Oligomerization of Ethylene and Ethanol into Fuel Through Heterogeneous Catalysis

by

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Abstract

The goal and ambition of this thesis has been to investigate a topic that could lead to a possible solution to the environmental crisis we are witnesses of. Replacement of fossil fuels is an essential step towards a renewable society that needs to be taken. This thesis will investigate one of those possible solutions, production of a biofuel from a renewable source. A large amount of research within the topic of ethylene oligomerization towards fuel hydrocarbons has already been conducted with variating results. During this work two noble metal catalysts were tested in experiments where both ethylene and ethanol were used as raw material in order to perform oligomerization to hydrocarbons used in fuels. The atmospheric pressure experiments that were performed showed that both catalyst are reactive and can upgrade both ethylene and ethanol. However most products were in the range of C_8 content, this is still not satisfactory for fuel implementation unless the C_8 products are branched. Furthermore, conversion of feedstock was up to 60%. Some conclusions about the correlation between the reaction temperature, product distribution and conversions were drawn and presented in the report. Impact of the ethanol on prevention of coke formation was observed and briefly discussed. This field of study has a lot of potential and there is still a lot to discover. The solution that the whole scientific world is trying to find may be hidden in this kind of process.

Sammanfattning

Ambitionen med den här studien har varit att undersöka ifall en katalytisk process har potentialen att lösa den världsomfattande krisen vi alla bevittnar. Under en längre period har människan varit medveten om att fossila bränslen måste ersättas med ett miljövänligare alternativ. Under förloppet av det här examensarbetet testades två olika katalysatorer och deras potentiella möjlighet att producera biobränslen från förnybara råvaror. Som råvaror användes eten och senare etanol, målet var alltså att uppgradera mindre molekyler till större kolväten med bränsleegenskaper. Idag finns det ren edan väl etablerad forskning där man försöker oligomerisera eten till bränslen men inte alls lika stor motsvarande forskning där etanol används för samma ändamål. De två katalysatorerna som är baserade på ädelmetallerna platina och palladium visade sig vara reaktiva och lämpade till att uppgradera både etanol och eten till föreningar med högre antal kolatomer vid atmosfärstryck. Resultaten av analysen visade att majoriteten av vätskeprodukterna bestod av C_8 föreningar. Samtliga produkter i vätskeform befann sig i intervallet av 7-11 kolatomer. Den högsta omsättningen nådde upp till 60 % och både gas och vätskeprodukter producerades. Genom att analysera resultaten kom vi fram till vissa samband gällande påverkan som reaktionstemperaturen utgör på produktfördelningen och omsättningen. Viktiga slutsatser angående etanolens roll på motverkandet av katalysatorernas deaktivering drogs och redovisades i rapporten. Även om den här studien inte gav de bästa resultaten det vill säga den kolväte blandningen som motsvarar dagens bränslen, finns det mycket utrymme för vidare forskning.

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1. Introduction

The government of Sweden has set up an ambitious goal of abolishing fossil fuels use in the vehicles by year 2030 (Anon., 2015). The situation in Sweden today is promising when compared to many other countries but the adequate large volume substitutes for the fossil fuels are not yet chosen. The current legislation is prescribing that all petrol sold in the country has to be a 95/5 % blend of petrol and ethanol. There is even a fuel brand called E85 which contains 85 % ethanol and is used in specialized ethanol driven engines. To make a short conclusion, emphasis on the substitution of petrol has been put on the larger implementation of ethanol as an alternative fuel (Anon., 2014).

However, the environmental friendly alternative for diesel fuel and kerosene has showed to be a greater challenge. Some of the presented possible solutions were blending with either FAME (fatty acid methyl esters), residue oil from the Swedish forest industry or biodiesel produced from rapeseed oil. Residue oil is suitable for fuel use since it could enhance the sustainability of the whole process but the limited available amount is hindering it from becoming the sought solution. On the other hand, biodiesel is hypothetically possible to produce in large quantities but there are other issues with it. Firstly, the discussion arises around the fact that feedstock for biodiesel synthesis could be used for the production of food. How should cropland be divided and is it acceptable that fuel should be prioritized to possible food production? The second drawback is not related to the public opinions but instead to the chemistry of the compounds it selves. The high presence of oxygen in the molecules (especially ethanol) is resulting in lower energy density than compared to the conventional fossil fuels. Some customers even reported the presence of algae growth and corrosion in the fuel tanks filled with biodiesel. This phenomenon is directly caused by the presence of water in the tank which can be explained by higher water solubility of biodiesel molecules. To summarize the issues, both the ethanol and biodiesel unfortunately lack the quality which fossil fuels possess (Anon., 2017).

A better solution for the set governmental goal would therefore be a “new fuel” that is produced synthetically, having the desired energy density of the fossil fuels and environmental friendliness of the biodiesel. By achieving these guidelines, a fuel that requires no drastic changes on the either vehicles or infrastructure would be produced and majorly facilitate the process of achieving the set goal of reaching the society’s fossil fuel independence.

1.1 Purpose

The aim of this study will be to investigate an alternative direct synthesis route of biodiesel and aviation biofuel from ethanol as starting material. The outcome of the synthesis will result in hydrocarbons with various length, however it’s needed to target those that have similar properties as biodiesel and aviation kerosene. To carry out this work two different heterogeneous catalysts, from Hulteberg Chemistry & Engineering AB, will be analysed regarding their selectivity and activity. All experiments will be carried out in lab scale with the focus of finding the most suitable catalysis for production. During the first experiments ethylene is going to act as the feedstock, only for the purpose of gaining an overview of the possibilities concerning the production of longer hydrocarbon chains.

Lastly a discussion, where the evaluation of implementing this kind of synthesis in larger scale, is going to set the foundation of further work involving optimization and effectiveness.

1.2 Disposition

A comprehensive amount of work, both of theoretical and experimental art, to investigate the synthesis of qualitative hydrocarbon chains in one single route is required. Therefore the study is divided into three parts. The first part concerns the literature study where the main focus is to map earlier known methods to synthesize longer hydrocarbon chains both from ethanol and ethylene as feedstock. Attention should only be held on articles involving heterogeneous catalytic reactions to give a solid groundwork.

The second part of the study gives details of the experimental outcome from the reactions performed under different conditions. In the third part a discussion section is presented including challenges during the work, error sources and finally the conclusions. At the end of the report the references are settled.

2. Literature review

2.1 Previous approaches regarding ethylene oligomerization

Ethylene oligomerization is the reaction which is supposed to produce longer hydrocarbon chains both during the usage of pure ethylene and ethanol as the feedstock to the reactor in this study. In the former case, catalyst is supposed to directly use the fed ethylene to arrange longer chains of carbon. In the latter case, oligomerization is preceded by ethanol dehydration which ought to produce ethylene that is needed for the oligomerization.

Ethylene oligomerization is already an established process which is exploited to produce more than 3 million tons of linear α-olefins annually. These product compounds are commonly used for manufacturing of for instance detergents and lubricants (Britovsek, et al., 2015). Linear and branched higher olefins are also of considerable importance as starting materials for other important chemicals as propylene, alcohol amines and acids.

The present, implemented processes of ethylene oligomerization involve usage of organic solvents and homogenous catalysts (Finiels, et al., 2014). Heterogeneous catalysis uses different metals (Ni, Cr, Zr, Ta, Ti Hf, Co and W) (Babu, et al., 2016) as active, catalytic components (Lallemand, et al., 2011). Reactions and mechanisms for these are thoroughly studied and have present implementations on industrial scale. The homogenous catalysis in this reaction often leads to formation of linear 1-alkenes. However, this procedure brings issues that require more environmental friendly, alternative solutions. The homogenous catalysis process involves both solvents that are not considered sustainable and large consuming of energy (Toch, et al., 2015). Since homogenous catalysts have the same state of aggregation as the substrate (hence homogenous), they are difficult to separate from the product and reuse again (Babu, et al., 2016).

Alternative type of catalysis, heterogeneous catalysis, is being investigated in order to develop robust and recyclable catalysts that can be reused several times. One of the greatest challenges alongside achieving high selectivity for the desired products has been preventing the deactivation of heterogeneous catalysts during the oligomerization process (Lallemand, et al., 2011). One of the countermeasures against deactivation is to use larger pores for the support material. The structure of heterogeneous catalysts involves putting the reactive metal complexes on support materials as silica, zeolites or MCM-41 (Mobile Composition of Matter no 41). Results of some scientific reports showed that catalytic systems for ethylene oligomerization tend to produce hydrocarbons according to Andersen-Schultz- Flory distribution which implies that the short chains are easily synthetized than longer ones. Modifications that result in selectivity towards hydrocarbon chains with 10 carbons or more is more challenging (Babu, et al., 2016).

This part of the literature study gave insight in which direction the research on ethylene oligomerization catalysts is going. There is undoubtedly a high interest in finding suitable heterogeneous catalysts for synthesis of longer hydrocarbon chains and many progressive results are being presented.

Many research teams focused on Ni based catalysts with various support materials since this transition metal showed promising catalytic properties under mild operating conditions. The first Ni-based heterogeneous catalyst for this application consisted of NiO inserted on the silica support material. Phillips Petroleum discovered that this configuration shows catalytic activity in the ranges between 0 and 150 degrees Celsius. Further studies that came during the

following years showed that the role of support material is important for the catalysis. For instance, density of acid sites was proven to be crucial for catalytic activity. Zeolites exchanged with Ni^{2+} attached to the oxygen anions were also tested for catalytic activity. Higher temperatures during ethylene reactions with these structures gave products with higher amount of carbon atoms. However, microporous zeolites showed some lack due to rapid deactivation with formed product.

Ion exchanged silica-alumina and sulfated alumina were also examined for feasible catalytic activity. Parameters which showed to be essential for the catalytic activity in this case are acid strength of the support (quantity of acid sites), temperature, pressure, catalyst composition and concentration of the active component.

A review about the Nickel based catalysis written by Finiels et al presents broad spectrum of different operational conditions and corresponding results from various studies. Temperatures between 20 and 360°C were tested in combination with pressures from 0.4 to 40 bars. The aforementioned NiO in supports showed to be not the optimal solution. Productivity was rather low for further consideration regarding eventual industrial application. Better results than these came from the studies where Ni-impregnated alumina was used and which gave enhanced productivity. Ni-zeolites category reported different results depending on the sizes of the pores of the support material. The overall conclusion is that larger pores result in less deactivation and therefore overall better activity for the catalyst. Overall, best results were reported with mesopores and MCM-41/MCM-48 support materials. High productivities between 110 and 158 g/gh (gram product per gram substrate and hour) were reported for this particular conformations. These high productivities were achieved with temperature of 158°C and pressure of 35 bars. Overall conclusion of the review is that temperature ranges of 100-150°C and pressure ranges of 30-40 bars are good operating conditions for Ni based catalysts. Results of the various studies with Nickel catalysts at different operating conditions are presented in Table 1 (Finiels, et al., 2014).

Especially interesting study regarding Nickel catalysts was conducted by Babu et al. This research team decided to perform the catalysis in two steps instead of one direct synthesis. The first part was oligomerization with Ni-AISBA-15 and this followed by a co-oligomerization over Amberlyst-35 dry ion-exchange resin. First oligomerization process was a reaction in the reactor with temperatures and pressure ranges of 150-200°C and 5-15 bars respectively. Products were condensed and separated from the gaseous products and these two were analysed separately. The condensed mixture was then set in an autoclave where it reacted in presence of Amberlyst-35 dry ion-exchange resin under pressures ranging from 10-30 bars and times from 12-48 h. The results brought this research group to different conclusions. Firstly, WHSV (weight hourly space velocity) is affecting the distribution of the produced olefins. When residence time of the gas in the reactor is prolonged there is a tendency for the system to produce mostly C_8 olefins with significantly reduced amount of C_4. At the higher rates of WHSV, distribution of olefins is following the normal Andersen-Schulz-Flory distribution where C_4 molecules are the mostly abundant ones. Temperature was also tested and the results showed that this parameter is crucial for the conversion of ethylene. Increase from 150 to 180° Celsius improved conversion from 87% to 99%. Test of various pressures conditions gave the conclusion that 10 bars is sufficient for producing an olefin mixture that defies the Andersen-Schulz-Flory distribution. The co-catalysis in an autoclave of the olefin mixture from the first step gave significantly improved results. The best results were achieved with 5w% catalyst loading, temperature of 100°C, reaction time of 24 h and a high 30 bars pressure. These conditions gave a high conversion to C_{5+} olefins (98%) where C_{10+} were present in significant amount (42%) (Babu, et al., 2016).

Other metals are examined too, a research performed by a group in Brazil examined chromium complexes with pyrazolyl-imine-phenoxy/pyrrolide ligands. All of the tested complexes were activated with methylaluminoxane (acting as co-catalyst) and were able to produce oligomers without a particular selectivity alongside some amount of polymers. In this study, it was also showed that a choice of ligand has effect on oligomers/polymers product distribution. For instance pyrazolyl-imine-phenoxy ligands were better suited for oligomer productions while pyrazolyl-imine- pyrrolide ligands led to polymerized product compounds. Most notable results are the cases where oligomerization products were majority (>90% wt) compared to the produced polymerized systems and when at the same time higher olefins were registered in considerable amounts. One example is one particular chromium complex which catalyzed ethylene to 99.4% oligomers of which whole36.2% were C_{12+} chains. These results were achieved with reaction temperature of 80 °C and pressure of 20 bars (Bergamo, et al., 2016).

One of the tactics to increase the efficiency of the catalysis was to use more than one active metal centre. The idea is to by a suitable ligand configuration achieve synergistic effect several metal centres. Therefore, development of binuclear systems has woken a lot of interest. Ambition is to achieve cooperation between more than one active centre; this in order to make the production of oligomers more efficient (Netalkar, et al., 2014).

Another research group from Korea tested sterically modulated binuclear palladium catalysts for ethylene oligomerization. Different designs of ligand structures were tested to optimize the environment around the active centres and facilitate the oligomerization. One of the interesting features in ligand design is the possibility to add phenyl and alkyl groups that create steric hindrances during the oligomerization process. These steric hindrances can result in chain termination at the desired carbon chain size. In this study, derived bis-imine ligands were tested for catalytic activity. All of these configurations showed the tendency to primarily dimerize the ethylene into C_4 products. Trimerization occurred to a less great extent than dimerization, creating a maximum amount of 13.6 % C_6 oligomers in one of the experiments. Higher olefins were found in even smaller amounts, for some experiments C_{12-20} content was down to trace level. These experiments were conducted under the conditions of low temperature, low pressure and short time (Budagumpi, et al., 2011). Less severe conditions tend to lead to mostly C_4 product formation once again.

Table 1. Summary of different Ni-based catalyst outcome results (Finiels, et al., 2014).

Catalyst	Ni (wt%)	T (°C)	P (bar)	C4	C6	C8	C10+
NiO/SiO_2-WO	3.9	275	1	81.8	16	1.7	0.5
	7.8	275	1	83.9	12.5	1.8	1.8
$NiO\text{-}ZrO_2/WO_3$	18	20	0.4	100	-	-	-
$NiO\text{-}ZrO_2/MoO_3$	3.9	20	0.4	100	-	-	-
$NiO/Al_2O_2\text{-}TiO_2/WO_3$	15.6	20	0.4	100	-	-	-
$NiO\text{-}ZrO_2/SO_4^{2-}$	18	20	0.4	100	-	-	-
$NiO\text{-}TiO_2/SO_4^{2-}$	36.5	20	0.4	100	-	-	-

NiO/Al_2O_3-SiO_2	4	40	20.7	50	16	13	21
NiO/Al_2O_3-SiO_2	3.6	150	28	85.4	9.6	2.3	2.7
NiO/silica-titanate	-	150	11-28	13.2	20.7	16.7	49.4
NiO/B_2O_3-Al_2O_3	3	200	10	73.8	20.2	5.1	0.9
	3	200	40	10	10	25	55
Ni-NaY	5.6	70	41	67.3	32.7	-	-
Ni-Y	5.6	60	28	67	13	5.5	14.5
Ni-NaY (Si/Al=2.8)	3.7	115	35	67	20	17	26
Ni-Y (Si/Al=31.5)	0.6	20	0.4	100	-	-	-
Ni-Y (Si/Al=30)	0.6	50	40	67	10	14	9
Ni-Beta (Si/Al=12)	1.7	120	26	72.3	13.4	7.2	3.1
	2.5	120	26	38.1	8.4	13.8	36.3
Ni-silica-alumina	0.27	300	11.5	72.2	14.1	6.2	3.4
Ni-silica-alumina	1.56	110	35	27	17.6	25	30.4
Ni-silica-alumina	1.6	160	35	31	17	19	33
Ni-MCM-22	0.55	150	40	81	5	13	1
Ni-MCM-36	0.5	70	40	81	8	6	5
	0.6	150	40	45	25	15	15
Ni-SBA-15	5	120	30	-	-	-	35.1
Ni-MCM-48	0.5	150	35	42	37	14	7
Ni-MCM-41 **(3.5 Å)**	2	150	35	45	33	15	7
Ni-MCM-41 **(10 Å)**	2	150	35	40	33	16	11
Ni-MCM-41	1.7	30	20	56	24	10	10
Ni/sulphated alumina	6.4	50	0.7	88.8	11.2	-	-
$NiSO_4/Al_2O_3$	3.1	20	0.4	100	-	-	-
$NiSO_4/Al_2O_3$*ZrO_2	3.1	20	0.4	100	-	-	-

2.2 Dehydration of ethanol

As earlier mentioned, the most important goal of this project is to successfully upgrade ethanol into longer hydrocarbons by a direct catalysis performed in one step. In order to achieve this, the ethanol that is fed to the reactor needs to be initially dehydrated to form ethylene. Ethylene is used in the first part of the experimental studying as the feedstock in intended oligomerization process to higher hydrocarbons and therefore the intention is to intend the same goal with "ethanol-derived" ethylene. Hence, ethanol dehydration is of crucial importance for the success of the intended fuel production.

Ethylene production is in itself an important chemical industrial process since the product is used as a raw material in the petrochemical industry. Broad spectrum of refined chemicals has their origin in ethylene processing and the estimation is that around 75% of all petrochemical products in the world are derived from ethylene. The solution that is primarily used today to satisfy this large need of ethylene is hydrocarbon-cracking of petro-hydrocarbon or natural gas as raw material. Almost all of the ethylene produced today is coming from this particular process but an alternative solution is needed since depletion of the fossil fuels used as feedstock in hydrocarbon-cracking process inevitably happen (Minhua & Yingzhe, 2013).

The crucial need for alternative solutions has driven researchers to consider the possibility to produce ethylene by catalytic dehydration of ethanol. Use of bioethanol for this purpose could further increase the environmental friendliness of all possible further implementations (Xian, et al., 2008). Instead of usual cracking of longer carbon chains into ethylene by a high temperature endothermic reaction, the catalytic dehydration of ethanol involves protonation of the hydroxyl group which leaves as a water molecule followed by the rearrangement of the hydrocarbon into ethylene (Denise, et al., 2013). This particular reaction takes place at the higher reaction temperatures but there is also alternative mechanism for ethanol dehydration. This second alternative reaction is favoured at the lower temperatures and results in diethyl ether instead of ethylene. It is important to note that ethanol dehydrogenation also can occur during the intended dehydration. This would result in acetaldehyde as a side reaction product (Xian, et al., 2008).

In the study performed by Xian et. al. an experimental setup similar to the one used for experimenting in this thesis was used to test ethylene producing capacities for 4 different catalysts. The results of these experiments showed that reaction temperature is of great importance for the conversion of fed ethanol but also for the amount of ethylene produced. Firstly, lower temperatures displayed inefficient conversion of ethanol alongside the unwished production of diethyl ether. Increase in temperature resulted in better conversion of ethanol and higher selectivity towards ethylene. The increase in ethylene production also brought the decrease in diethyl ether production, which is undesired for this purpose. However, the positive outcomes of temperature increasing reached a peak since the continued temperature increase eventually gave other results. Even larger temperatures opened up the possibility for another reaction mechanism to take place, namely ethanol dehydrogenation. This pathway resulted in decreased selectivity for ethylene production and introduced the formation of acetaldehyde. It can be concluded that optimal reaction conditions are essential for achieving the high selectivity for the desired product, in this case ethylene. The optimal temperature conditions for the purpose of producing hydrocarbon fuels ought to be tested in the experimental part of the thesis.

In one study published in 2008, a research group that intended to find optimal conditions for hydrogen production by catalytic steam reforming reported interesting results. When letting

the gas mixture of ethanol, vapour and helium pass through the Pd catalytic bed no produced ethylene was detected. However, saturated ethane was present as product at higher reaction temperatures and the possible explanation given by the researchers was that hydrogenation of the initially produced ethylene took place during reaction. This occurrence should be taken into consideration since one of the catalysts that are to be tested in the experimental part of this thesis is based on Pd. Same research team reported that ethylene was produced and detected after the reaction with Rh based catalyst (Aristides, et al., 2008).

In order to achieve higher possible production of potential hydrocarbon mixtures resembling diesel/kerosene it is important to achieve feasible conversion of ethanol to ethylene and avoid undesired side products. In the ethanol experimental part of this thesis, gaseous alcohol/nitrogen blend will be driven through catalytic bed of the reactor at the different temperatures. The optimal outcome of the experiments would be a discovery of particular reaction temperature that enables high conversion of ethanol to ethylene (ethanol dehydration) and at the same time favours the desired oligomerization process for the synthesis of longer carbon chains. However, the main purpose of this project is still to produce possible diesel/kerosene blends at large amounts as possible. Even though the ethanol dehydration is essential part of the planned fuel production, the actual hydrocarbons are the main focus. Therefore the reaction temperature that gives highest amounts of the liquid hydrocarbon product will be preferred as the future recommendation even if this particular temperature would not yield optimal ethylene selectivity.

2.3 Deposition of carbon and coke onto the catalyst

During catalytic reactions deposition of various components occur onto the surface of the catalyst, resulting in activity loss due to blockage of sites and pores. This kind of proceeding, in general termed as fouling, may lead in its advanced stages to terminal consequences in form of disintegrating the particles in the catalyst and plugging the voids. One highly discussed form of fouling is deposits of carbon and coke in porous catalysts. The interpretation of carbon and coke deposition is somewhat loose in its definition and related to their origin. For instance coke produced by decomposition and condensation of hydrocarbons differs in their structure onto the catalyst surface. The outcome can vary form longer polymerized hydrocarbons chains to layered structure as graphite. Carbon fouling is however a characteristic product of CO disproportionation, a specific type of redox reaction. It should also be emphasized that the chemical structure of deposited species are varying depending on type of reaction, catalyst and conditions during formation (Bartholomew, 2001).

Today there is an ordering which classifies catalytic reactions followed by coke and carbon formation, as structure-sensitive or structure-insensitive. Regarding the coke-sensitive reactions the unreacted coke will cover the active phase and the activity drops. Reactions including that category are catalytic cracking and hydrogenolysis. In the coke-insensitive reactions the reactive deposition can be removed by hydrogen or through other gasifying agents to a large extent. Examples of that kind are methanol synthesis, methanation, steam reforming and Fischer-Tropsch synthesis. The author, with the classification as support, concluded that structure and location of coke is of huge importance rather than the effects of the catalytic activity (Rostrup-Nielsen, 1974).

How supported metal catalysts are affected by coke or carbon fouling is illustrated in Figure 1. There are three different scenarios that are possible. In the first one carbon chemisorb on the metal surface sites and hinders access for reactants, second one is about encapsulating the whole metal particle which cause fully deactivation. The last case regards plugging of the

micro- and mesoporous and thereby denying access to those sites. Another case is steam methane reforming catalysts which consist of nickel as active phase supported on alumina with alkaline oxide. In that case observation has shown growth of carbon filaments from the backside that eventually pushed the active particle off the support surface (Farrauto & Bartholomew, 1997) (Lyle F. Albright, 1982).

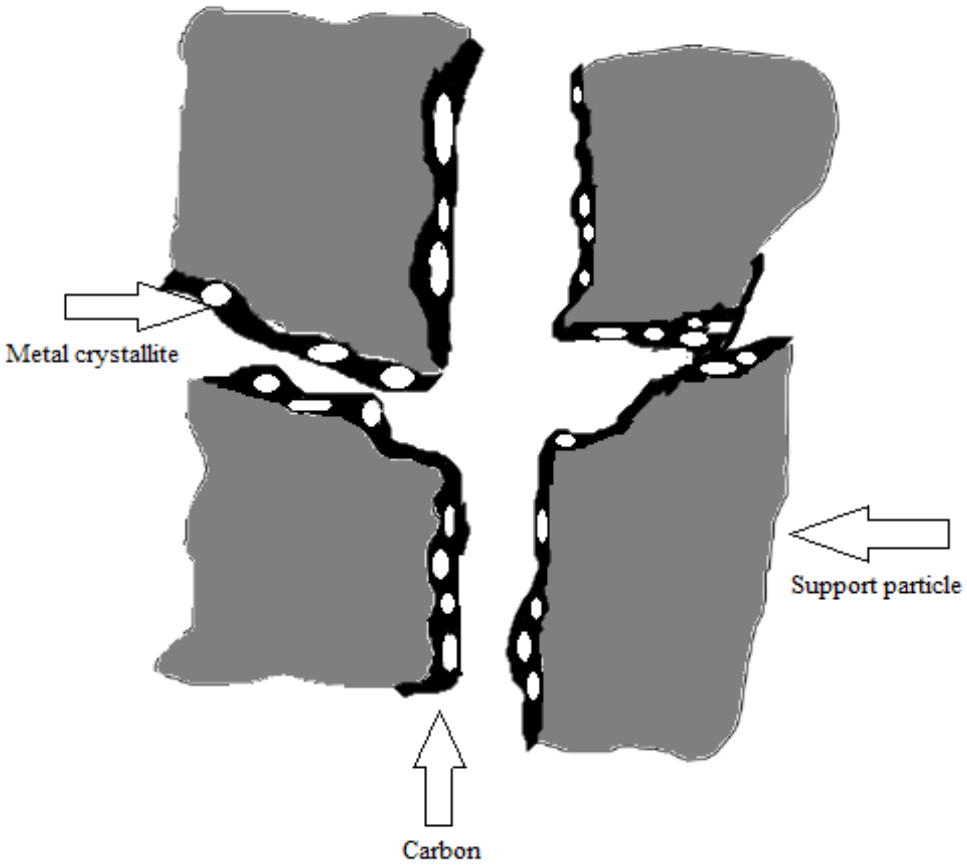

Figure 1. A picture of how a typically coke formation onto a catalyst can look like. The picture is modified version of an illustration taken from a research article (Bartholomew, 2001).

At which rates the deactivation proceeds for particular catalyst and reaction depends significantly on the conditions, such as reaction temperature. For instance in coke-insensitive reactions on metals, see steam reforming, the rate of deactivation depends essentially in the difference between the rates of formation and gasification of carbon or coke precursor. Deposition of carbon or coke won't occur if the rate of gasification is equal or greater than the formation. Both rates increase with elevated temperature, however the difference between them varies during intervals of temperature and activation energies must be taken into consideration. To avoid deposition it's therefore recommended to operate in temperature zones in which gasification rate surpasses the formation rate (Bartholomew, 2001).

The rate build-up of carbon or coke is also, beside reaction conditions, influenced by the structure of the catalyst with respect to its metal type, metal size, and support material. Supported active phase metals as Fe, Ni and CO are reported to have growth of filamentous carbon from CO and hydrocarbons at their active temperature around 350-400 C. At that temperature region the activity decreases in following order Fe>CO>Ni (Lyle F. Albright,

1982). On the other hand metal active types as Pt, Ru and Rh, has shown to produce insignificantly little coke or carbon in steam reforming. Noble metals have shown properties of hindering the mobility and solubility of carbon which halts the deposition process. Adding noble metals as Pt in Ni decreases the formation rate of carbon during methanation. In steam reforming, deposition can be lowered by addition of Cu or Au to Ni (Bartholomew, 2001) (Lyle F. Albright, 1982). Comparing this with adding Sn to cobalt, in absence of any noble metal, the rate of filament formation from ethylene increases. This case demonstrates the importance of selecting a noble active phase (Bellare & Dadyburjor, 1993).

Beside the choice of active phase, modifications in catalyst structure in terms of support material can alter the rate of unwanted carbon or coke build-up. Adding oxide additives or having oxide supports are some modifications for enhancing the resistance of species deposition. During methanation at 350° C it was found that the formation of filamentous carbon on nickel decreased in order of Ni/TiO_2, $NiAl_2O_3$ and Ni/SiO_2 (Bartholomew, 2001) (Uguina, et al., 1993). How the metal crystallites are oriented by the support is an explanation to its inhibiting behaviour, for instance selecting silica prevents both CO dissociation and carbon hydrogenation. Furthermore in methane reforming the rate of carbon formation decreased in the order of Pt/gamma-Al_2O_3, Pt/TiO_2 and Pt/ZrO_2, which clarifies the preventing effects when selecting oxide supports (Fuentes & Bartholomew, 1997).

Regarding the size of metal crystallites, smaller sizes of nickel in steam reforming of methane have showed a pattern of lowering the rate of filamentous carbon (Lyle F. Albright, 1982) (Bartholomew, 2001). Researchers found also out that larger size of the active crystallite Pt deactivates faster than those of smaller size (Fuentes & Bartholomew, 1997).

In metal oxide and sulphide catalysts, when reactions of hydrocarbons are present, the coke forms not only in the gas phase and on the catalytic surface but also on the non-catalytic part. Different kind of reactions involving hydrocarbons can take place. Common types of those are polymerization of olefins, cyclization of alkenes and formation of polynuclear aromatics, all of them condenses on the catalyst surface as coke.

2.4 Discussion of the literature study

The literature study had the intension of giving insight in the past and present research on the relevant topic of ethylene oligomerization. Many articles from different parts of the world are presented on the subject. This seems rather reasonable if the urgent demand for fossil fuel substitution is regarded. Particularly innovating and interesting for this study are those who are describing the research with the heterogeneous catalysis.

When it comes to the choice of substrate for these heterogeneous catalyst reactions, it seems as ethylene is vastly preferred over ethanol. There were no difficulties in finding articles that described how ethylene was used as a feedstock for the oligomerization research. However, there are not nearly as many if any research reports where intension is to produce hydrocarbons directly from ethanol.

The vast majority of scientific work which was investigated during the literature study is not referring to Platinum or Palladium catalysts which are tested during this thesis. The articles which were encountered focused mostly on Nickel and partly on Chromium based catalysts with varying support materials, loadings, reaction conditions etc. Especially prominent results were presented in a nickel catalyst review where several studies that used nickel based

catalysts for ethylene oligomerization were summarized. In this review, several good productivities for C_{10+} compounds were reported alongside good conversions of ethylene.

Regarding the reaction conditions, several conclusions can be drawn from the results of the previously conducted studies. Overall it seems like the more harsh conditions are suitable for higher oligomerization and production of higher olefins. Increasing the temperature led in many cases to the higher conversion of the ethylene while higher reaction pressures enabled oligomerizations of longer carbon chains. One research group even divided the catalysis process into two steps, where the second step involved high pressure treatment. Yield of longer chains was greatly improved by this interesting approach (Babu, et al., 2016).

When it comes to catalyst deactivation, a solution for delaying this experimental occurrence was presented in one of the read articles. This particular research group introduced the water as a way of reducing the catalyst cooking by preventing the formation of polymerized structures on the catalyst surface (Denise, et al., 2013).

Even if the study of this thesis has not yet been conducted in a similar research, some lessons can be obtained from already published articles. Temperature ought not to be too low in order to achieve successful ethylene conversion. Furthermore, the possible deactivation of coking could be countered by water addition to the inlet mixture.

3. Method

3.1 Preparatory calculations

Noble metal catalysts that will be tested in this study are highly reactive. Estimation given by the manufacturer is that both of them possess a space velocity of approximately 22000/h. This figure means that a single volume of catalyst bed can treat up to 22000 equivalent volumes of feed during each hour of the reaction.

Therefore, each feed expressed as volume/time has a corresponding volume of catalyst that will fulfil the maximum conversion of the inflowing reactant.

Therefore the least needed volume of catalyst can be expressed as:

$$\frac{F_{feed}}{V_{cat}} = SV \rightarrow V_{cat} = \frac{F_{feed}}{SV} \quad (1)$$

In Figure 2, volume of catalyst are calculated for different total flows of feed input.

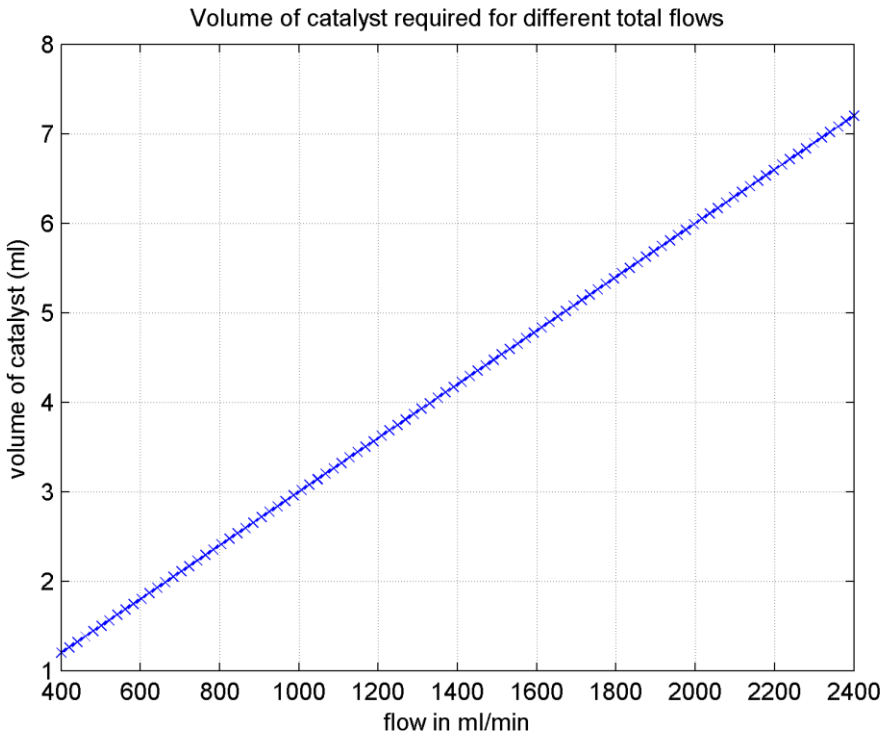

Figure 2. Graph showing the correlation of total feed flow and required volume of catalyst.

3.1.1 Design of packed bed

The catalytic bed will be placed in the middle of continuous reactor (diameter 16mm & length 300mm) used for synthesis.

As suspected a relatively little volume of catalyst is required since the space velocity is rather high and therefore catalyst is able to convert large volumes of feed.

It was decided in the beginning that inlet flow to the reactor should be 1000ml/min with a composition of 75% nitrogen gas and 25% ethylene. As can be seen in the Figure 3 this volume flow roughly corresponds to 3 ml of catalyst. Hypothetically, 3 ml of active catalyst should be enough for the conversion of 1000 ml gas each minute but the matter is not yet solved.

First of all, catalyst particles are roughly 2 mm in diameter. Therefore, a 3 ml volume occupied by catalyst particles will not resemble 3 ml of catalyst only since one part of the occupied volume is taken by the void. Assumption must be made to compensate for this loss of volume.

It is assumed that approximately 50% of the volume that catalyst takes up is void. Thus, the catalyst volume required for flow of 1000ml/min is doubled to 6 ml.

Furthermore, one must be aware of the fact that the void fraction of a packed bed is greatest at the walls of the reactor. Larger void fraction contributes to the greater velocities at the walls and hence worse conversion for one part of the inlet gas. Short catalytic beds are especially tendentious to suffer from this problem. Logically, possibility that wall region channels are able to allow the inlet flow free passage through the catalytic bed is much higher if the bed itself is rather short.

One of the rules for the minimum bed length and avoidance of dispersion effects is Mears criteria:

$$\frac{L}{d_P} > \frac{20n}{Pe} \ln\left(\frac{1}{1-x}\right) \qquad (2)$$

Peclet number can be assumed as 2 if Reynolds number for the flow is greater than 2, which is assumed as valid. In this case also reaction order (n) is assumed to be 1 and conversion (x) to 0.5. Particle diameter is as previously stated approximately 2mm.

The results of the calculations show that the minimal length of the catalytic bed should be approximately at least 1.4 cm. The reactor which is used during the experimental studies has a diameter of 1.6 cm. With this in consideration, Figure 3 is showing the correlation between the catalytic bed length and volume taken by the catalyst.

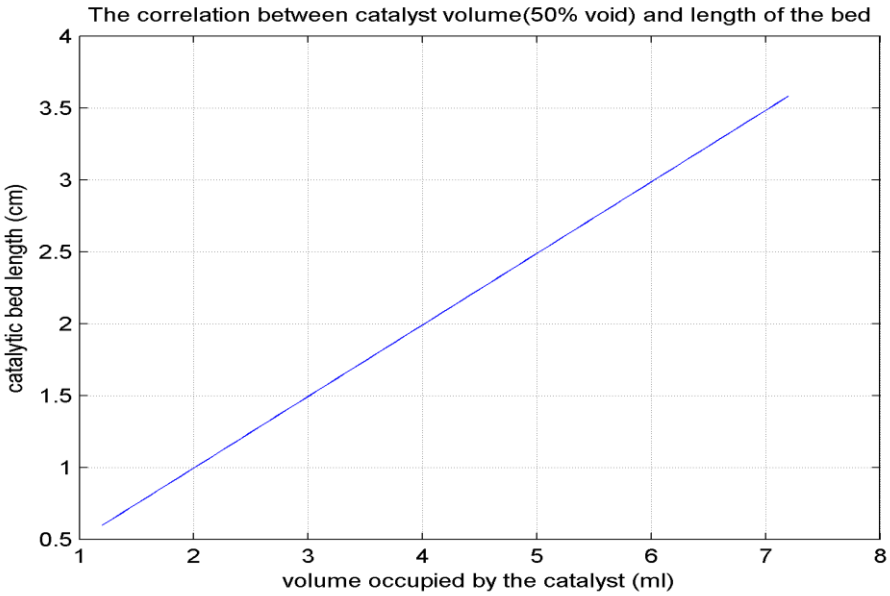

Figure 3. Illustration of how catalyst volume is correlated to the length of the catalyst bed.

A fast checking in the Figure 3 assures that 6 ml of catalyst correspond to 3 cm bed length for this particular reactor and this is not violating the Mears criteria. However, it was decided that catalytic bed volume should be doubled once more to ensure that all problems regarding channels or dispersion will not have any effect on the course of the results. Therefore, 6 ml of catalyst was blended with 6 ml of alpha phase aluminium oxide. Aluminium oxide was broken down to the approximate size of the catalyst particles.

It was also decided that a layer of pure alpha aluminium oxide will be placed above and beneath the catalytic bed. This is done to ensure good heat transfer to the catalytic bed in the reactor. The schematic picture of the reactor including the design of the catalytic bed is presented in Figure 4. Be aware that reactor is placed vertically during the actual experimental work; the horizontal presentation here in the report is due to the space convenience.

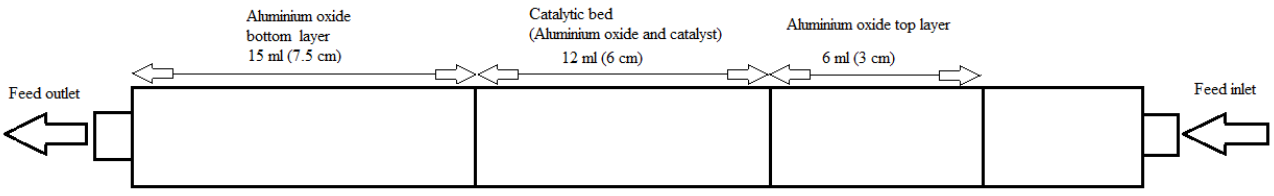

Figure 4. This picture shows how the porous bed in the plug flow reactor is constructed.

3.1.2 Pressure drop

When designing the packed catalytic bed, pressure drop needs to be taken into the consideration. Packed bed is providing resistance for the inlet gas flow that is entering the reactor. Therefore, it is of great importance that potential pressure drop over the reactor is not too high. A high pressure drop will prevent achieving desired outflow. To avoid this, inlet pressure of the gas mixture needs to be sufficiently high, so that it will not be reduced below the value of atmospheric pressure while passing through the packed bed. Pressure drop of the packed bed is calculated with following expressions:

$$f_p = \frac{150}{Re_p} + 1.75 \tag{3}$$

$$f_p = \frac{\Delta p}{L} * \frac{D_p}{(\rho V_s^2)\left(\frac{\boldsymbol{\varepsilon^3}}{1-\boldsymbol{\varepsilon}}\right)} \tag{4}$$

$$Re_p = \frac{D_p V_s \rho}{(1-\boldsymbol{\varepsilon})\mu} \tag{5}$$

These were rearranged to an expression for calculation of pressure drop:

$$\Delta p = \frac{(1-\varepsilon) * \mu * 150}{D_p * V_s * \rho} * \frac{L * \rho * V_s^2}{D_p} * \left(\frac{1-\varepsilon}{\varepsilon^3}\right) \tag{6}$$

Pressure drop for the 10 cm long catalytic bed was calculated to 7.3211 Pa. This pressure drop is not significant and there should not be any stop of the flow throughout the reactor as long the pressure of the inlet gas is slightly larger than atmospheric pressure.

3.2 Calculation of ethanol amount needed

During the ethanol experiments, it is decided that the ethanol vapour volume entering the reactor will be the same as the volume of the ethylene entering the reactor previously. Since the dehydration of one mole of ethanol is resulting in one mole of water and one mole of ethylene the calculations of needed mass of ethanol that is equivalent to 250 ml/min are as following:

$$M_{EtOH} = 46.06844\ g * mol^{-1}$$

To calculate the amount of moles which is equivalent the volume of 250 ml, the ideal gas law is used:

$$PV = nRT \rightarrow n = \frac{PV}{RT} \tag{7}$$

When temperature of evaporation (393.15 K), gas constant ($8.3144598 m^3 Pa K^{-1} mol^{-1}$), atmospheric pressure (101325 Pa) and the desired volume ($250*10^{-6}$ m^3) are applied to the equation, the amount of 0.007749 moles/min is calculated.

From this mole amount (7), the needed mass of ethanol per minute is derived:

$$m_{EtOh} = 0.007749 * 46.06844 \approx 0.357\ \text{g/min}$$

3.3 Calibration of flowmeters

3.3.1 Calibration of ethylene & N_2 flow meters

It was previously decided that the inlet flow to the reactor will be 1000 ml/min. The composition of that flow is 750 ml/min of nitrogen and 250 ml/min of ethylene. In order to adjust the desired values for flows, flow meters are necessary. These are connected to a box that regulates their flows as percentages of their maximal flows. Flows for different percentages are measured by a flow meter and correlations are obtained. Calibration curves are created and the corresponding equations are found in order to precisely regulate the flows in terms of percentages. These Figures 5 and 6 are showing how flows and percentages of the maximum flows are related to each other.

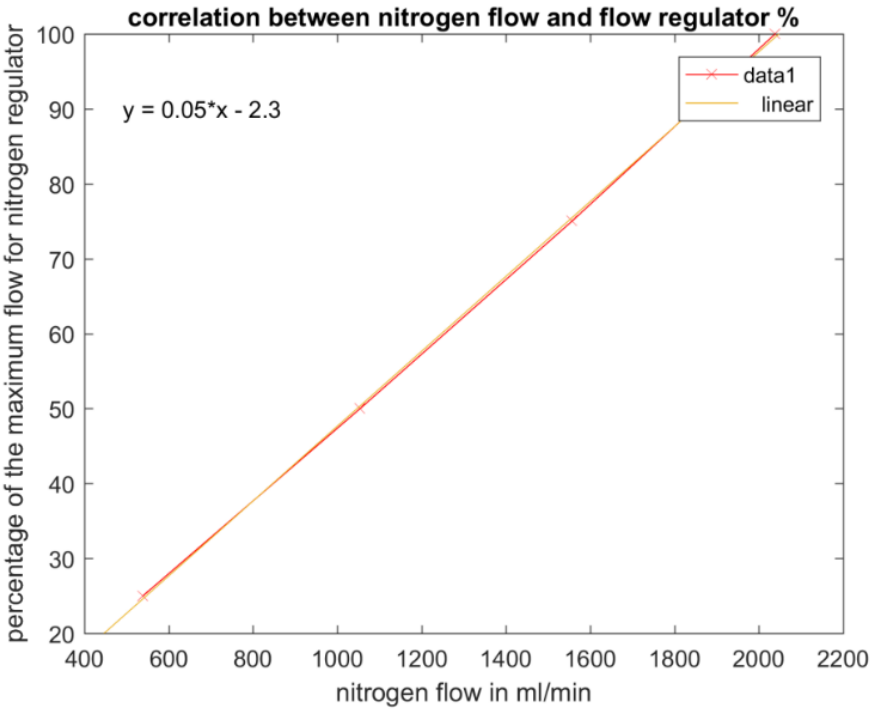

Figure 5. Description of how the nitrogen flow is correlated to the percentage of the maximum flow of the regulator.

The correlation between flow percentage and actual nitrogen flow is explained by expression:

$$y = 0.05 * x - 2.3 \quad (8)$$

According to this, the required flow percentage to get 750 ml/min is 35.2%.

The same procedure was conducted for the ethylene flow meter; the calibration curve is presented in Figure 6.

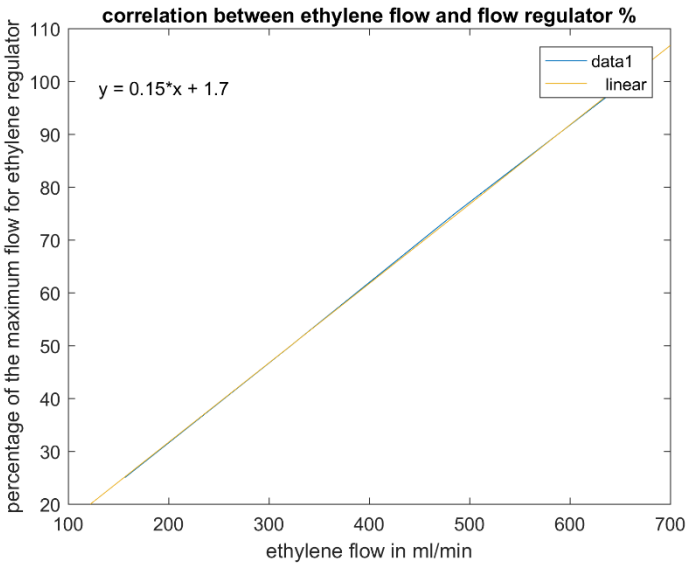

Figure 6. Graph showing the relation between ethylene flow and percentage of the maximum flow of the regulator.

According to the equation from Figure 6, 39.2% is corresponding to 250 ml/min. During the experiments, 35.2% is used for the nitrogen regulator and 39.2% for the ethylene regulator.

3.3.2 Calibration of ethanol/water flow meter

Flow meter and evaporator used for the water and ethanol addition are originally intended for the ethanol only. If same equipment is to be used to add water in a decided amount, flow meter needs to be calibrated. The calibration was conducted by weighting the outlet water at regulated time intervals for different percentages of the maximum flow. Results are presented in Figure 7. The linearity of the correlation is assuring its reliability.

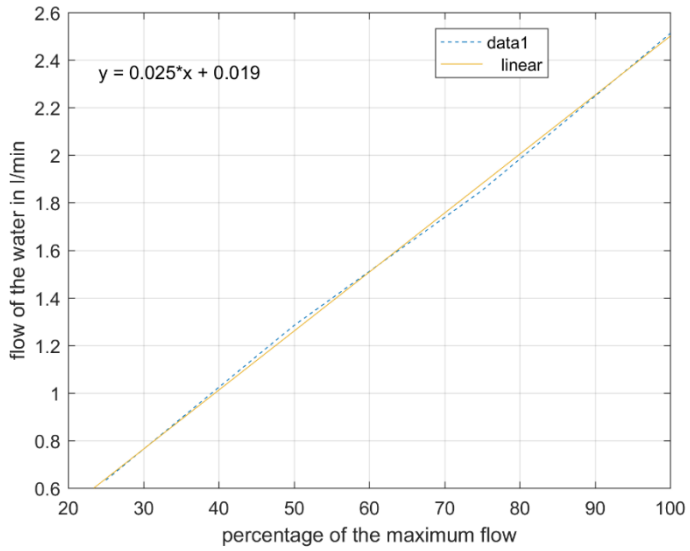

Figure 7. In this figure the water flow is calibrated to the percentage of the maximum flow of the mass flow meter.

In ethanol experiments flow meter is used in accordance to the maximum flow rate displayed on it, the apparatus is intended for ethanol used.

3.4 Calibration curve for identification of hydrocarbons

Analyses of the condensed liquid products for the different ethylene/ethanol experiments were conducted resulting in chromatograms with different separated peaks. However, the performed analysis of the produced liquids is of no value if these compounds remain unidentified. Therefore, a calibration curve method is used to estimate the boiling temperatures and carbon number of the products. Since the ambition of this study is primarily to produce straight hydrocarbon chain compounds, four pure hydrocarbons in the range of interest are used to derive a calibration curve that correlates retention time on the chromatograms to the boiling temperatures. Compounds that were used to design this curve, their boiling temperatures and retention times on the analysing chromatography are shown in Table 2 (Schmidt, et al., 2014).

Table 2. The four different alkanes used to derive a calibration curve for identifying unknown hydrocarbons

Compound	Boiling temperature (°C)	Retention time on chromatography (min)
Heptane	98.4	1.4194
Octane	125.7	1.879
Decane	174.1	2.725
Undecane	195.9	3.57

These values were used to design a curve shown in Figure 8. Different polynomial fittings were tested and the cubic one was chosen as the most suitable for the temperature estimations of the unknown compounds. Equation of the curve is displayed in the figure bellow.

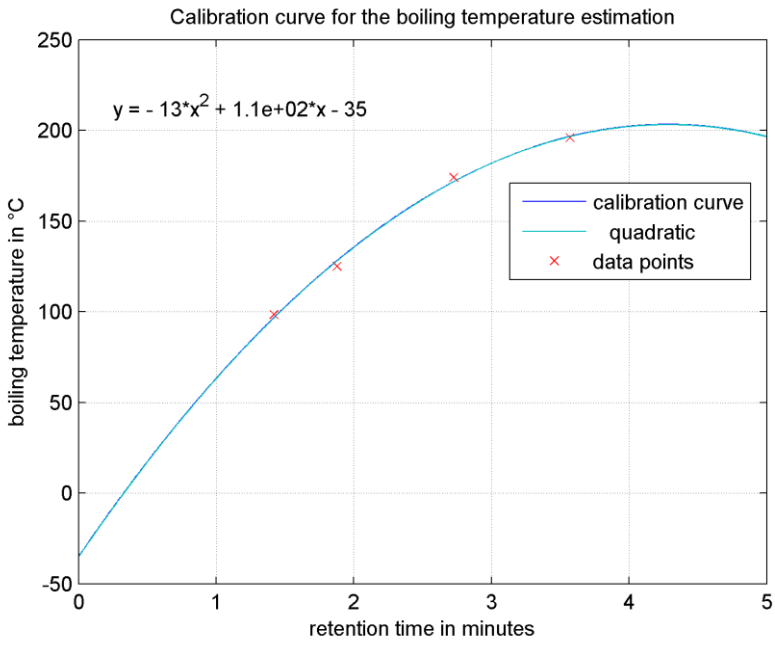

Figure 8. Displays the calibration curve for the chromatography retention times and boiling temperatures

3.5 Choice of analysis equipment

The GC model type Varian CP-3800 was chosen to analyse both the gas and liquid species from the ethylene oligomerization reaction, present in the bed reactor. As organic compounds are to be dealt with, the flame ionization detector (FID) is a suitable choice for the purpose of this study. At the beginning a capillary column of the model Agilent J&W DB-23 performed the separations. This kind is designed to reach very satisfactory separation of fatty acid methyl esters (FAME). It can handle large operating temperature and is appropriate when working with isomers as cis and trans FAME. However the capillary column needed to be changed into one suited for gaseous organic compounds, since the previous one wasn't able to manage larger hydrocarbons than ethylene (Anon., 2017) (Zielinski & Kettle, 2013).

To characterize the physical properties of the catalyst, gas adsorption was utilized. By implementing two different methods, BET and BJH, the surface area, pore volume and pore sizes are determined. It is a necessity to analyse the catalyst during two different circumstances, one at initial condition and the other when it's coked, to study how the properties are altered

3.5.1 Gas chromatography

Gas chromatography is a very reliable separation technique, used worldwide in the chemistry sector, which distributes and separates unknown or identified compounds between a stationary phase and mobile phase. The stationary phase can be of solid or liquid state, while the mobile phase is always an inert gas fulfilling its purpose of transporting solutes through the column. The solutes vapour pressure influences the residence time (retention) in the column. On the other hand the vapour pressure is dependent on the temperature and the molecular forces between the solutes and the stationary phase.

Today GC is among the most trusted and economically feasible separations method with an application range from the analysis of permanent gases to heavy petroleum products. Regarding efficiency and selectivity no other separation technique can compete with the supreme GC. A schematic draw of a general GC is illustrated in Figure 9.

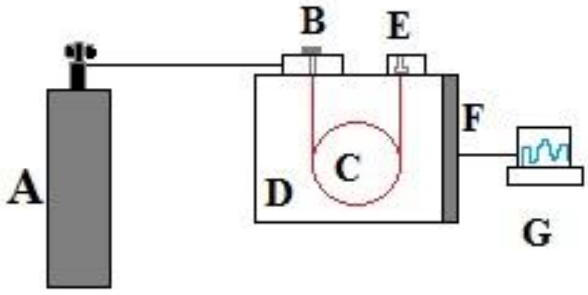

Figure 9. A view over the basic components of a Gas Chromatography. The picture is inspired by an image in (Sandra, 2001).

In Figure 9 the basic parts can be seen. The high pressure cylinder (A) supplies the carrier gas. A regulator is connected to regulate the pressure. At the controller (F), different running modes can be set and altering operating conditions is possible. The compounds to be analysed are introduced in the injector (B), where they are vaporized and transported into the column

by the carrier gas. Separation occurs in the column (C) which is placed in an oven (D). The temperature in the oven can either be constant or modified. When separation is completed the components leave the column and are recorded as a function of time by a detection device, point e. The results are viewed at a computer (G) as a chromatogram. The chromatogram provides data about the solutes residence time and the interaction in the stationary phase, which is used to identify compounds.

Selecting a carrier gas depends on several factors, both the column and the detector need to be taken into consideration but also, most importantly, on the desired speed of the analysis and detectability (efficiency). There are three common universal carrier gases to be selected, nitrogen, helium and hydrogen. Nitrogen for instance has a high density relative to the other gases and the longitudinal diffusional distribution of the solutes is small in the carrier gas. Though the mass transfer resistance for the solutes in nitrogen is high. However, hydrogen and helium shows contrary properties. They are low-density gases with large longitudinal diffusional spreading and their mass transfer resistance is small.

The most vital component for achieving a highly satisfactory separation is the choice of GC column. Packed column and capillary column are the types to be selected and which one is preferred depends on the nature and complexity of the analyse sample. The differences between these two types of GC column is interpreted from the resolution equation

$$R_s = \frac{\sqrt{N}}{4} \frac{\alpha - 1}{\alpha} \frac{k}{k+1} \tag{9}$$

where N represents the column efficiency, α is the column selectivity and K denotes the retention factor. By increasing these parameters the separation enhances. Packed column is general a low-resolution due to its low number of theoretical plates (low efficiency). But this hasn't decreased its usage in the analytical area since the resolution is improved by the high selectivity of the stationary phase. Several different stationary has been develop and improved for GC packed column because of that motive. For capillary columns the selectivity isn't central because this kind has very high efficiency (large number of theoretical plates) which enhances the separation resolution. In general the majority of the separation issues require only four basic stationary phases for reaching desired target.

Identification of the compounds depends on what kind of detector is applied in a GC. The purpose of a detector is to sense the compounds in the carrier gas and transform this into an electrical response which is recorded and sent to a computer. There is several existing detector devices used today but the common one are flame ionization detector (FID) and thermal conductivity detector (TCD).

How a FID proceeds is very simple, it can sense carbons from 10 pg per second with a linear range of 10^7. Beside its good stability the device provides fast response. During the analysis the carrier gas mixed with the carbons are combusted in air at the flame jet, with hydrogen included. Electrodes will then pull together the ions that are formed and provide an electric current proportional to the amount of inserted compounds to be analysed. However, non-carbon compounds and permanent gases like CO_2 and CS_2 want result in any response from the FID detector. The TCD on the other hand has another work mechanism; it measures the difference in thermal conductivity between pure carrier gas (reference gas) and analyte gas (sample gas). The difference occurs due to the drop of thermal conductivity when sample compounds are present in the carrier gas. When this occurs, the detector filament operating at constant voltage is heated and its resistance will elevate. This change in resistance, which is

measured electronically and recorded, is proportional to the amount of analytes in the sample gas. Regarding the choice of carrier gas for TCD, it's important to select one with high thermal conductivity and that doesn't mix with the sample gas during carrying (Sandra, 2001).

3.5.2 The Brunauer-Emmet-Teller (BET) – technique

A frequently used method to characterize the physical properties of a catalyst is gas adsorption analysis. The study of physical properties before and after reaction is of great importance, since differences can have a huge impact on the catalyst quality and performance. With above mentioned technique several parameters can be determined, for instance surface area, porosity, pore volume and pore size distribution. Shortly, gas adsorption involves exposing the catalyst to gases at different conditions and thereby values the amount uptake.

The Brunauer-Emmet-Theller-(BET) theory is built on the purpose of explaining the physical adsorption of gas molecules on a solid surface and provides tools to measure the specific surface area of powders and porous materials. With the measured surface area it can be determined how the solids dissolve or react with other species, therefore a conclusive aspect to be taken into consideration when designing catalyst. The analyse starts with a pre-treatment operation by applying a combination of heat, vacuum or flowing gas onto the catalyst, to clear away adsorbed contaminations at atmospheric pressure. After pre-treatment the catalyst cools down to cryogenic temperature (-195°C) under vacuum conditions. During that state an adsorptive is applied, usually nitrogen, to the catalyst at controlled rate doses. When the pressure reaches equilibrium after each dose, the amount nitrogen adsorbed is calculated. With the help of adsorption isotherm, the quantity of absorbate (N_2) required to create a monolayer over the external surface is determined. Through this covered area the surface area can be calculated (Zielinski & Kettle, 2013).

4. Experimental approach

In this section explanation of the experimental setup will be given. A schematic picture of the whole experimental setup will also be presented.

4.1 Description of the experimental set up

To begin with all reactions are performed in a 16(diameter) x 300(length) mm tubular, continuous reactor. The reactor is placed inside a heating jacket which has the purpose of setting the desired reaction temperature. Temperature is controlled with an external heating control box that is in direct contact with the heating jacket.

In the case of ethylene experiments, feed to the reactor is as previously mentioned composed of 75% nitrogen and 25% ethylene. Nitrogen and ethylene are supplied from separate sources and blended into a single pipeline. Mixed gas is then passing through the water evaporator which is used to add water vapour to the blend if needed. Before entering the evaporator, the liquid water is supplied to the gas mixture from a pressurised water tank connected to the gas pipeline. Afterwards, the mixture is entering the reactor.

In the case with ethanol experiments the mixing of inlet feed is slightly different. Ethanol is added to the gas mixture in the same manner as water in ethylene experiments. To be precise, liquid ethanol is added to the gas mixture from the same tank. The ethanol is then vaporized when the mixture is passing through the evaporator. Now completely gasified mixture is entering the reactor and getting in physical contact with catalyst.

Since the product leaving the reactor can consist of both liquid and gaseous compounds, a condensation step is needed in order to trap the liquid product. For this purpose a bubble flask containing toluene is used. A small amount of toluene (7 ml) is used in order to facilitate the future analysis of the toluene/liquid product mix. On the other hand, this amount should be sufficiently large to ensure that everything that leaves the pipeline is bubbling through the toluene. The flask itself is placed in an improvised cold bath to condense the less volatile synthetized compounds with potential fuel properties.

The unreacted ethylene and potential synthetized gases continue from the flask since their temperatures of condensations are far lower than the temperature in the cold bath. Gases then continue to the fume hood where the flow is measured and samples for analysis are taken during the reaction. Detailed simplified overview of the reaction set up is shown in Figure 10.

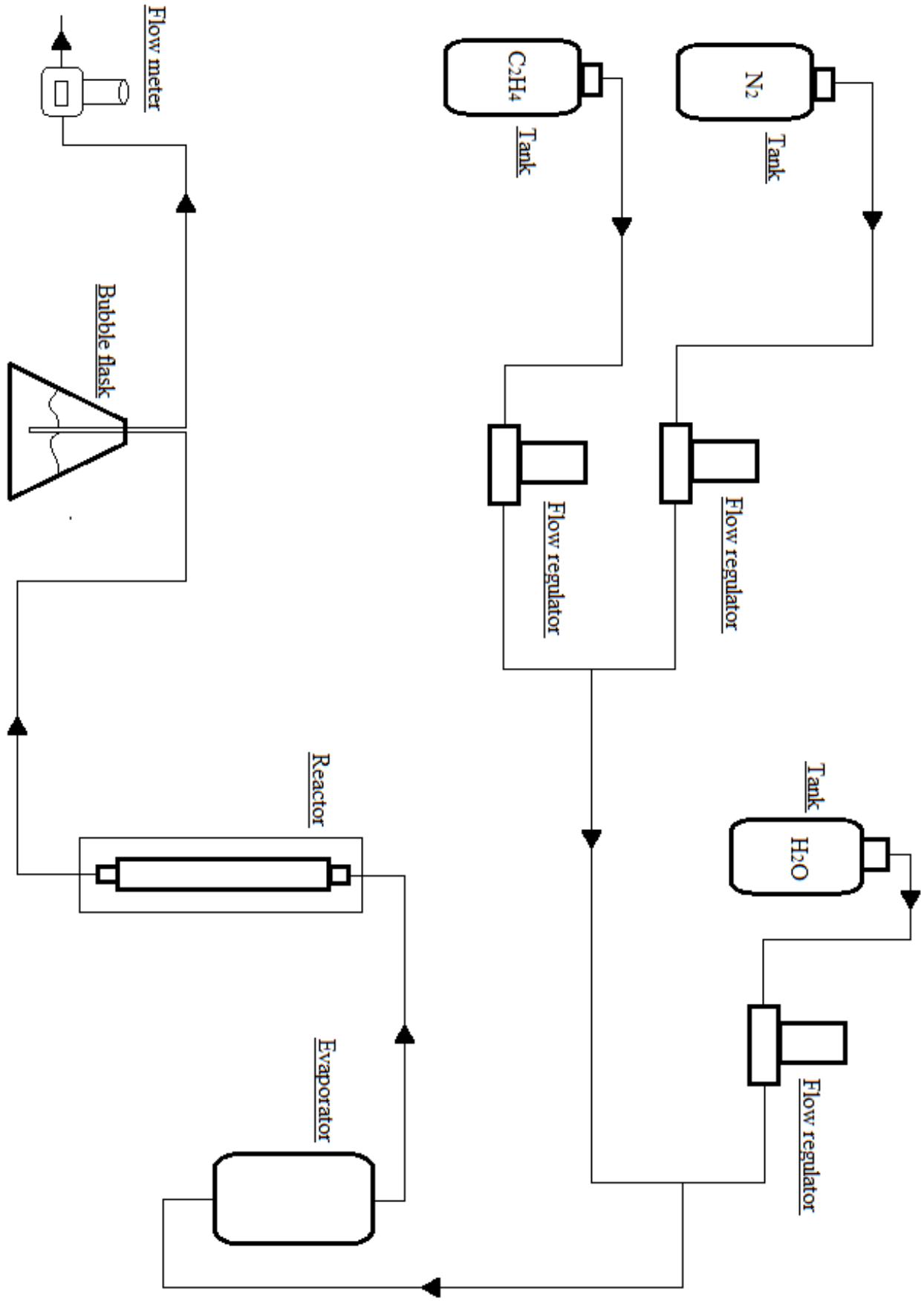

Figure 10. A schematic view of the experimental set up

4.1.1 Continuous process

All of the experiments are to be conducted in the same tubular reactor and with continuous operating condition. This implies that feedstock addition to the catalyst filled reactor and product extraction from it will happen simultaneously during reaction periods of between 30 and 60 minutes. The reaction parameter that will be particularly altered in order to achieve optimal conditions is the temperature in the reactor. Even if literature study gave insight in the importance of high pressure conditions for this particular type of reaction, high pressures will not be maintained during the reaction due to the equipment limitation. The feed will enter the reactor at the top, pass through the whole length of the vessel exit at the bottom and is led away to the separation step. As previously stated, gaseous outlet samples will be taken and analysed with even time intervals during the actual reactions.

It is expected that catalyst will be at least partially deactivated after each time a reaction is conducted. Therefore, the reactor will be emptied and then filled with fresh catalyst 50/50 volume % blend following every finished reaction. The old catalyst is regenerated through heat treatment.

Heating of the vessel will be accomplished by placing it in a heat jacket with spiral heat wire. The heat delivery is regulated by a control box that is measuring the temperature of the heating wire. It is assumed that both reactor vessel and the catalytic bed will attain the temperature of the wire after short time of exposure to the radiating heat. Therefore, if temperature of the wire has been 250°C for some time, assumption that the temperature of the catalytic bed is 250°C too will be made.

4.1.2 Addition of Water

In order to prevent or at least postpone the catalyst deactivation by coking, water is added during the experiments with ethylene. During the experiments with ethanol, water will be "added through the pre-reaction" since dehydration of ethanol is resulting in water alongside the produced ethylene. In the case with ethylene feedstock, water is mixed with the nitrogen/ethylene gas mixture before entering the reactor. When ethanol/nitrogen mixture is fed to the reactor, water is created when ethanol has reacted in the presence of catalyst. During the experiments with ethylene, the nitrogen, ethylene and water mix was decided to be 50, 12.5 and 37.5 volume% of the reactor feed. This amount of water in relation to the ethylene (3:1) is assumed to be sufficient for prevention of the catalyst deactivation. The temperature in the evaporator is set to 150 °C to ensure that sufficient amount of water is added to the gas inlet or that water vapour is not condensed on the way to the reactor.

4.1.3 Condensation of liquid products

As previously mentioned, products are condensed in a bubble flask with a solvent. Toluene is used to capture the eventual liquid products in bubble flask so that they can be analysed later with the aid of liquid chromatography. Since alkanes do not have polar properties, it is supposed that they will be easily captured by non-polar toluene. Water, on the other hand should form a second phase in liquid blend of the bubble flask. Assumption is that liquid products in range of C_{5+} are going to be produced. N-pentane is a liquid at room temperature (BP 36° C) and the larger alkenes are having even higher boiling points. It is therefore assumed that the cold bath that keeps a temperature of approximately 0° C will be sufficient to condense the produced liquids (source). According to an article in "Fluid Phase Equilibria",

solubility of ethylene in toluene is rather low. Therefore, there is no great risk that unreacted ethylene or other produced gases will be absorbed by the toluene solvent (Satoa, et al., u.d.).

4.2 Sampling approach

As previously stated gas outlet samples are taken in the fume hood during the reaction, with 5 minutes intervals. For this part of the experiments a gas sampling syringe is used to collect the gas mixture from the outlet and inject it into gas chromatography. This approach is open to many sources of error but the gas sample is always taken slowly in order to avoid air inserting into the syringe. Furthermore, the same volume of 1.4 ml of gas is taken each time. The flow of the outlet gas is also measured before each sample is taken.

When it comes to the liquid products, these are condensed and collected in a bubble flask. The blend in the flask is containing 7 ml of non-polar solvent (toluene), polar water (used to prevent the deactivation of the catalyst) and the potentially produced hydrocarbons. Immediately after the finished reaction, the content of the flask is transferred to a smaller container which is closed, shaken and left in the fume hood during some time. The liquid in the container will eventually separate in two phases, one polar which consists mainly of water and one non-polar with the solvent and hydrocarbons. This non-polar phase has lower density than water and will therefore form the upper layer.

A small volume of this upper layer is carefully pipetted into a sampling tube for chromatography. The analysis of the liquid products is then conducted.

5. Results & Discussion

This section of the rapport will present to the reader the experiment results of this thesis. The section is divided into two main parts, one part regarding the ethylene experiments and one part for ethanol experiments. Results for the different catalysts and reaction conditions will be presented in tables to illustrate the outcome of the experiments and convey the suggested conclusions. These illustrations will be followed by brief comments while the more thorough discussions will be present at the end of each separate section.

Results will regard both the analysis of the gases leaving the reactor in the fume hood and the captured liquids from the bubble flask. Measured outlet gas flows and gas distribution on the chromatograms are used to determine the amount of unreacted feedstock and thus the overall conversion rate. It is presupposed during all those calculation that the inlet nitrogen is not reacting nor accumulating anywhere during the process, same amount of nitrogen is thus leaving the reactor as it initially entered.

Each individual experiment with unique combination of catalyst and reaction temperature is presented in two tables. First table is presenting what actually happened with the feedstock during the reaction at different time phases. In ethylene cases, yields for gas and liquid/coke products are expressed in percent, selectivity for gas and liquid/coke products are also displayed. Furthermore, overall conversion of the ethylene is presented in the last column. In the case with ethanol feed, gas yields are presented at the different time rates. Selectivity was not calculated since the amount of unreacted ethanol is not possible to determine.

In the second table for each experiment, brief summary of the liquid product analysis is displayed. The first two columns are telling the retention times and corresponding estimated boiling points of the compounds. Based on this information, suspected number of carbons in each compound and distribution based on their chromatographic areas are conveyed in following two columns of this table format. Note that there is no guarantee that solemnly alkanes/alkenes are produced, aromatic or iso-structured compounds are also possibly produced. Boiling temperature estimations in the table are however based only on alkanes/alkenes.

Regarding the analysis of the liquid products, a calibration curve is used to approximately determine boiling temperatures of produced carbohydrates. This is done with four pure hydrocarbons with known retention times on the same chromatography apparatus. Unfortunately, internal standard method was not used for the quantification of the products. Therefore, the exact amount of products from the bubble flask is not determinable. Instead the product amounts are compared to each other in an approximate manner using chromatogram areas as references.

Calculations methods are described in Appendix B and the chromatograms can be seen in Appendix A.

5.1 Ethylene as feed

5.1.1 Catalyst 1 (ZrO_2-CeO_2 / 2% Pd)

The first reaction was carried out at 200°C with a continuous feed flow of 1020 ml/min into the plug flow reactor, at atmospheric pressure. Table 3 summarizes the results from that reaction occasion. During those conditions both yield and selectivity for liquid & coke products are greatly favoured. The conversion of the ethylene feed is however very low, not satisfying, but the possibility of recycling the reaming ethylene must be considered when designing for large scale production.

Table 3. A summary of the results from the oligomerization reaction at 200 °C, consisting of yield(Y), selectivity(S) and conversion (X).

Measured outlet flow (ml/min)	Time on stream (minutes)	$Y_{gas\ products}$ (%)	$Y_{liquid\ \&\ coke\ products}$ (%)	$S_{gas\ products}$ (%)	$S_{liqiud\ \&\ coke\ products}$ (%)	$X_{Ethylene}$ (%)
979	0 (30seconds)	16	16	50	50	32
970	5	----	----	----	----	----
969	10	0.44	21	2.1	98	21
968	15	0.34	21	1.6	98	21
956	20	0.33	25	1.3	99	26
973	25	0.12	19	0.66	99	19
968	30	0.75	21	0.34	97	22
					Mean conversion:	23

The liquid products formed at 200 °C are analysed for identification of hydrocarbons synthesized. Table 4 illustrates at which time each of the carbon-chains are eluted, the suspected number of carbons in the chain-skeleton and the distribution of them. Form Table 4 it can be seen that chains with carbon number of 9 are more selective than those with 7.

Table 4. Illustration of the estimated boiling temperatures, suspected number of carbons and the distribution for the produced liquids when Pd catalyst at 200 °C is tested with ethylene feed.

Retention time (min)	Obtained boiling point from the model (°C)	Suspected C_n	Distribution relationship between the compounds (%)
1.393	95	7	11.5
1.422	97	7	10.88
1.994	135	8-9	5.17
2.026	137	8-9	5.30
2.235	153	9	19.5

Table 5 displays the results from the oligomerization reaction at 250 °C and atmospheric pressure. The feed inlet flow was at 995 ml/min. The conversion of ethylene at this condition is still low as in the previous case. The same behaviour also remains regarding selectivity and yield for liquid & coke products since earlier case, but with a slightly increase of gas products.

Table 5. A summary of the results from the oligomerization reaction at 250 °C, consisting of yield (Y), selectivity (S) and conversion(X).

Measured outlet flow (ml/min)	Time on stream (minutes)	$Y_{gas\ products}$ (%)	$Y_{liquid\ \&\ coke\ products}$ (%)	$S_{gas\ products}$ (%)	$S_{liqiud\ \&\ coke\ products}$ (%)	$X_{Ethylene}$ (%)
960	0 (30seconds)	13	14	47	52	27
975	5	----	8	----	----	----
973	10	5.4	8.8	38	62	14
968	15	----	11	----	----	----
967	20	1.9	11	6.5	39	29
962	25	----	13	----	----	----
973	30	3.5	8.8	28	71	12
					Mean conversion:	21

The results from the GC-analysis for the liquid outcome show, see Table 6, that hydrocarbons chains with 10-11 carbons are formed. A remarkable fine result, which shows that production of petrol and aviation kerosene, is highly possible, though the low obtained amount compared to the rest. Chains with carbon numbers in the interval 8-9 is the produced majority.

Table 6. This table displays the estimated boiling temperatures, suspected number of carbons and the distribution for the produced liquids when Pd catalyst at 250 °C is tested with ethylene feed.

Retention time (min)	Obtained boiling point from the model (°C)	Suspected C_n	Distribution relationship between the compounds (%)
1.419	96.7	7	14.1
2.022	137	8	54.38
2.215	148	9	2.15
2.321	153	9	16.3
2.357	155	9	3.3
2.466	160		0.15
2.525	163		0.36
2.838	176	10	0.33
2.883	178	10	1.5
2.915	179		1.23
3.111	185		1.06
3.445	194	11	5.1

Not until the oligomerization reaction was performed at 300°C with a feed inlet flow at 997 ml/min, which a significant change in the outcome results could be observed. In Table 7 the results are presented. A remarkable 87% increase compared to previous case (350 °C) regarding conversion was noticed. The yield and selectivity shifted towards favouring the formation of gas products, an opposite behaviour present in contrast to earlier occasions.

Table 7. A summary of the results from the oligomerization reaction at 300 °C, consisting of yield(Y), selectivity(S) and conversion (X).

Measured outlet flow (ml/min)	Time on stream (minutes)	$Y_{gas\ products}$ (%)	$Y_{liquid\ \&\ coke\ products}$ (%)	$S_{gas\ products}$ (%)	$S_{liqiud\ \&\ coke\ products}$ (%)	$X_{Ethylene}$ (%)
983	0 (30seconds)	42	5.6	88	12	48
958	5	----	16	----	----	----
966	10	35	12	74	26	48
974	15	----	9	----	----	----
971	20	17	10	62	38	28
971	25	----	10	----	----	----
977	30	20	8	72	28	28
					Mean conversion:	38

Table 8 present the results when liquid obtained at 300 °C was analysed. According to the calibration model, two identified peaks from the chromatogram is similar in boiling points with hydrocarbon chains consisting of 7-8 carbons. The distribution is though very high for the one with 8 carbons.

Table 8. Presentation the estimated boiling temperature, suspected number of carbons and the distribution for the produced liquids when Pd catalyst at 300 °C is tested with ethylene feed.

Retention time (min)	Obtained boiling point from the model (°C)	Suspected C_n	Distribution relationship between the compounds (%)
1.418	96.648	7	17.51
2.021	136.808	8	82.49

At higher temperature, the conversion of ethylene increases even more, nearly 60% converts into products and coke formation. This is illustrated in Table 9, when the oligomerization was performed at 350 °C with a feed inlet flow of 1025 ml/min. At these conditions the yield of the gas products are nearly the same as in the reaction performed at 300 °C, see Table 7. The difference here is that due to increase of conversion, more of ethylene is converted into liquid products, see Table 9.

Table 9. A summary of the results from the oligomerization reaction at 350 °C, consisting of yield (Y), selectivity (S) and conversion (X).

Measured outlet flow (ml/min)	Time on stream (minutes)	$Y_{gas\ products}$ (%)	$Y_{liquid\ \&\ coke\ products}$ (%)	$S_{gas\ products}$ (%)	$S_{liqiud\ \&\ coke\ products}$ (%)	$X_{Ethylene}$ (%)
981	0 (30seconds)	47	18	72	27	66
958	5	----	27	----	----	----
912	10	29	45	39	61	74
987	15	----	15	----	----	----
972	20	35	21	62	38	56
981	25	----	18	----	----	----
985	30	33	16	67	33	50
					Mean conversion:	62

From the liquid sample analysis, see Table 10, the identified carbon chain in majority regarding quantity consisted of mostly 8 carbons. The longest chain with 9 carbons was however greater in amount in relationship with the one identified as $C_{7.}$

Table 10. Shows the estimated boiling temperature, suspected number of carbons and the distribution for the produced liquids when Pd catalyst at 350 °C is tested with ethylene feed.

Retention time (min)	Obtained boiling point from the model (°C)	Suspected C_n	Distribution relationship between the compounds (%)
1.418	97	7	11.92
2.022	137	8	62.99
2.320	153	9	25.10

The reactor conditions 400 °C and a feed continuous inlet flow has been shown to be a turn-off point for the reaction. Table 11 illustrates the results with an inlet feed of 994 ml/min and reactor temperature at 400 °C. The conversion has decreased significantly compared to the reaction carried out at 350 °C. When conversion declined the reaction shifted more into synthesizing more gas products, the selectivity for compounds at gaseous state increased.

Table 11. A summary of the results from the oligomerization reaction at 400 ℃, consisting of yield(Y), selectivity(S) and conversion(X).

Measured outlet flow (ml/min)	Time on stream (minutes)	$Y_{gas\ products}$ (%)	$Y_{liquid\ \&\ coke\ products}$ (%)	$S_{gas\ products}$ (%)	$S_{liqiud\ \&\ coke\ products}$ (%)	$X_{Ethylene}$ (%)
918	0 (30seconds)	32	30	52	49	63
977	5	----	6.8	----	----	----
989	10	41	2	95	4.6	43
985	15	----	3.6	----	----	----
956	20	23	15	60	39	38
946	25	----	19	----	----	----
991	30	14	1.2	92	7.8	15
					Mean conversion:	40

The results from the analysis, see Table 12, showed to identify the same hydrocarbons compounds as the one in Table 10. Even the distribution of the carbon species is the same both for the reaction carried out at 350 °C and this one carried out at 400 °C. This means variating the temperature in the interval 350-400 °C doesn't alter the composition of the obtained liquid products.

Table 12. This table displays the estimated boiling temperature, suspected number of carbons and the distribution for the produced liquids when Pd catalyst at 400 ℃ is tested with ethylene feed.

Retention time (min)	Obtained boiling point from the model (°C)	Suspected C_n	Distribution relationship between the compounds (%)
1.418	97	7	11.46
2.022	137	8	60.56
2.321	153	9	24.13

Since the reaction performed at 250 °C resulted in the creation of the longest hydrocarbon chains the synthesis was carried out again but with some modification. By lowering the feed flow inlet with 30% the residence time is increased. The reactants have then longer time to detain in the packed bed and react. The conditions for obtaining desired results should thereby be enhanced duo to the modification. Table 13 illustrates the consequences of performing the reaction a decreased inlet flow. The measured input flow of 718 ml/ml seems to increase the conversion comparing to the reaction performed at same temperature and regular input flow, see Table 5. Another difference noticed was how both the selectivity and yield for liquid & coke decreased compared to the one with normal inlet flow, see Table 5. In that reaction the main ethylene to react, was converted into only liquid & coke products.

Table 13. A summary of the results from the oligomerization reaction at 250 °C with 30% reduced total inflow, consisting of yield (Y), selectivity (Y) and conversion (X).

Measured outlet flow (ml/min)	Time on stream (minutes)	$Y_{gas\ products}$ (%)	$Y_{liquid\ \&\ coke\ products}$ (%)	$S_{gas\ products}$ (%)	$S_{liqiud\ \&\ coke\ products}$ (%)	$X_{Ethylene}$ (%)
675	0 (30seconds)	40	25	62	38	65
677	5	33	23	58	42	56
682	10	3.6	21	15	85	24
700	15	9.3	10	47	52	20
641	20	0.6	44	1.34	99	45
710	25	2.2	4.5	32.8	67	6.7
678	30	12.3	22.9	35.0	65	35
					Mean conversion:	31

Even the GC-analysis showed that shorter chains were obtained at these conditions, see table 14, comparing to the one with 100% inlet flow. Table 14 displays the results where the outcome distribution was the highest for those consisting 8-9 carbons.

Table 14. Presentation of the estimated boiling temperature, suspected number of carbons and the distribution for the produced liquids when Pd catalyst at 250 °C is tested with ethylene feed. In this experiment total feed to the reactor is decreased by 30%.

Retention time (min)	Obtained boiling point from the model (°C)	Suspected C_n	Distribution relationship between the compounds (%)
1.393	95	7	3.7
1.418	97	7	12
2.026	137	8	61
2.326	154	9	23

During the period when experiments were carried out at different circumstances with the Pd-catalyst, the behaviours through the temperature interval 200-400 °C were examined and mapped. Some results are straight forward and follow expected patterns, theories that are supported by the literature study. Then there are those results gained from the experiment that

don’t follow any “logical” or common path. They are unpredictable and the cause is difficult to point mark. Independently if the outcome follows any hypothesis or cannot be explained, there is a fundamental base for investigation towards improvement.

Regarding the relationship between the temperature and the conversion of the precursor ethylene some certain conclusions can be drawn. The increase in conversion is followed by elevating the temperature. Therefore lower temperatures aren’t desired since a large amount of the feed has to be recirculated into the system again of environmental issues. Though a deviation was observed during the 250 °C it showed a conversion of 20.6% lower than the experiment performed at 200 °C that reached 23.5. However both of these results are miles from being satisfactory for the investigators. The highest conversion (61%) was reached during the 350 °C reaction and at 400 °C it declined into 39.8 %. This is not an odd progress path but more of a logical one. The ethylene oligomerization is an exothermic process which releases heat energy from its system to the surroundings. If the temperature is increased the more heat is supplied to the process so the reaction should shift the equilibrium to left, at the site of the reactant, to consume some of the heat. Therefore this kind of reaction would produce more hydrocarbon chains if it was operated at lower temperature. But this is contradictory since lowering the temperature also declines the rate of the process. So in practice the optimum temperature for this case is 350 °C, a compromise value that allow reactants to be consumed at reasonable rate an equilibrium heat content that’s not to unfavourable.

Another observation made, common for all the experiments, was how the conversion declined with respect to the time on the stream. An explanation could be that catalyst deactivation occurs due to coke or carbon formation hindering the reactants reaching the active phase. So the added water wasn’t sufficient enough to prevent it.

Regarding the yield of the compounds in gaseous state it increases with elevated temperature. Maximum yield for gas products is reached in the temperate range 300-350 °C, whereas yield from the 400 °C reaction was in comparison decreased with 23.4 %.

5.1.2 Catalyst 2 (20% CeO_2/Al_2O_3/ 0.5% Pt)

In this subsection results for the experiments with Pt catalyst and ethylene feed are presented. The initial experiment was the one below where reactor temperature was set to 250 °C. The gas samples were taken in the beginning and each tenth minute until the end of experiment. According to the data presented in Table 15, this lower temperature reaction condition is favouring the liquid/coke production. Yields are notably lower for gas products and the selectivity is following the same reasoning. Ethylene conversion with the average value of approximately 34% is not satisfactory.

Continuous input flow (CIP) was measured as 1015 ml /min in the beginning

Table 15. A summary of the results from the oligomerization reaction at 250 °C, consisting of yield (Y), selectivity(S) and conversion (X).

Measured outlet flow (ml/min)	Time on stream (minutes)	$Y_{gas\ products}$ (%)	$Y_{liquid\ \&\ coke\ products}$ (%)	$S_{gas\ products}$ (%)	$S_{liqiud\ \&\ coke\ products}$ (%)	$X_{Ethylene}$ (%)
958	0 (30seconds)	9.6	23	30	70	32
926	5	----	36	----	----	----
935	10	6.1	32	16	84	38
937	15	----	31	-----	-----	----
935	20	3.2	32	9	91	35
937	25	----	31.2	----	----	----
954	30	4.5	24	16	84	29
					Mean conversion:	34

Results from the liquid analysis of 250 °C experiment with Pt catalyst and ethylene feed are presented in Table 16. First of all, one can observe that 4 different products were detected with strong dominance of the guessed C_8 product with the retention time of 2.022 minutes. This major product is placed in the middle of the size scale for all the observed produced compounds in this experiment. The size range is 7-9 carbon atoms.

Table 16. Displays the estimated boiling temperature, suspected number of carbons and the distribution for the produced liquids when Pt catalyst at 250 °C is tested with ethylene feed.

Retention time (min)	Obtained boiling point from the model (°C)	Suspected C_n	Distribution relationship between the compounds (%)
1.418	97	7	10
2.022	137	8	63
2.320	153	9	21
3.445	194	11	6.8

The next experiment in this series was conducted with reaction temperature of 300 °C, thus 50 degrees temperature increase being the only change in regard to the preceding experiment. However, this slightly hotter environment caused drastic difference in the gas results presented in Table 17. Yields and selectivity for the gas products increased notably to the cost of liquid/coke products. This higher temperature also increased the overall conversion of the ethylene. Continuous input flow (CIP) was measured as 1011 ml /min in the beginning of the experiment.

Table 17. A summary of the results from the oligomerization reaction at 300 °C, consisting of yield(Y), selectivity(S) and conversion(X).

Measured outlet flow (ml/min)	Time on stream (minutes)	$Y_{gas\ products}$ (%)	$Y_{liquid\ \&\ coke\ products}$ (%)	$S_{gas\ products}$ (%)	$S_{liqiud\ \&\ coke\ products}$ (%)	$X_{Ethylene}$ (%)
985	0 (30seconds)	34	10	77	23	45
949	5	----	25	----	----	----
975	10	26	14	64	36	40
985	15	----	10	----	----	----
975	20	27	14	65	35	41
982	25	----	12	----	----	----
985	30	23	10	69	31	33
					Mean conversion:	40

Information in the Table 18 is showing which liquid carbohydrates the 300 °C reaction condition was able to synthetize. The dominance of the C_8 is preserved with higher temperature with even a slight increase in the distribution percentage (note 62.63% in Table 16 and 67.17% in Table 18). Otherwise, the disappearance of C_{11} product is noted alongside the unquestionable reduction in C_9 product. The C_7 product is on the other hand increased indicating that this condition favours the shorter chains more than the previous. The almost identical retention times in Tables 16 and 18 are indicating that the same products are obtained.

Table 18. The table shows the estimated boiling temperature, suspected number of carbons and the distribution for the produced liquids when Pt catalyst at 300 °C is tested with ethylene feed.

Retention time (min)	Obtained boiling point from the model (°C)	Suspected C_n	Distribution relationship between the compounds (%)
1.418	97	7	16
2.021	137	8	69
2.320	153	9	15

The trend of increasing temperature was continued and this experiment was testing the oligomerization possibilities of Pt catalyst at 350 °C. The information in the Table 19 is clearly stating that the same trends as that were previously observed are still valid. The further increasing of the reaction temperature is enhancing the favouring towards the gaseous

products. Yield of the gases exiting the reaction have increased but at the same time selectivity for the same is slightly lower. Ethylene conversion is further increased but is dropping during the reaction. Possible explanation is the occurrence of the catalyst deactivation by coke formation. Trend of increasing conversion with increased temperature is still kept.

Continuous input flow (CIP) was measured as 1025 ml /min when experiment started.

Table 19. A summary of the results from the oligomerization reaction at 350 °C, consisting of yield (Y), selectivity(S) and conversion(X).

Measured outlet flow (ml/min)	Time on stream (minutes)	$Y_{gas\ products}$ (%)	$Y_{liquid\ \&\ coke\ products}$ (%)	$S_{gas\ products}$ (%)	$S_{liqiud\ \&\ coke\ products}$ (%)	$X_{Ethylene}$ (%)
956	0 (30seconds)	49	28	64	36	76
940	5	----	34	----	----	----
972	10	38	21	64	36	59
986	15	----	16	----	----	----
956	20	26	28	48	52	53
947	25	----	31	----	----	----
964	30	21	24	46	54	46
					Mean conversion:	59

Results from the liquid product analysis for 350 °C experiment are shown in Table 20. Reduction of C_8 product is observed, breaking the previously stated trend where increased temperature gave more of this compound. Other interesting fact is the reappearance of C_{11} product, this time with more than 100% larger distribution among the other products when compared to Table 16. The almost identical retention time is quite assuring that the C_{11} products from Tables 16 and 20 are in fact the same compound. Furthermore, C_7 distribution decreased while the C_9 compound experienced almost a doubling of the disposition in the mixture when compared to previous experiment. All of the retention times in the Table 20 have been previously seen indicating that the products are the same.

Table 20. The estimated boiling temperature, suspected number of carbons and the distribution for the produced liquids when the Pt catalyst at 350 °C is tested with ethylene feed are presented.

Retention time (min)	Obtained boiling point from the model (°C)	Suspected C_n	Distribution relationship between the compounds (%)
1.419	97	7	15
2.021	137	8	56
2.320	153	9	28
3.442	194	11	15

The final experiment in this section is at the reaction temperature of 400 °C with other conditions unchanged. Yields, selectivity and conversion are presented in Table 21. Yield for the gas products is slightly decreased at the beginning when compared to the 350 °C experiment and the corresponding Table 19. Interesting change is that the yield for the gas products is decreasing less with the increasing running time of the reaction when compared to previous cases. At the same the selectivity for the liquid/coke products is increasing less during the later stages of the experiment when compared to for instance Table 19 and 350 °C experiment. It is therefore possible that the increased reaction temperature is reducing the rate of deactivation in this particular case. This cannot be stated for certain since there is no way of calculating the selectivity for coke only from the available information.

Continuous input flow (CIP) was measured as 1013 ml /min in the beginning of the experiment.

Table 21. A summary of the results from the oligomerization reaction at 400 °C, consisting of yield (Y), selectivity (S) and conversion (X).

Measured outlet flow (ml/min)	Time on stream (minutes)	$Y_{gas\ products}$ (%)	$Y_{liquid\ \&\ coke\ products}$ (%)	$S_{gas\ products}$ (%)	$S_{liqiud\ \&\ coke\ products}$ (%)	$X_{Ethylene}$ (%)
993	0 (30seconds)	42	23	65	35	65
925	5	----	29	----	----	----
984	10	43	16	73	27	60
958	15	----	11	----	----	----
968	20	34	23	60	40	57
1009	25	----	26	----	----	----
988	30	32	20	62	38	51
					Mean conversion:	58

Results for the liquid analysis of 400 °C are presented in Table 22. A completely new product is observed at the retention time of 1.610 which was not previously detected. This new compound has a significant distribution of almost 20% which is excluding the possibility of impurity detection. The other three products have already been seen in the other experiments. The C_{11} compound disappeared from the product blend once more while the C_7 and C_9 are still present with approximately same distributions as in 350 °C experiment.

Table 22. The estimated boiling temperature, suspected number of carbons and the distribution for the produced liquids when Pt catalyst at 400 °C is tested with ethylene feed, are presented.

Retention time (min)	Obtained boiling point from the model (°C)	Suspected C_n	Distribution relationship between the compounds (%)
1.419	97	7	13
1.610	110	8	20
2.022	137	8	54
2.320	149	9	20

Some overall conclusions for the ethylene experiments with the Pt catalyst can be drawn from the obtained results. Firstly, yields for the produced gases are increasing with the increased reaction temperature. The fast comparison between second columns of Tables 15, 17, 19 and 21 indicates that the absolutely worst gas yields are observed at the lowest temperature. Contrary they are higher at higher temperatures, for instance highest gas yields are generated from 350 °C and 400 °C experiments.

Logically, the lower gas yield implies that liquid/coke yields are higher and this is happening since the ethylene can end up in only one of these two product categories. For the lowest temperature of this experimental part (250 °C) selectivity towards liquid/coke products in range of 70-90% is observed. Contrary to this, the same result parameter attains values between 27-40% for the 400 °C experiment. A hastily drawn conclusion could therefore be that lower temperatures are generally better for the oligomerization but this premise cannot be seen as true until more analysis is done.

Unfortunately it is impossible to distinguish liquid product from coke and precisely assure that higher temperature conditions are producing more liquid products. Further development of this experimental plan is essential in order to achieve definitive results regarding the produced amounts of liquid hydrocarbons which are not available at the moment. Only then will it be certain if the low temperatures tend to favour the formation of longer chains.

On the other hand, some definite conclusions can be made about the relation between the temperature and the conversion of fed ethylene. At lower temperatures, conversion of ethylene is generally lower and vice versa. During the first experiment, at the 250 °C, conversion of ethylene did not reach values higher than 38 % which is rather low. Best results were observed at 350 °C when conversion was about 76% in the initial stages of the experiment. Temperature conditions of 400 °C also gave one of higher conversions (65%). One occurrence regarding conversion, common for all experiments, is that conversion is gradually decreasing with the time of reaction. This phenomenon could happen due to the catalyst deactivation and implies that the water addition was not sufficient to prevent it.

When it comes to the production of hydrocarbons, neither of the individual experiments succeeded in producing higher carbon number than 11. This C_{11} compound was observed after 250 °C and 350 °C experiments but not at all detectable for the other two. Throughout all the experiments, the most abundant component has been C_8 at retention time of about 2.020 minutes. However, it is hard to draw any straight conclusion about the distribution of products and its correlation with the temperature.C_8 seems to have achieved its peak of production at the 300 °C since its distribution is decreased for both lower and higher temperature than this point. C_9 reached its top production at 350 °C but the difference is not too great in comparison with other reaction conditions. It is unclear why $C_{11}$is produced during some instances but not during others.

5.2 Ethanol as feed

In this section, results are presented from those experiments where vaporized ethanol was used as a feed. The two used catalysts are tested for one low (250 °C) and one high (400 °C) temperature. Gas samples are taken in 5 minute intervals. As in the previous ethylene results, results for the each experiment are presented in two tables which are commented separately. Overall conclusions are discussed at the end of the section.

5.2.1 Catalyst 1 (ZrO_2-CeO_2 / 2% Pd)

Gas product results for the ethanol experiments with Pd catalyst at 250 °C are presented in Table 23. The only obtainable information was the yield of gas products since it was not possible to determine the amount of unreacted ethanol that condensed in the bubble flask. Gas yields are generally the same during the reaction which could imply the reduced deactivation.

Table 23. A summary of the results from the oligomerization reaction at 250 °C with EtOH as feed.

Measured outlet flow (ml/min)	Time on stream (minutes)	$Y_{gas\ products}$ (%)
780	0 (30seconds)	12.0
855	5	42.0
833	10	33.2
843	15	37.2
842	20	36.8
827	25	30.8
838	30	35.2

In the Table 24 liquid products for this experiment are presented. Identification of these compounds has been a harder task than the identification of liquid products from the ethylene experiments. When used in the temperature estimation model that was constructed, some of the retention times are resulting in boiling temperatures that are hard to place in a defined size category. For instance, retention times 1.524 and 2.036 minutes are identified as either 7 or 8 carbon compound in the case of former and 8 or 9 carbon compound in the case of latter. Their estimated boiling temperatures are values that are in between values for two alkane boiling temperatures. They are therefore presented as 7-8 and 8-9 carbon sized.

Table 24. The estimated boiling temperature, suspected number of carbons and the distribution for the produced liquids when Pd catalyst at 250 °C is tested with ethanol feed, are presented in the table.

Retention time (min)	Obtained boiling point from the model (°C)	Suspected C_n	Distribution relationship between the compounds (%)
1.351	92	7	9.15
1.524	104	7-8	24.92
1.597	110	8	30.6
1.704	17	8	22.6
2.036	138	8-9	12.8

The following Pd experiment was conducted during 400 °C reaction conditions. Yields for gas products are presented in Table 25 and it seems that higher temperature conditions resulted in higher production of gases. It is also observable that the gas yield is experiencing lesser decrease during the course of the reaction.

Table 25. A summary of the results from the oligomerization reaction at 400 °C with EtOH as feed.

Measured outlet flow (ml/min)	Time on stream (minutes)	$Y_{gas\ products}$ (%)
820	0 (30seconds)	28.0
963	5	85.2
941	10	76.4
948	15	79.2
930	20	72.0
941	25	76.4
939	30	75.6

Hydrocarbon production results for the Pd catalyst at higher temperature are presented in Table 26. The immediate observation is that this particular experiment resulted in a larger number of produced individual compounds. There are totally 9 different compounds that are in a supposed range of 7-9 carbon atoms. Once again it is hard to determine the true carbon contents for several produced compounds since their boiling temperatures are placed in the middle of those for two different alkenes. The compound with the highest distribution (23.21 %) is the one that could supposedly contain 8 carbon atoms, the following one (21.66%) contains supposedly 7 carbons since its boiling point is close to the one of heptane.

Table 26. This table illustrates the estimated boiling temperature, suspected number of carbons and the distribution for the produced liquids when Pd catalyst at 400°C is tested with ethanol feed-

Retention time (min)	Obtained boiling point from the model (°C)	Suspected C_n	Distribution relationship between the compounds (%)
1.433	98	7	21.7
1.461	100	7	11.4
1.526	105	7-8	12.8
1.589	109	8	7.7
1.612	111	8	4.6
1.744	120	8	23.2
2.023	137	8-9	8.6
2.084	140	8-9	2.5
2.507	162	9	7.6

First observation falling into one's eyes when comparing the two Pd experiments is that gas yields are vastly different. The 250 °C experiment is averaging around 32 % for the gas yield while the corresponding value for the 400 °C is around 70%. This fact is strengthening the previous conclusion from the ethylene experiments where it was stated that increasing temperature is driving the reaction towards gas formation. Another observation is that these

yields do not drop significantly as the reaction is approaching its ending. This occurrence is implying that lesser degree of catalyst deactivation is taking place during the ethanol experiments than previously when ethylene was utilized as the feedstock. Although catalyst deactivation is a field of study on its own which this thesis was not intended to investigate thoroughly, possible explanation of observed behaviour is suggested to occur due to the dehydration of ethanol to ethylene and water. Ethanol dehydration is possibly supplying the needed water for the deactivation prevention in a more effective manner than addition of water by evaporation before the actual reaction. Another explanation is the much lower concentration of ethylene during the ethanol experiments. There is a large difference in ethylene concentration during experiments when ethylene is fed directly to the catalytic reactor and during the ethanol experiments when ethanol is dehydrated to ethylene to the limited extent. This lower presence of ethylene in the reactor could be the reason for the lesser extent of deactivation.

When it comes to the identification of the synthetized compounds one must admit that the presence of ethanol is adding a whole new dimension to the speculations regarding the number of carbon atoms. The oxygen atoms which are present in each one of ethanol molecules are opening opportunities for synthesis of larger number of compounds than it was case when ethylene was used as a feed. Therefore some of the guesses that Tables 24 and 26 are highly uncertain. The conclusions are that Pd catalyst with ethanol feed was not able to produce compounds that contain more than 9 carbon atoms. Another analysing method besides boiling temperature curve based on alkanes is needed in order to tell more about the content and the structure of the produced compounds.

5.2.2 Catalyst 2 (20% CeO_2/Al_2O_3/ 0.5% Pt)

The two experiments for the Pt catalyst and ethanol as a feed were conducted in the same manner as those for the Pd catalyst. One low (250 °C) and one high (400 °C) temperature were tested with dense gas sampling.

Gas yields for the 250 °C ethanol experiment with Pt catalyst are shown in Table 27. Overall these yields are notably higher than those for the Pd catalyst at the same reaction conditions, shown in Table 23. Average value for the yields in Table 26 was calculated to approximately 41% which is considerably higher than the average 32% for previous 250 °C Pd experiment. The minor changing of the gas yield over the course of the reaction is noted, same suggestion of ethanol dehydration impact could be applied as an explanation.

Table 27. A summary of the results from the oligomerization reaction at 250 °C with EtOH as feed.

Measured outlet flow (ml/min)	Time on stream (minutes)	$Y_{gas\ products}$ (%)
778	0 (30seconds)	11.2
830	5	32
879	10	51.6
873	15	49.2
863	20	45.2
860	25	44.0
888	30	55.2

Table 28 demonstrates the hydrocarbon products from the Pt 250 °C experiment. As in the case with Pd 250 °C experiments, products are few and are not containing more than 9 carbon atoms. Product with the largest distribution is the one with retention time of 1.6 minutes and the approximate carbon content of 8 atoms. The second most present compound is supposedly also containing 8 carbon atoms which indicate that this oligomerization confirmation is favoured. One of the produced compounds with retention time of 1.527 minutes is identified as either C_7 or C_8 due to the reasons previously stated.

Table 28. Presentation of the estimated boiling temperature, suspected number of carbons and the distribution for the produced liquids when Pt catalyst at 250 °C is tested with ethanol feed.

Retention time (min)	Obtained boiling point from the model (°C)	Suspected C_n	Distribution relationship between the compounds (%)
1.527	105	7-8	18.1
1.6	110	8	42.
1.707	117	8	31.9
2.303	152	9	7.8

Gas yields were once again higher at the higher temperatures as can be seen in Table 29. Values for yields were ranging between 57-84 % with no notable drop towards the reactions ending. The average gas yield was 72 % compared with the 41 % for the same catalyst and feed at lower temperature.

Table 29. A summary of the results from the oligomerization reaction at 400 °C with EtOH as feed.

Measured outlet flow (ml/min)	Time on stream (minutes)	$Y_{gas\ products}$ (%)
893	0 (30seconds)	57.2
960	5	84.0
943	10	77.2
931	15	72.4
939	20	75.6
929	25	71.6
924	30	69.6

Temperature increase yielded more different products even in the case with Pt catalyst. The estimated temperatures and their distribution among each other can be observed in Table 30. The compound with highest distribution (22.67 %) is the one with retention time of 1.747; this particular compound is believed to be a C_8. Rest of the compound are as in previous cases in size range between C_7 and C_9. Unfortunately, no hydrocarbons of higher order (C_{10+}) were obtained.

Table 30. Shows the estimated boiling temperature, suspected number of carbons and the distribution for the produced liquids when Pt catalyst at 400 °C is tested with ethanol feed.

Retention time (min)	Obtained boiling point from the model (°C)	Suspected C_n	Distribution relationship between the compounds (%)
1.423	97	7	12.83
1.463	100	7	4.8
1.543	106	7-8	17.23
1.592	109	8	4.2
1.612	111	8	5.7
1.747	120	8	22.7
2.026	137	8-9	13.8
2.325	153	9	9.5
2.361	155	9	9.31

The overall conclusion for this section's experiments with both catalysts is firstly that the gas yield is increasing with the increasing reaction temperature. These changes are significantly high with almost 38% increased average gas yield for the Pd catalyst and corresponding 31% increase for Pt catalyst when temperature is changed from 250 °C to 400 °C. The phenomena of stable gas yield values throughout the whole reaction time lapse was also noted in all the

experiments. One of the conclusions is therefore that addition of water through ethanol dehydration is a more suitable approach for catalyst deactivation prevention.

Another detected impact of the temperature increase was the number of compounds that were produced. For both catalysts number of produced compounds was notably increased. In the case with Pd 4 more compounds were detected after the temperature increase, in the case with Pt catalyst 5. Interesting fact is also that the retention time of the 250 °C products are not observable in the 400 °C. This means that temperature increase delivered a set of whole new compounds with a clear distinction to the previous ones. This stands quite opposite to the results from the ethylene experiments where several identical compounds reappeared and were detected again in spite of the temperature increase. This high reactivity of the system with production of different compounds depending on the reaction temperature is one more reason that is evidencing that the calibration curve currently used is not sufficient for the identification of the produced chemicals. Previous statement about the role of the oxygen in generating compounds during the reaction is the main reason.

Furthermore, neither of the experiments succeeded in synthetizing C_{10+} compounds which were the primary aim and hope of this thesis. Products from all of the experiments were in the range of C_7 to C_9. As with ethylene experiments, reactions tended to grant C_8 compounds highest distribution percentages in the blends. Recommendations for the future work and the existing experimental set-up will be given in a separate section.

The idea that was not realized during this thesis but which is a good recommendation for future studies is to measure and analyse polar phase from the bubble flask in order to determine the amounts of ethanol that condensed. This information will greatly improve the possibilities for generating deeper conclusions. Corresponding yields, selectivities and conversions for ethanol could be calculated.

Overall, Pd catalyst had the better performance out of the two tested. The possible reason for this occurrence is the presence of Al_2O_3 as a support material. This support compound contributes to the additional acidic catalytic sites that enhance the rate of ethanol dehydration (Deutschmann, 2002) (Denise, et al., 2013).

5.3 Physical characterization of the catalysts

The two different types of catalysts were characterized with respect to their physical properties. Gas adsorption analysis was carried out for measurements of surface area, pore volume and pore size. By implementing the Brunauer-Emmet-Teller (BET) technique, which explains the physical adsorption of the gas nitrogen molecules in the surface area of the catalyst, the parameters could be determined. In Table 31 & 32 the results from the BET-technique are displayed. Both catalysts are analysed during two different circumstances. One regards the catalyst at fresh conditions and the other is analysed after the ethylene oligomerization when getting exposed of coke deposition.

Table 31. A summary of the BET-results consisting of surface area, micropore area, pore volume and pore size for the catalyst 20% wt CeO_2/Al_2O_3 0.5% Pt .

Characterization of 20% wt CeO_2/Al_2O_3 0.5% Pt		
Condition of the catalyst :	**Fresh**	**Spent**
Surface Area		
BET Surface Area	117 m^2/g	118 m^2/g
t-Plot Micropore Area	6.73 m^2/g	7.04 m^2/g
BJH Adsorption cumulative surface area of pores	117 m^2/g	117 m^2/g
BJH Desorption cumulative surface area of pores	134 m^2/g	136 m^2/g
Pore Volume		
t-Plot micropore volume	0.00228 cm^3/g	0.00243 cm^3/g
Pore Size		
BJH Adsorption average pore width	156 Å	193 Å
BJH Desorption average pore width	139 Å	167 Å

Table 32 A summary of the BET-results consisting of surface area, micropore area, pore volume and pore size for the catalyst 2% Pd.

Characterization of ZrO_2-CeO_2 / 2% Pd		
Condition of the catalyst :	**Fresh**	**Spent**
Surface Area		
BET Surface Area	116 m^2/g	117 m^2/g
t-Plot Micropore Area	10.5 m^2/g	4.49 m^2/g
BJH Adsorption cumulative surface area of pores	110 m^2/g	114 m^2/g
BJH Desorption cumulative surface area of pores	137 m^2/g	139 m^2/g
Pore Volume		
t-Plot micropore volume	0.00420 cm^3/g	0.00103 cm^3/g
Pore Size		
BJH Adsorption average pore width	264 Å	250 Å
BJH Desorption average pore width	213 Å	207 Å

It’s important to emphasize that the catalyst wasn’t analysed at its initial condition, at the very beginning before being exposed of several cycles of same reaction. Therefore the condition of being “fresh” applies for regenerated catalyst, after removal of coked sediment.

At the first case, see Table 1, there are some few significant differences between fresh and cooked catalyst. But for the most part no substantial changes arose after coke fouling. However the BET surface area, the area for the micropores and the micropore volume were increased for the coked one. An increased BET surface area confirms the formation of coke or carbon but doesn’t clarify the rest. The structure of the deposit is of huge importance because the increase in micropore area and volume is due to creation of new micropores in the coked residue. A coked deposit of porous structure is obtained. On the other hand this motive is contradictory since the average pore size increases and one should think that the increase of micropores should reduce the size. This is explained by the distribution of pore sizes. If the existing smaller micropores are plugged by coke formation and larger ones are conceived in the coke structure then it legitimates the increase of average pore size.

The physical properties of the catalyst with palladium as active phase, see Table 2, are affected in larger scale by the coke than the previous one. For instance, the micropore area is decreased nearly with 60% and the micropore volume is reduced with 75%. The BET surface doesn’t show any distinctive change. This trend appears to characterize a formation of non-porous deposit which clogs the existing micropores but leaves the mesopores.

6. Summary

6.1 Conclusions

The initial performed ethylene experiments with Pd-catalyst revealed that the optimal conversion temperature is 350 °C which also governs the rate of the process without shifting the reaction towards reactants. The conversion for this reaction condition was 61%, satisfying considering the lack of pressure. Products in the range of 8-9 carbon atoms were mostly abundant throughout all the experiments. The longest carbon chain was identified after the 250 °C reaction with Pd-catalyst.

The above stated conclusions imply also for the Pt-catalyst except that this particular catalyst produced generally C_8 compounds throughout the corresponding experiments. Furthermore C_{11} was produced at 250 °C but also at 350 °C.

Regarding the ethanol experiments it was observed that high temperature gave large spectra of products and the yield for gas was increased with elevated temperature. C_8 compounds were the major outcome in all four ethanol experiments. The longest chain, C_9, was obtained at 400 °C. All of these observations are valid for both catalysts used.

It was also observed that yields for the gas products went through minor or almost none alterations during the time elapse of the reactions. This is in sharp contrast to the notable gas yield drops for the ethylene experiments. Water derived from ethanol dehydration is clearly a better solution for the deactivation prevention than addition of water vapour.

6.2 Limitations (Challenges & Error sources)

The experimental limitations and possibilities of error in this study were numerous and serious. To begin with the actual reaction, setting the desired reaction temperature was a challenge in itself. The control unit box which was hand made some year ago had troubles in correcting the actual temperatures to the desired one. This issue deprived a lot of time since a minimum of half an hour was needed to achieve the desired temperature point. At some instances temperature dropped even during the actual reactions and even if this was rapidly corrected there is no security that these occurrences did not alter the results.

Another large error source could possibly be the flow meter that was used to measure the outlet flow of the gases that exited the reactor. This apparatus gave at some points measured values that were higher than the inlet flow to the reactor, which could depend on ethylene splitting to methane but this is uncertain. At some points, measuring button was pressed up to 5 times to get a reasonable value. But even these values cannot be taken for granted as accurate due to the unpredictable behaviour of the flow meter. The fact that these measurements were used throughout the whole results sections of the report is putting a dose of uncertainty to the actual conclusions of this work.

The most serious limitation in this report has undoubtedly been the lack of analysing methods to distinguish the amounts of coke and liquid products separately. Therefore, yields and calculated selectivity for these two different products are given as one figure instead of two separate. This lack of proper analysis has also limited the formation of more deep and concrete conclusions and recommendation.

The calibration curve method for determination of boiling temperatures of the products had also its limitations. This curve is designed and adapted to the pure saturated alkanes and there is not any proof or indication that only these are produced during the course of the reactions.

Flow regulators that are used to feed the desired amount of gas mix to the reactor showed a tendency to fluctuate in their performance. This could also possibly contribute to the aforementioned errors regarding the flow measurements.

Finally, the contribution of the human error factor to the limitations and error cannot be excluded. To remind, the gas samples were taken manually and there is no guarantee that these samples that were injected into the gas chromatography did not contain surrounding air which could easily have been drawn in into the syringe by a mistake. Transferring of the non-polar phase to the chromatography sample tube was also performed manually and the risk of impurities in the sample tube is always present.

6.3 Future work

During this master thesis a lot of challenges have been encountered and solved with a mix of knowledge, intuition and creativity. However this rapport isn't the final destination or the final product of the investigation. Several modifications are possible to improve this alternative direct synthesis route of fuel from ethanol as starting material. It requires patient, time and of course financial needs to advance further.

The following ideas for improvement to take into the future work are listed:

- Implementing pressure to the process. The oligomerization reaction is favoured by pressure and from several articles (see literature review) it's shown how longer hydrocarbon chains are synthesized by having pressure between 10-30 bars. But since the reactions in this study are carried out in atmospheric pressure it is reasonable to elevate the pressure. For instance by starting to apply 5-10 bars in the early stages and make an evaluation to see if it is benefiting.

- To repeat the reactions at the same temperature interval as in this study, but with a lower total inlet flow. In this investigation only one reaction was performed with lower inlet flow. The results were very promising. Lowering the inlet flow elevates the residence time, reactants have then longer time to detain in the packed bed and react.

- Optimization of the reactor design to ensure optional conditions for oligomerization. As previously mentioned it is important to maintain suitable reaction temperature but at the same time lead off the excess heat produced by exothermic reaction. This favours the reaction thermodynamically by preventing the shifting towards the reactants.

- The importance of improving both the quantity and quality analysis for the product sample. This means using internal standards precisely identifying the concentration of the compounds produced. One additional qualitative analysing method besides the present calibration curve is essentially needed to determine exactly which compounds are produced.

- Renewing some of the measurement equipment to gain both reliable and accurate results.

- Explore more temperatures for the ethanol experiments since only two temperatures are tested in this thesis. Just to get a wider view of the reaction outcome.

- Measure the volume of the liquid attained from the ethanol experiments. Separate and analyse the polar phase from the bubble flask, determine its composition with liquid chromatography in order to calculate conversion, yield and selectivity.

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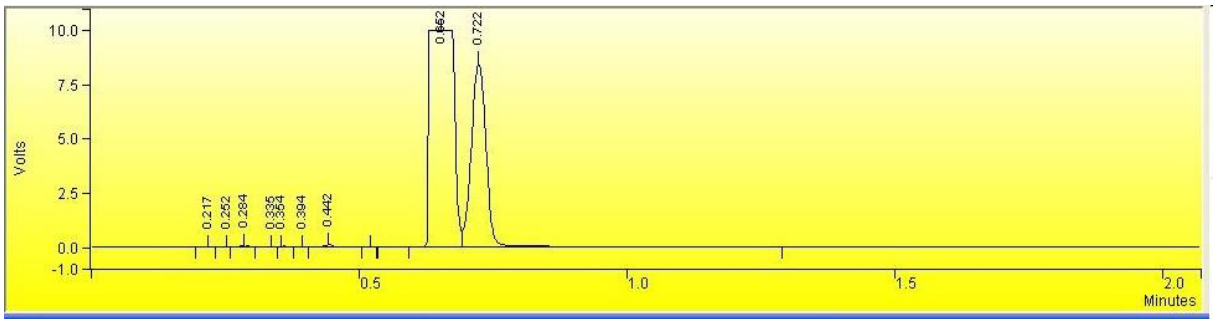
8. Appendices

8.1 Appendix A – Chromatograms

In appendix A, two chromatogram examples are shown. One shows how the analysis of gas samples looked like and the other how corresponding results for liquid analysis were.



Channel Middle = FID - Results

Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		0.0031	0.217	0.000	1491	BV	0.3	
2		0.0022	0.252	0.000	1039	VV	0.2	
3		0.0217	0.284	0.000	10347	VV	1.4	
4		0.0213	0.335	0.000	10189	VV	0.8	
5		0.0144	0.354	0.000	6878	VV	1.1	
6		0.0038	0.394	0.000	1838	VV	0.4	
7		0.1485	0.442	0.000	70922	VP	0.9	
8		66.3619	0.652	0.000	31690484	BV	3.1	
9		33.4231	0.722	0.000	15960863	VB	1.8	
	Totals:	100.0000		0.000	47754051			

Figure 11. A chromatogram from the gas analysis, analysing the outcome from reaction performed at 250°C and with 30% reduced inlet flow.

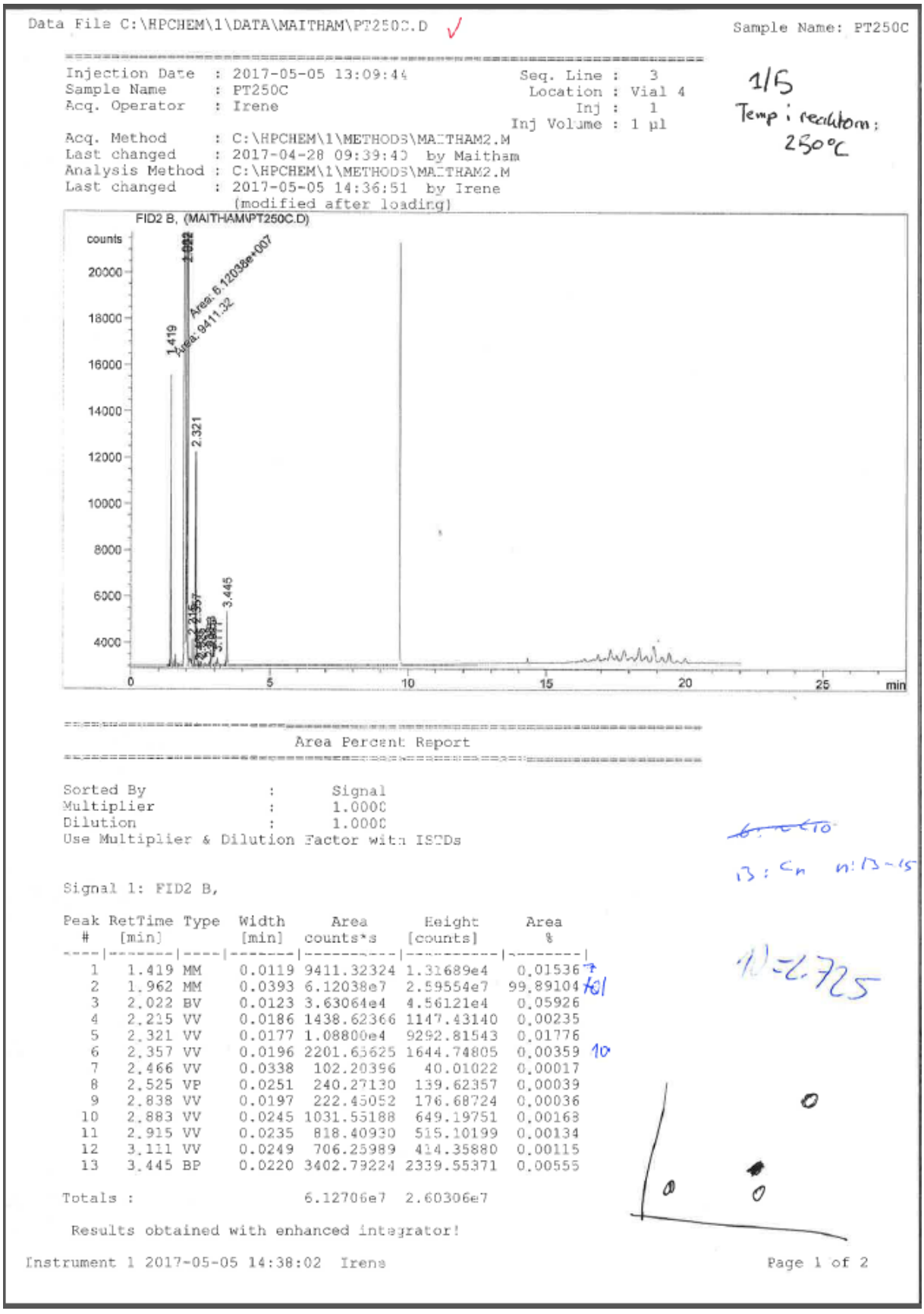


Figure 12. The analysis from a liquid sample. These products are the outcome from a reaction performed at 250°C and with 30 % lover reduced inlet flow.

8.2 Appendix B – Calculations

All the results are based on the chromatograms. This appendix is a template of how the calculations are carried out.

Products in gas state (ml/min) are calculated by following expression:

P_{gas} = (Total outlet flow – N_2)* area percentage of selected peak

where the total outlet flow represents the flow out from the plug flow reactor, the N_2 is the inert gas which does not accumulate in the reactor. The area percentage of selected peak is the size of the desired peak in the chromatograms for the gases.

Products in liquid and coke state (ml/min) are calculated by following expression:

P_{liquid} = Input flow – Total outlet flow

where the input flow is the inlet flow to the plug flow reactor and the total outlet flow is the flow out from the reactor.

The yields for all the different conditions are calculated by following expression:

$Y_i = P_i$ / Inlet flow of ethylene

where P_i stands either for the products in gas state or products in liquid state and the inlet flow of ethylene is the total amount of C_2H_4 entering the reactor.

Conversion is calculated by dividing the sum of all the products produced with the initial flow of C_2H_4.

Lastly the selectivity is carried out by dividing the products yield with the conversion:

$S_i = Y_i/X_E$

where the index i stands for particular product type.