed are not immediate, and the residence time of methane has to be rather seconds than fractions of it.

It was also mentioned in Section 4.3.2, that the methane decomposition rate seemed to increase along with the space velocity. Results show that at the same time the space velocity has a negative effect on methane conversion percentage. As a conclusion, this seems to become an optimization problem with respect to the desired parameters (for example maximum conversion or the fastest reaction rate).

As the density of the carbon catalyst is needed in the volume calculations, attempts to measure it were made. The reliability of the method used was found to be questionable, so the value given in literature was used instead. The bulk density for the BP2000, according to Lázaro et al. [72], is

$$\rho_{cat} = 0.24 \frac{g}{cm^3}.$$ (8.1)

When the catalyst is weighed and the inlet gas flow rate is known we can calculate the gas hourly space velocity (GHSV) for the runs by modifying the formula 4.17:

$$GHSV = \frac{\rho_{cat}(\dot{V}_{N_2} + \dot{V}_{CH_4}) \cdot 60\,000}{m_{cat}}, \tag{8.2}$$

where the gas flow rates are $\dot{V}_{N_2}$ and $\dot{V}_{CH_4}$ are given in *l/min*. Table 8.2 shows the parameters used in the runs.

Table 8.2. *Parameters used in runs to determine the effect of space velocity.*

temperature	T	900	°C
pressure	p	1	atm (amb.)
methane flow rate	$\dot{V}_{CH4}$	0.206	l/min
nitrogen flow rate	$\dot{V}_{N2}$	3.925	l/min
methane mole fraction	x_{CH4}	5	%

	run 1	run 2	run 3
catalyst mass	30 g	40 g	50 g
GHSV	1983 1/h	1487 1/h	1190 1/h

Figure 8.3 illustrates the three runs in terms the % of methane converted.
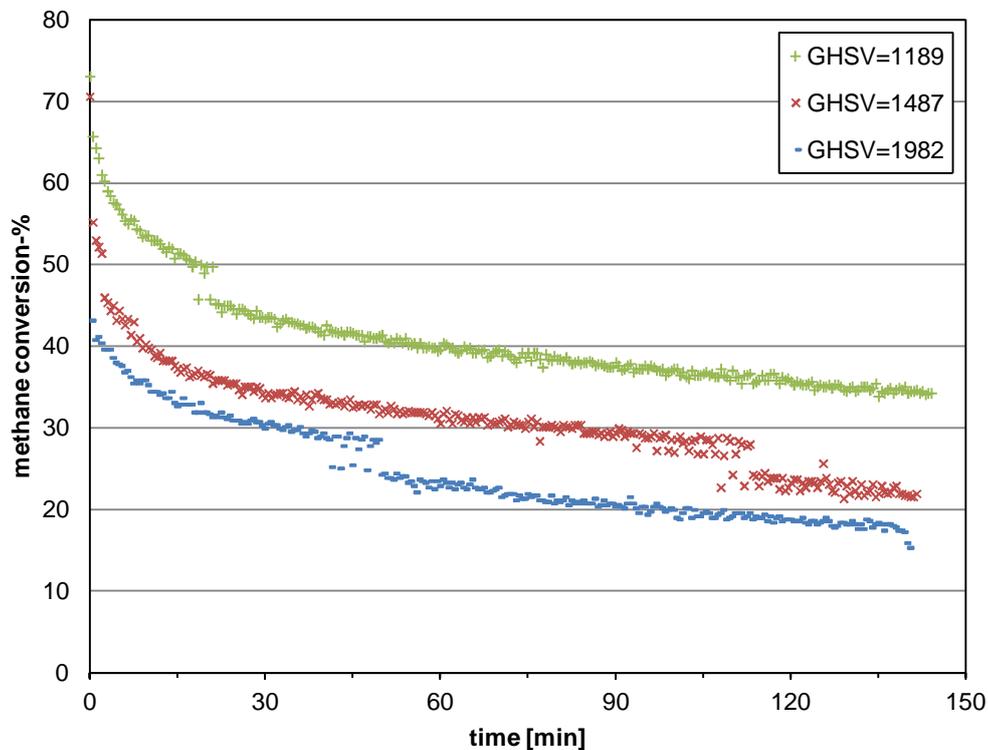
Figure 8.3. *The effect of space velocity on the % of methane converted.*

It is obvious from the figure, that space velocity is a key parameter in the reaction. Similar kinds of behavior can also be expected with lower GHSV-values. In order to scale up the process, it is also clear that the residence time in the reactor has an upper boundary value limited by techno-economic factors, which could be the subject of future studies.
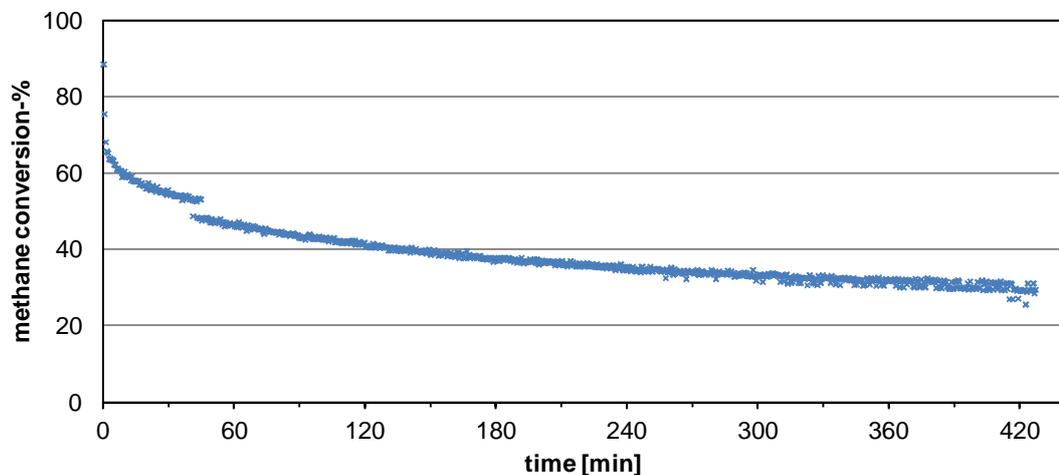
8.1.5 Long duration run

An attempt to monitor the catalyst behaviour during a long test run was also made. From the decomposition curves it could be deduced that the conversion percentage asymptotically approaches a constant value. Still, a question arises if the activity drops drastically after a certain time. This information could be used in the future catalyst life time estimations. Table 8.2 shows the parameters used in the long duration run.

Table 8.3. *Parameters used to determine the catalyst behaviour during a long duration run.*

temperature	T	925	°C
pressure	p	1	atm (amb.)
methane flow rate	$\dot{V}_{CH4}$	0.206	l/min
nitrogen flow rate	$\dot{V}_{N2}$	3.925	l/min
methane mole fraction	x_{CH4}	5	%
catalyst mass	m_{cat}	50	g
space velocity		1190	1/h

It can be seen from Figure 8.4 that during the length of the run, the conversion percentage reduces quite predictably. It is interesting that the conversion percentage has values similar and even better compared to the values in the run conducted in 950 °C (see Section 8.1.3). It could indicate, that it is possible to achieve same conversion in lower temperatures (here 925 °C), depending on the reactor conditions. In laboratory scale it can refer to even catalyst distribution in the bed, careful clamping of the grates etc., but same laws apply on the larger scale as well.

Figure 8.4. *Methane conversion percentage behaviour during a long duration run.*

With the current catalyst, even longer run is suggested and similar test should be conducted with all new catalysts taken into use in the future.

8.1.6 Methane decomposition rate

Daud et al. calculate values for the methane decomposition rate (R) using the following formula (e.g. [17]):

$$R = \dot{n}_{CH_4} \cdot \frac{\chi_{CH_4}}{m_{cat}}, \tag{8.3}$$

where $\dot{n}_{CH_4}$ is the molar flow rate of methane in units *mmol/min*, χ_{CH_4} is the measured methane conversion percentage and m_{cat} is the weight of the catalyst. Thus R has units of *mmol/g$_{cat}$ min^{-1}*.

For easier calculation, Equation 8.3 can be modified as follows

$$R = \frac{\rho \dot{V}_{CH_4}}{M_{CH_4}} \cdot \frac{\chi_{CH_4}}{m_{cat}}, \tag{8.4}$$

where ρ is methane density, $\dot{V}_{CH_4}$ is the methane flow rate in units of *ml/min* and M_{CH_4} is the methane molar mass.

The temperature dependence of density can be taken into account by applying the ideal gas law when the working pressure is close to the atmospheric:

$$R = 10^{-3} \cdot \frac{p \dot{V}_{CH_4}}{R_u T} \cdot \frac{\chi_{CH_4}}{m_{cat}}. \tag{8.5}$$

Now p is the operating pressure, R_u the ideal gas constant and T the operating temperature. The decomposition rates are calculated for both the temperature and space velocity cases and the following figures can be created:
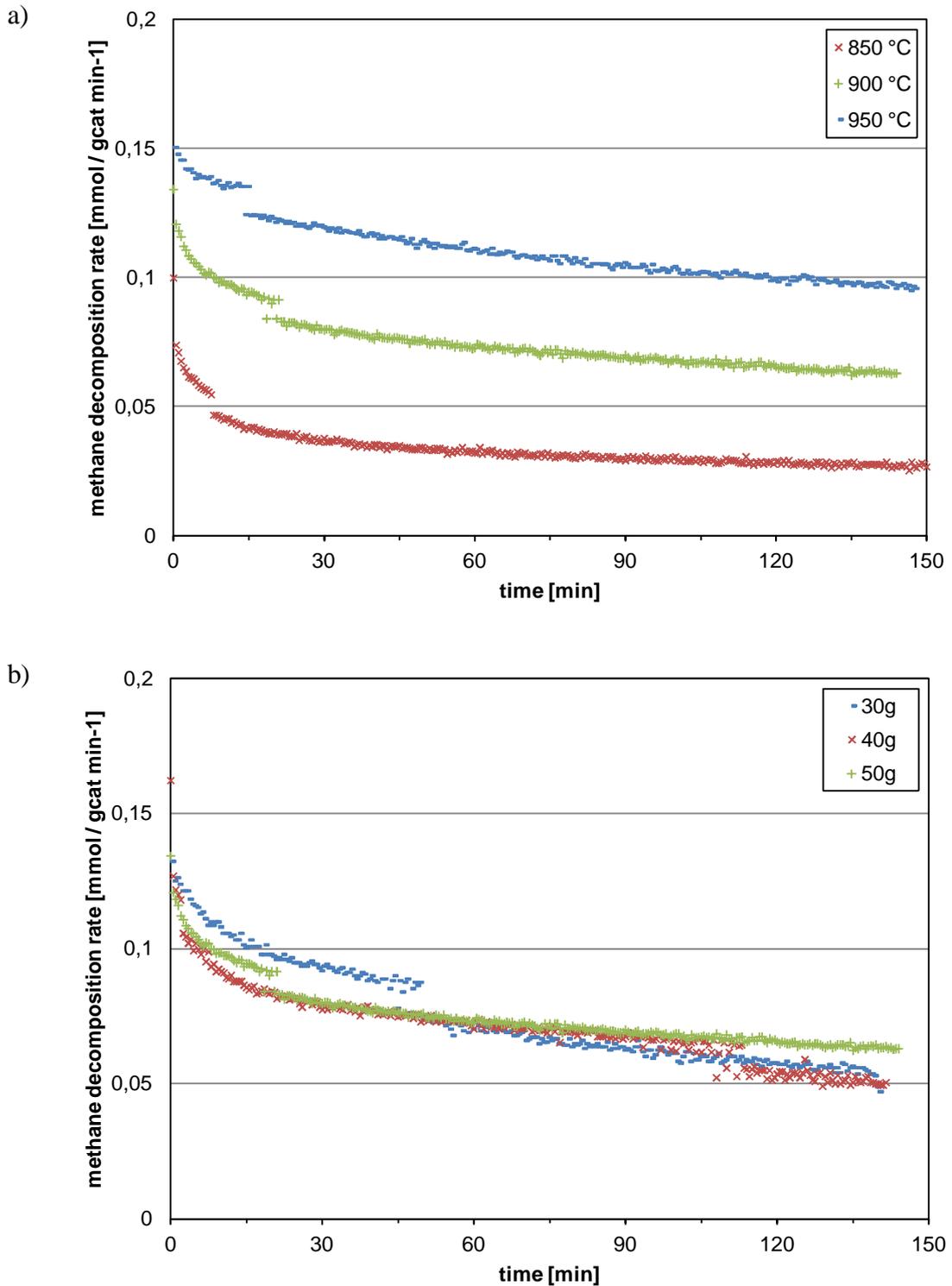
Figure 8.5. *Methane decomposition rate as a function of a) temperature and b) space velocity.*

Figure 8.5 shows that the decomposition rate values are low compared to the ones in the literature (e.g. [17],[72]). In Figure 8.5a, elevating the temperature can also be seen as higher decomposition rates. However, the effect of the catalyst amount on the decomposition rate seems to be somewhat low. In Figure 8.5b the decomposition rate curves even overlap each other.

There is no mentioning whether the authors have calculated the decomposition rates using NTP-conditions or not, which would result in higher decomposition rate – values. Furthermore, in order to for clarify thoroughly for example the space velocity contribution on the decomposition rate the current experimental setup needs further enhancing.

8.2   Suggestions from the experiments

In general, the experiments showed results which were surprisingly comparable to those in the literature. In order to reduce the systematic error, the experimental apparatus is to needs to be updated.

Set points for the methane mass flow controller had to be determined experimentally, which lead to some uncertainty and reduced the range of gas flow rates available.

Determining the mass increase of the catalyst due to the deposited carbon turned out to be problematic and inaccurate. Despite the quartz wool used as a filter above the upper quartz frit, some carbon was able to escape from the reactor. A new method for preventing this is necessary.

The reactor lid rapidly lost – after one or two runs- the ability to prevent air leaking into the reactor. This was detected through the presence of fractions of CO and CO_2 in the outlet gas. In the calculations, these were treated as 'unconverted methane'. A solution has probably been found and will be tested during future experiments.

With the current setup, the highest test temperature seemed to be 950 °C at which point the reactor core started to flake, and the quartz frits showed signs of deformation. In order to conduct experiments at higher temperatures, a new apparatus has to be considered.

8.3   Future research areas

It is evident, that in order to reduce anthropogenic carbon dioxide emissions via the method described in the thesis, an alternative catalyst or a sustainable catalyst regeneration method has to be found. One solution could be a carbon catalyst based on otherwise difficult to use biomass.

As further tests are made, the suitability of the existing power plant technology will be evaluated. Circulating fluidized bed –technology and regenerative heat exchangers may have potential on an industrial scale. Some compromise between the desired conversion of methane and the process pressure probably has to be made, for increased pressure enables plant size to be reduced.

Techno-economic assessment and realistic process efficiency calculations are essential in the future as they will define the boundary conditions within which to act. Fluctuating and still somewhat immature legislation and regulation concerning CO_2 emissions mean that this is not an easy field in which to conduct cost comparisons.

Whether the plant location would be better at the user-end or at a more communal location still needs to be investigated. The selection of the reaction heat input method depends on the local conditions. Electric heating is a good option when it is available CO_2 free and economically. Otherwise burning a portion of either the feedstock or the product gas are options.

9   CONCLUSIONS

Methane thermocatalytic decomposition has been examined as a possible way to reduce CO_2 emissions in the natural gas combustion process in the future. The purpose of the thesis is to give an insight into the topic for the reader and to offer a basis on which it is possible to draw up the guidelines for the future. The bibliography contains most of the literature published in the field. This area of research is relatively new so that more information is needed in order to scale-up the process with the emphasis being in finding an efficient catalyst as well as a low-emissive method for regenerating it.

The results showed that the reaction already takes place at reasonable rates with a relatively modest experimental setup and without further optimization of the process parameters. This encourages future research, and has given new ideas for future work.

It may be that this path towards reducing carbon dioxide emissions ends as a result of some unexpected difficulty in the future, but that would be a result itself showing that this is not the solution and new areas are then explored. Or it may be that this method, on a national scale, will decrease the fossil-fuel based carbon dioxide emission by almost ten percent, support a new business area and make Finnish green technology a desirable export product. Reality, most likely, lies between these two alternative scenarios. It has to be emphasized, that no single technology, improvement or invention can make a difference on its own. In order to reduce the greenhouse gas emissions and change the current course, a contribution from numerous solutions will be needed. Even if the technique described in the thesis turns out to be unpromising, on the way to that conclusion, knowledge will have grown, and people will be inspired by the new ideas which evolve during the research process These in turn can be of help in finding novel ways to reduce the environmental effects and provide better opportunities for future generations.

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