Fuel and Chemicals from Renewable Alcohols
Part 1+2

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Publication date: 2008

Document Version
Publisher's PDF, also known as Version of record

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Ph. D. Thesis
DTU, Department of Chemistry, Kgs. Lyngby
September 2008
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Fuel and Chemicals from Renewable Alcohols


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Preface

The present thesis is submitted in fulfillment of the requirements for the Ph. D. degree at the Technical University of Denmark. The work has been carried out in Center for Sustainable and Green Chemistry (CSG) at the Department of Chemistry from September 2005 to August 2008 under supervision of Prof. Claus Hviid Christensen. The Ph. D. scholarship was funded by The Danish National Research Foundation. The thesis contains in the appendix eight relevant papers published in international peer-reviewed journals. Additional manuscripts to which I have contributed are also listed in the appendix.

The initial objective of this study was focused on the production of hydrogen from renewable resources for a future hydrogen society. In relation to this topic the catalytic production of hydrogen from bioethanol by steam reforming process was investigated. However, the study of bioethanol brought many interesting perspectives regarding the production of different renewable chemicals from bioethanol, and the scope of the thesis was shifted toward aiming at producing value-added chemicals by catalytic reactions of renewable alcohols.

First of all I would like to thank all my great colleagues for a pleasant and enjoyable time at CSG. I would also like to thank my colleagues for all the time spent on sharing laboratory experiences. I would like to thank and give my respect to the two professors who guided me through these three years. Claus H. Christensen and James A. Dumesic have both been very inspiring, and I have learned a lot about science and life from the time in their company. Finally I would like to thank Rasmus Fehrmann for taking care of all the practical issues in the finalization of my Ph. D. after Prof. Christensen has left CSG.

Kgs. Lyngby, September 2008

Jeppe Rass-Hansen
Abstract

The present work entitled *Fuel and Chemicals from Renewable Alcohols* covers the idea of developing routes for producing sustainable fuel and chemicals from biomass resources. Some renewable alcohols are already readily available from biomass in significant amounts and thus the potential for these renewable alcohols, together with other primary renewable building blocks, has been highlighted in the introductory chapter.

While the first chapter covers the general potential of a renewable chemical industry, the other chapters deal with particular possibilities. It is shown how ethanol and glycerol can be converted into hydrogen by steam reforming over nickel or ruthenium based catalysts. This process could be important in a future hydrogen society, where hydrogen can be utilized in high efficiency fuel cells. Hydrogen produced from biofeedstocks can also be used directly in the chemical industry, where it can compete with hydrogen production from natural gas. Similar substitution possibilities are emerging in the case of conversion of renewable alcohols to synthesis gas, which is used for instance in the manufacture of methanol and synthetic fuel. Here it is illustrated how glycerol can be converted directly to diesel fuel in a one pot reaction consisting of: conversion of glycerol to synthesis gas over a Pt-Re/C catalyst followed by conversion of the produced synthesis gas to liquid hydrocarbons by Fischer-Tropsch synthesis using a Ru/TiO$_2$ catalyst.

Oxidation of aqueous solutions of ethanol over gold catalysts with air as oxidant yields acetic acid selectively. This process is perhaps one of the most promising ways of utilizing cheap renewable alcohol to produce high value chemicals. Moreover, the process will most likely be able to compete economically with existing process routes to acetic acid, and it is significantly more environmentally friendly.

A final type of reactions examined in this thesis is the dehydration of different renewable alcohols over solid acid catalysts to yield olefins or aromatic compounds. It is
shown that ethanol can be dehydrated into ethylene with high selectivity at temperatures below 200 °C. This reaction also seems to have potential for competing with the present non-catalytic production of ethylene from steam cracking of naphtha carried out at temperatures around 800 °C. The price of ethylene is about twice that of fuel grade bioethanol, and this reaction is another example of a possible production of value-added chemicals from renewable resources. High temperature dehydration of methanol and ethanol results in a range of different hydrocarbons, which can be used either as gasoline fuel or, by altering process conditions, as a way to produce important olefin products which can be used in the manufacture of plastics etc.
Dansk resumé

Foreliggende afhandling med titlen *Brændstof og kemikalier fra fornybare alkoholer* omhandler idéen om at udvikle måder, hvorpå biomasseresurser kan omdannes til brændstof eller kemikalier på bæredygtig vis. Visse fornybare alkoholer udvundet fra biomasse findes allerede i dag i betydelige mængder, hvorfor potentialet i disse fornybare alkoholer og andre primære fornybare byggesten er fremhævet i introduktionskapitlet.


Eddikesyre kan dannes med høj selektivitet ved oxidation af vandige opløsninger af ethanol over en guld katalysator med luft som oxidationsmiddel. Denne proces er måske en af de mest lovende for udnyttelse af billige fornybare alkoholer til produktion af kemikalier med en øget værdi. Desuden vil processen sandsynligvis kunne konkurrere økonomisk med den nuværende produktion af eddikesyre, samtidig med at den er betydeligt mere miljøvenlig.
En sidste type af reaktioner, som er undersøgt i denne afhandling, er dehydrering af forskellige alkoholer til olefiner eller aromatiske forbindelser over katalysatorer bestående af faste syrer. Det vises, hvordan ethanol kan dehydreres til ethylen med en meget høj selektivitet ved temperaturer under 200 °C. Denne reaktion ser også ud til at have potentielle til at konkurrere med den nuværende ikke-katalytiske produktion af ethylen ved steam cracking af naphtha, som udføres ved temperaturer omkring 800 °C. Prisen for ethylen er omkring dobbelt så høj som brændstof ethanol, reaktionen er dermed endnu et eksempel på at der kan skabes merværdi af et kemikalie produceret fra fornybare resurser. Ved dehydrering af methanol og ethanol ved høje temperaturer dannes en række forskellige kulbrinter, der kan anvendes som benzin-brændstof eller - ved at ændre på reaktionsbetingelserne - som en måde til at producere de vigtige olefiner, der blandt andet anvendes til produktion af plastic.
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1 Renewable chemical industry

1.1 Introduction

1.1.1 Energy demand

Before the discovery of crude oil in the 19th century the global energy demand was covered almost entirely by the use of biomass. With the discovery of crude oil, inexpensive fossil fuel and chemicals were developed and the industrialization accelerated. More than 100 years with a society based on fossil resources and chemicals have set its marks on the society and environment. The use of fossil resources has led to an incredible progress and development of the industrialized world with an enormous impact on living standards and human health. However, with these progressing steps came also a continuously increasing demand of energy, a demand that is even more pronounced in recent years with the economic booms seen particularly in Asia. Actually, the world energy demand is expected to rise with more than 50% by 2025 with most of this demand emerging from these rapidly developing nations. ¹

One of society’s major challenges today is to eliminate poverty. But, raising living standards for people in the third world and in developing countries like India and China will result in an increased demand for energy. Along with the projected industrialization of the non-industrialized world the population is also increasing in these parts of the world and is expected to reach more than 9 billion people in year 2050, cf. Figure 1-1, a four time increase compared to the 1950 level. The increasing world population and hopefully success in decreasing poverty, are both leading to the same conclusion – the world demand for energy will keep growing.
1.1.2 Oil depletion

The world oil reservoirs are, beyond any doubt, at present depleting with a high rate resulting in a foreseeable end of our society as it is today; primarily built on oil resources. It is, however, difficult to predict the exact time for depletion, but the most likely scenarios proclaim that the global oil production will peak between 2020 and 2040.²

As a consequence of the predicted lack of crude oil available there have in recent years been a dramatically rise in the cost of crude oil, *cf.* Figure 1-2, with prices for a barrel of oil as high as 140 US$. 

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The oil price is closely related to the economic growth. Very simplistically it could be said that when the cost of fuel and chemicals rises dramatically in a short time frame, as seen in recent years, a resulting increase in the price of almost any product is expected as well. This will again give less purchasing power for customers and lead to economic stagnation. There are naturally a lot of other factors that influence the economic situation, but the price of fuel and chemicals, which is directly correlated to the crude oil price, definitely has significant importance. For the same reasons there have been growing governmental concerns about the oil depletion and a very important message and goal from different governments has been to obtain security in fuel and energy supply.

One of the ways to gain security in supply has been to expand the uses of biomass utilization. In particular the fermentation of biomass to bioethanol, for substituting some gasoline, has become an important industry. Other possibilities lie in the use of different renewable resources like wind and solar power, though the easiest way to substitute oil probably lies in the non-renewable but rather abundant coal resources available. However, a change from oil to coal means increasing CO$_2$ emissions to the atmosphere.

Figure 1-2 Crude oil price history during the last 30 years. Data from Energy Information Administration (EIA).
1.1.3 The CO₂ issue

The increasing world population and its demands for energy, fuel and chemicals have resulted in a fast depletion of the available fossil resources. At the same time it is argued that the use of these resources has resulted in increasing levels of CO₂ in the atmosphere, which are possibly leading to an increased global warming.

![Figure 1-3]( Temperatur e and CO₂ concentration in the atmosphere over the past 400,000 years. Data received by analyzing the Vostok ice core in Antarctica. )

Figure 1-3 illustrates the trend between temperature and CO₂ concentration in the atmosphere during the last four hundred thousand years. The data source is from the Vostok ice core in Antarctica. From the figure it seems very likely that there is a correlation between the CO₂ concentration in the atmosphere and the temperature. Nevertheless, the alarming thing is that these data scale from prehistoric time to the beginning of industrialization, since then the atmospheric concentration of CO₂ has
increased from around 280 ppm to 385 ppm in 2008. This level of \( \text{CO}_2 \) is far beyond any earlier measured value, and if the trend in Figure 1-3 with an intimate correlation between temperature and carbon dioxide is true, an increased global warming must be expected.

Under these assumptions it seems like a step in the wrong direction to increase the use of coal to generate energy, fuel and chemicals. It is most likely, though, that it is exactly what will happen. A possible use of coal in a more environmental way could be to capture the released carbon dioxide. Various types of carbon sequestration can be imagined; among many others are physical absorbance in large underground caves or in deep oceans or chemically absorbance as carbonates.

One of the most efficient ways to utilize fossil (and biomass) resources for energy today is the combined heat and power plants (CHP) wherein up to around 95 \% fuel efficiency can be achieved. A typical coal fired power plant has, on the other hand, an electrical efficiency of around 40 \% and produces 1000 g of \( \text{CO}_2 \) per kWh. This carbon release can be lowered to less than 700 g of \( \text{CO}_2 \) per kWh by using the newest technological improvements whereby also the electrical efficiency can be increased to about 50 \%. With the use of both CHP and carbon sequestration coal firing could actually be a very good midterm solution to solve our energy needs. However, in the long term a more sustainable way to generate energy is needed, which is possible through the use of renewable resources. In particular solar, water and wind power seem to be interesting alternatives to generate electricity, whereas biomass has the potential of substituting fossil resources in the chemical industry.

1.2 Routes to a renewable chemical industry

Around 3-5 \% of a barrel of crude oil is on average used as chemical feedstock. An equal amount is used in the conversion of this oil for the production of the many industrial chemicals that our society relies so deeply on. There are several reasons to focus on producing chemicals rather than fuel from biomass. Generally these chemicals are significantly more valuable than transportation fuels and it will therefore be easier to
compete with fossil chemicals than fuel. Important is also that most chemicals contain carbon, and the only renewable carbonaceous feedstock is biomass. Fuel on the other hand could be non-carbonaceous like electricity for battery driven cars or hydrogen for fuel cells. Finally, the production of chemicals from crude oil often requires so much energy that the simultaneous production of CO$_2$ exceeds the actual amount of the chemical produced. These chemicals can instead be produced in a fully renewable way from CO$_2$ neutral biomass resulting in the utmost reduction in CO$_2$.

One economic incentive to start using biomass as a feedstock for chemicals instead of crude oil is illustrated in Figure 1-4, wherein the historical corn to oil price ratio is plotted during the last 60 years. From the figure it is seen that in recent years this ratio has been historically low indicating that the use of technologies for converting biomass into chemicals at present time would be more competitive to fossil chemicals than ever before.

![Graph: Historical corn/oil price ratio](image)

**Figure 1-4** Historical corn/oil price ratio based on weight/weight with 15 % moisture in the corn. The numbers are averaged over a 3 year period. The changes in the corn/oil price ratio during the last 60 years show how biomass (corn) has become relatively cheaper and by that economically more interesting as an alternative to oil for the chemical industry.
1.2.1 Value chains

To illustrate the value of different chemicals produced from fossil resources compared to the actual feedstock, a fossil value chain was prepared. The value chain is shown in Figure 1-5. In the value chain the three important fossil resources; coal, crude oil and natural gas are marked in red. It is seen that some of the simplest molecules like hydrogen from steam reforming of natural gas or methanol from carbonylation of synthesis gas (available either from reforming of natural gas or from coal gasification) can be derived quite cheaply from these feedstocks. Also gasoline and diesel fuel are relatively cheap products which by simple, efficient and inexpensive steps are available from crude oil. On the other hand, the primary chemicals from which most other chemicals are produced (ethylene, propylene, benzene etc.) are profoundly more expensive. Relative to these primary chemicals come all the commodity chemicals which have an increasing value and therefore are found even further out to the right in the value chain. The value chain is based on actual prices relative to each other and it is primarily the production costs involved in the different chemical transformations that decide the position of a chemical.

Figure 1-5  The fossil and renewable value chains indicate the values of different commodity chemicals relative to the feedstock. A direct comparison between the two chains depends on the actual cost of the feedstocks.
In the same way a renewable value chain can be imagined, where the most important chemicals are produced from biomass possibly via primary renewable building blocks like glucose, ethanol and glycerol. This scenario is also illustrated in Figure 1-5. On the fossil value chain the relative prices can be expected to be fairly accurate, but this is not necessarily the case for the renewable value chain. First of all large differences in the biomass composition must be expected from different feeds and qualities around the world. Secondly most of the processes for converting biomass into large scale chemicals are only on lab scale or perhaps not invented at all. This of course means that significant improvements are foreseeable in optimizing the processes. The relative values in the renewable value chain are rough estimates for expected prices for some significant renewable building blocks which are on, or are on the way to the market.

The illustrations of the two value chains are mainly qualitative since a number of factors influence the position of the different chemicals. Particular important is the origin of the coal, crude oil and biomass, whose composition differs from region to region and for biomass it differs widely with the type of biomass. The purity of the feedstock is equally important and has a tremendous impact on the price, which again decides the two value chains relative to each other. Importantly, as long as the price ratio of biomass to crude oil declines, closely related to the availability of crude oil, and improvements in biomass transformations are seen, the use of new biomass resources for producing chemicals are developed in a continuously more competing way to that of the fossil routes. In that way the goal of adding value to biomass feeds is achievable.\textsuperscript{7,8}

\subsection{Contemporary chemical industry}

The carbonaceous chemical industry today is, as illustrated in Figure 1-6, primarily based on seven important chemicals derived from fossil resources. From these seven chemicals almost all other commodity chemicals are produced.\textsuperscript{7,9} To give a few examples; benzene is used to produce styrene and adipic acid, which again is used for the manufacture of polystyrene and nylon 6,6, both important co-polymers with the latter for instance used for producing Kevlar\textsuperscript{®}. Terephthalic acid is produced from xylene and used in the co-polymerization with ethylene glycol, available from ethylene, to produce PET (poly
Renewable chemical industry

ethylene terephthalate) plastics, which among many other uses is found in almost every drinking plastic bottle. Ethylene, propylene and butadiene are also used as monomers in the production of various rubbers and plastics most often in combination with other monomers; for example, styrene butadiene rubber which is used for the manufacture of auto tires. Toluene is an important organic solvent but is mainly used for foam polyurethanes, which can be found all over where a foam material is needed. Finally, methanol is mainly used to make formaldehyde and from there plastics, paints, explosives, etc. It is also used for the production of acetic acid, as fuel for internal combustion engines, and as an important laboratory chemical and solvent.

![Diagram of chemical compounds]

**Figure 1-6** The seven primary building blocks in contemporary chemical industry - almost entirely based on fossil resources.

The fossil chemical industry has been developed and optimized through the last 100 years. Most of the processes are therefore very efficient, which makes it rather difficult to compete with for new and sustainable chemicals production. However, one of the important issues in the current chemical industry is to introduce functionality into the chemicals. Biomass derived building blocks, on the other hand, are usually highly functionalized and could therefore be advantageous to the fossil building blocks in producing chemicals with particular oxygen functionalities.
1.2.3 Strategies for a renewable chemical industry

Turning the chemical industry into one based on renewable chemicals requires a whole new set of chemical reactions. Where many of the traditional reactions in the fossil chemical industry are about inserting functionality into a hydrocarbon, the opposite is often the case in the renewable chemical industry where highly functionalized carbohydrates are defunctionalized. Two strategies could be imagined for the conversion of biomass resources into valuable chemicals; one where biomass is converted to the same chemicals as known for the existing fossil chemical industry and one where it is converted to a whole new set of chemical species, which can substitute the previously used chemicals. In Figure 1-7 these two strategies are illustrated with some highlighted examples.

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**Figure 1-7** Biomass Chemicals. Two strategies for producing commodity chemicals from biomass. The grayish hatched area shows some of the most important commodity chemicals produced from fossil resources. In strategy 1 these same chemicals are produced from renewable building blocks. Strategy 2 covers the idea of producing “new” chemicals which potentially can substitute some of the “old” ones. Together strategy 1 and 2 cover the shaded green area.
To explain the idea behind the two strategies carefully a pedagogical illustration is shown in Figure 1-7. The grey area describes the fossil chemical industry as it is built up today. The three main resources are oil, natural gas and coal. These are transformed into the previously mentioned seven important chemicals, which together with synthesis gas are denoted the primary fossil building blocks. From these building blocks the remaining commodity chemicals are produced in one or several steps, with only a few examples listed in the figure. To the right in the figure a comparable situation is illustrated with different renewable resources all covered in the green shaded area. Biomass (carbohydrates, lipids, oils, lignin, etc.) can be converted directly into some primary renewable building blocks where ethanol, glycerol, xylose, fructose, glucose and bio-syngas probably could be the most important ones. From these primary renewable building blocks all the same chemicals known from the fossil chemical industry can be produced in one or multiple steps. This scenario covers the first strategy and is noticed in Figure 1-7 where the green and the grayish shaded areas are overlapping. The second strategy covers the idea of finding new chemicals, which potentially can substitute some of the existing chemicals. This scenario is illustrated at the bottom right of the figure.

To illustrate the concept in Figure 1-7 with a few examples, it could be interesting to look at the synthesis of acrolein. Acrolein is produced by oxidation of propylene (Figure 1-8) but it is usually immediately reacted further into acrylic acid and its esters due to the toxicity and unstable nature of acrolein. It could also be produced directly by dehydration of glycerol (Figure 1-8), one of the primary renewable building blocks. Recently it has been reported that the heterogeneous glycerol dehydration over solid acid catalysts gives acrolein in high yields in continuous processes,\textsuperscript{12,13} an example in agreement with the first strategy for a renewable chemical industry.
The second approach towards a renewable chemical industry can be exemplified with the production of lactic acid and its polymer PLA (poly lactic acid). This example is particularly interesting because PLA has already entered the marked as potential substitute to polymers like PET (poly ethylene terephthalate) and PS (poly styrene). Importantly PLA has the advantage over the conventional polymers that it is completely biodegradable and compostable and the degradation products are easily absorbed in the biological systems. Lactic acid is produced from bacterial fermentation of starch and sugars and PLA mainly from polymerization of its cyclic dimer lactide.

A conversion of the chemical industry into one based on renewables differs widely between the two strategies. The first strategy will by far be the easiest to pursue since many of the chemicals, industrial plants and processes are the same. The only important new processes are the conversion of biomass either directly or through the primary renewable building blocks into the well known petrochemical industry. The second strategy will be more innovative and visionary, and it will be significantly more challenging for chemicals following this strategy to enter the market. First of all the manufacture of these chemicals will have to compete with existing and optimized processes, but also the industries that are using the chemicals might have to change their procedures to substitute the petrochemicals used today. Thus implementation of new chemicals in the society will be challenging but possibly also the most sustainable way of using bioresources available.
For a more comprehensive discussion of the renewable chemical industry some interesting reviews on the area have been published by Lipinsky\textsuperscript{9}, Corma \textit{et al.}\textsuperscript{14}, Eisen \textit{et al.}\textsuperscript{15}, Elliott \textit{et al.}\textsuperscript{16}, Dumesic \textit{et al.}\textsuperscript{17} and Christensen \textit{et al.}\textsuperscript{18} and a schematic presentation of a somewhat more detailed and reaction orientated renewable chemical industry is shown in Figure 1-9.

1.2.4 \textit{C-factors}

A way to illustrate a chemical process’ impact on the surroundings is the E-factor or environmental factor first introduced by Sheldon\textsuperscript{19,20} The E-factor describes how much waste an overall process produces per amount of product (equation 1.1). Table 1-1 shows the typical E-factor for production of various chemicals, in general the most efficient are also the ones produced in the largest amounts.

<table>
<thead>
<tr>
<th>Industry segment</th>
<th>Product tonnage</th>
<th>E Factor (kg waste/kg product)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil Refining</td>
<td>$10^6$-$10^8$</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Bulk chemicals</td>
<td>$10^6$-$10^6$</td>
<td>&lt;1-5</td>
</tr>
<tr>
<td>Fine chemicals</td>
<td>$10^2$-$10^4$</td>
<td>5-50</td>
</tr>
<tr>
<td>Pharmaceuticals</td>
<td>$10$-$10^3$</td>
<td>25-100</td>
</tr>
</tbody>
</table>

In a similar fashion it can be interesting to look at the C-factor (equation 1.2) or climate factor indicating how much CO\textsubscript{2} a given process produces\textsuperscript{11}. By comparing the C-factor for different reactions it is possible to point out which process will lead to the most substantial CO\textsubscript{2}-reduction upon substitution with a renewable feedstock.

\[
E_{factor} = \frac{m_{\text{waste}}}{m_{\text{product}}} \quad (1.1)
\]

\[
C_{factor} = \frac{m_{\text{CO}_2}}{m_{\text{product}}} \quad (1.2)
\]

In the following chapters these C-factors will be used to examine the climate influence by exchanging different fossil chemicals with potential renewable ones.
Primary Renewable Building Blocks

Synthesis gas (H₂, CO, CO₂, CH₄)

Fischer-Tropsch products

Methane
Ethanol
Glycerol
Xylose
Fructose
Glucose

Ethyl acetate
Acetic acid
Dihydroxyacetone
Glycerol
Butadiene
Malonic acid
3,4-Dihydro-2H-pyran
Tetrahydrofuran
Methyl acrylate
Acrolein
Lactic acid
Methyl furoate
2-Methyl furan
Malonic acid
1,3-Propanediol
Tetrahydrofurfuryl alcohol
1,2-Propanediol
Tetrahydrofurane

Commodity Chemicals

C1 C2 C3 C4 C5 C6

Glycric acid
Tartronic acid
Pyruvic acid
Hydroxyypyruvic acid
Malonic acid
Methyl fumarate
Butyrolactone
Methyl 3-hydroxypropionate
1,4-Butanediol
Tetrahydrofurfuryl alcohol
1,4-Pentanediol
2-Methyl furan
1,4-pentanediol
2-Methyl tetrabutylfuran

Fermentation
Hydrogenation
Oxidation
Dehydration
Other
1.3 Fuel and chemicals from renewable alcohols

Today 80-90 % of all crude oil products are used as transportation or combustion fuels and about 13 % are used for non-fuel chemical production in the US. From all the previously mentioned reasons and the fact that most crude oil is used for fuel, a lot of effort has been put in trying to produce renewable liquid fuel. In particular bioethanol and biodiesel have received significant attention, though also bio-gas, -methanol, -DME (dimethyl ether), -MTBE (methyl tert butyl ether), -ETBE (ethyl tert butyl ether) -hydrogen and others have been investigated.

The particular interest in bioethanol and biodiesel has resulted in a relatively cheap industrial production of two renewable alcohols; namely ethanol and glycerol. In the following sections the possibilities with these two renewable alcohols will be highlighted and a couple of the possible applications will be thoroughly described in the remaining of the thesis.

1.3.1 Ethanol

1.3.1.1 Production

One of the oldest biological processes known to mankind is the fermentation of biomass into ethanol. The process has been known since prehistoric time for the production of alcoholic drinks but has lately gained growing importance due to the interest in producing fuel ethanol. Industrial production of fuel ethanol started in Brazil during the oil crisis in the 1970s, and has ever since been widely important there. The knowhow and achievements from Brazil have been used and further developed around the world. Today ethanol is produced from all sorts of biomass rich in sucrose, starch and cellulose. These are easily hydrolyzed by acids or enzymes to C\textsubscript{6} sugars (mainly glucose), which are fermented into ethanol and CO\textsubscript{2}. The largest producers of bioethanol are Brazil and the USA using sugarcane and corn respectively as feedstock. Mainly wheat crops and sugar beet have so far been used in Europe. The world production of fuel ethanol in 2007 was around 50 billion liters. The energy in this ethanol corresponds to less than 1.2 % of the total fuel consumption of 88.2 quadrillion Btu in 2005. In the USA (the largest
producer of bioethanol) the production of bioethanol has more than three doubled from 2002 to 2007.\textsuperscript{34} The most efficiently produced bioethanol is however made in Brazil from sugarcane, where the fossil energy used in the manufacture pays back around 10 times\textsuperscript{36} compared to only around 1.4 times from the maize ethanol in the USA.\textsuperscript{36,37}

The types of feedstock used today for production of bioethanol are primarily based on edible bio-resources, which can also find use as food for humans and animals. This has together with increasing food prices resulted in an almost religious debate about the ethics in using food for fuels.\textsuperscript{34,38,39} Furthermore it has also increased the interest in the next generation of bioethanol. Second generation bioethanol or cellulosic ethanol as it is also called is made from biomass like agricultural waste, straw and wood. These consist of large amounts of cellulose, hemicelluloses and lignin (termed lignicellulose) and much less starch and sugar compared to the feeds for first generation bioethanol. Due to the complex structures in which glucose is bound in lignocellulosic biomass more energy is required to release the glucose for fermentation.\textsuperscript{33}

In most places of the world, it will only be reasonable to produce bioethanol from non-food resources like household waste, straw, corn stover and wood. These resources are often considered to be waste materials and are thus significantly less valuable than edible ones. The use of such resources will not interfere with food production and importantly, it will also greatly reduce the greenhouse gas (GHG) emissions and feedstock costs from the ethanol production.\textsuperscript{28} In particular rice straw in Asia has a huge potential as lignocellulosic feed for second generation bioethanol production.\textsuperscript{40} These new improved technologies for biomass conversion use less non-renewable energy and give both a higher $\text{CO}_2$ reduction and a higher product yield than first-generation plants due to a higher utilization of the feedstock. Therefore, there is globally an intense research on developing this so-called second generation bioethanol. However, only a few companies have reached the point of demonstrating the process in a pilot plant.

In the second generation biorefinery, the highest $\text{CO}_2$ reduction is reached by co-producing other valuable products. In the Danish bioenergy concept this is achieved by co-producing methane and hydrogen.\textsuperscript{41} Another significant aspect is that abundant coal resources are the primary source of the non-renewable energy in conversion of biomass
into ethanol. In that way, a premium liquid transportation fuel is produced from a less valuable energy resource, which further reduces the need for import of petroleum.  

1.3.1.2 Uses

The large production of ethanol is almost entirely made for the use as fuel for internal combustion engines (ICE) where it is mixed with gasoline in up to 85 % ethanol.

Bioethanol can certainly have some positive influence on CO$_2$ emissions from the transportation sector, but it might prove possible to achieve an even better environmental effect by using it as a feedstock for the chemical industry. Finding effective catalytic reaction pathways for producing commodity or specialty chemicals from bioethanol rather than using it to substitute the least expensive fossil products, such as fuel, will most likely hold the greatest economic promise. Thus, the optimal use of bioethanol, in terms of efficiency, could well be to incorporate it into high-value materials otherwise produced from fossil resources.

Figure 1-10 illustrates a range of chemicals which could be produced from ethanol. The steam reforming to hydrogen is probably the area which has received the most attention, and the subject will be thoroughly examined in the following chapter. Other interesting possibilities could be found in oxidation to acetic acid, acetaldehyde and ethyl acetate or perhaps low temperature dehydration to diethyl ether and ethylene. Dehydration at high temperatures over solid acid catalysts yields aromatic compounds like benzene and ethylbenzene. Other reactions that could find interest are ethanol condensation to butanol or perhaps the conversion of ethanol to yield butadiene.

Ethanol seems to be particularly promising as a feedstock for other renewable chemicals, when distillation to fuel grade ethanol is not necessary. Even though the cost of distillation has come down recently it is still a major energy intensive process. Therefore the best economic prospects lie in the use of crude bioethanol or only light distilled bioethanol where most of the remaining sugars and enzyme leftover from the fermentation have been removed.
A new study suggests an annual increase of the world biofuel market of approximately 12.3 % from 2007 to 2017, and an annual production of bioethanol of more than 100 billion liters already in 2014. With this amount of bioethanol available, there is great promise in partly converting the chemical industry to one based on renewable resources. Instead of using bioethanol for transportation fuel purposes where it has a relatively low value, it could instead be used as feedstock for other important chemical products with a much higher value. Besides bioethanol use for hydrogen production by steam reforming or the direct use as a fuel or fuel additive, it could be utilized for producing acetaldehyde, ethylene, butadiene and acetic acid, among others. The annual amount of these chemicals produced worldwide is around 1.4, 120, 7.5 and 8.5 million metric tons (MT), respectively. A significant amount of these petrochemical products could thus be produced from renewable ethanol if efficient catalytic reaction pathways are developed. For this to be economically viable, the products produced from bioethanol must obviously be more valuable than the bioethanol itself. Moreover, it is necessary to keep the conversion processes as inexpensive as possible, but one advantage here is that distillation to fuel grade ethanol is usually not crucial.
1.3.2 Glycerol

1.3.2.1 Production

Glycerol, also known as 1,2,3-propanetriol or glycerin is synthetically produced from propylene. Far more important today is, however, the formation of glycerol from animal fats and vegetable oils. Glycerol is therefore already a good example of an original petrochemical, which has been almost completely transformed into a renewable chemical. Fats and oils consist of triglycerides from where formation of either glycerol and soap is achieved through saponification, glycerol and fatty acids by hydrolysis or glycerol and fatty acid methyl esters (FAME) by transesterification with methanol, cf. Figure 1-11

\[X-OH + Na \rightarrow \text{sodium carboxylate (soap)}\]
\[H = \text{free fatty acid}\]
\[CH_3 = \text{FAME (biodiesel)}\]

Glycerol has become a very interesting renewable chemical due to the growing production of biodiesel. Biodiesel consists of fatty acid methyl esters, which are formed by transesterification of animal fats or vegetable oil with methanol according to Figure 1-11. Glycerol is a byproduct in this process and about 100 kg of glycerol is formed per ton of biodiesel. The largest production of Biodiesel is currently in the EU, where around 6 million MT were produced in 2006 with an expected growth to 12 million MT in 2010. Also for biodiesel there exist first and second generation, where first generation for instance can be rapeseed oil, second generation refers to the non-edible fats and oils like algae oil and waste fat from abattoirs and restaurants.
Another possible way to produce glycerol as a renewable chemical is by fermentation of carbohydrates, in a similar way to the fermentation processes leading to bioethanol. But, where bioethanol is only obtained in around 10 wt% aqueous solution then glycerol, from fermentation, yields about 25 wt%, which possibly decreases the need for consuming energy on distillation. A glycerol solution with 80-90 % purity is usually obtained from the transesterification process.

1.3.2.2 Uses
Glycerol has more than 2000 applications mainly in the food and cosmetics industry, though also used in significant amounts in pharmaceuticals, plastics and tobacco industry. Even though there are many applications of glycerol, there is today an oversupply resulting from the production of biodiesel, and it has been estimated that the production of glycerol would be six times higher than the demand in 2020.\textsuperscript{49} This also indicates that glycerol could possibly be a very inexpensive chemical, which opens up for a potential use for the manufacture of other commodity chemicals from glycerol.

Glycerol has received tremendous interest in literature and several reviews on adding value to glycerol by converting it into other products have recently been published.\textsuperscript{48,51} There are many possible chemicals which can be produced from glycerol and some of them are illustrated in Figure 1-12. Among these are hydrogenation to propanediols, oxidation to dihydroxy acetone or glyceric acid, dehydration to hydroxy acetone (acetol), acrolein or poly glycerols, reforming to hydrogen or synthesis gas and the formation of for instance glycerol carbonate and its esters or glycidol.
1.4 Conclusion

The very high CO₂ levels in the atmosphere at present time can be partly explained by the amounts of fossil energy and chemicals consumed in the industrialized world. In the 21st century the fast depletion of these fossil resources together with environmental concerns and concerns about security in energy supply will drive the society back towards a renewable energy, fuel and chemicals production. A central point is that all available resources, both fossil and renewable, are limited and it is essential that we carefully consider how each is used best. This is a future key challenge for chemical research and development.
2 Hydrogen

Hydrogen is very important in the manufacture of many large scale chemicals like ammonia (120 million MT/y) and methanol (30 million MT/y) as well as for hydrotreating in refineries.\textsuperscript{52} Hydrogen can be produced from almost any kind of feedstock as illustrated in Figure 2-1. Steam reforming of natural gas is the predominant way of producing hydrogen today but many alternatives have been examined, in particular electrochemical production of hydrogen from electrolysis of water. The optimal way for producing hydrogen in a renewable society would be by water electrolysis using wind-power, solar-power or other renewable alternatives for generating the necessary electricity.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2-1.png}
\caption{Possible ways to produce hydrogen from fossil and renewable resources.\textsuperscript{53}}
\end{figure}

2.1 Steam reforming of natural gas

Catalytic steam reforming (SR) is a process wherein typically hydrocarbons are reacted with steam at high temperatures over a catalyst. The main product is hydrogen. The industrially most important SR process today is the conversion of natural gas into...
hydrogen. The endothermic reaction is shown in equation 2.1, and a more general expression for the SR of hydrocarbons is shown in equation 2.2. The catalysts used for the SR processes are also active for the exothermic water gas shift reaction (WGS) shown in equation 2.3.

\[ \text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \quad (\Delta H^\circ = 206 \text{ kJ/mol}) \quad (2.1) \]

\[ C_n\text{H}_m + n\text{H}_2\text{O} \rightarrow n\text{CO} + (n + \frac{m}{2})\text{H}_2 \quad (\Delta H^\circ > 0) \quad (2.2) \]

\[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \quad (\Delta H^\circ = -41 \text{ kJ/mol}) \quad (2.3) \]

Industrial SR is performed over nickel-based catalysts at temperatures of around 800-950 °C and steam pressures of around 20 bar and results in a mixture of hydrogen, carbon dioxide and carbon monoxide called synthesis gas or syngas.\textsuperscript{52} For optimizing to hydrogen production the syngas is usually reacted further over a copper catalyst in a low temperature WGS reactor operated at 210-330 °C to convert almost all the CO.\textsuperscript{52}

An alternative way of producing hydrogen is to use a renewable feedstock. As shown in Figure 2-1 this can be done for example by electrolysis of water with wind or solar powered electricity or by gasification of biomass. But it could also be achieved through SR of the ethanol or glycerol produced from biomass fermentation and/or biodiesel waste, respectively.

### 2.2 Ethanol steam reforming

Today bioethanol is produced for the use as a fuel. Combustion of ethanol in an ICE has an efficiency of the fuel limited by the Carnot efficiency and can only reach around 25 %.\textsuperscript{54} This energy efficiency can theoretically be significantly increased, if ethanol is first converted to hydrogen and then used in a fuel cell stack with a likely energy efficiency of more than 50 %.\textsuperscript{54,55,56} Moreover, three mol of water (steam) is necessary for each mol of ethanol for the complete ethanol steam reforming (ESR) as shown in equation 2.4. It is therefore not needed to produce the highly pure and expensive fuel grade ethanol required for ICEs, where a distillation to 99.5 % is required. Instead an inexpensive flash
Distillation to remove sugars and enzyme leftovers in the fermentation broth will be sufficient.

\[ CH_3CH_2OH + 3H_2O \rightarrow 2CO_2 + 6H_2 \ (\Delta H^\circ = 174 \text{ kJ/mol}) \]  

(2.4)

Catalytic conversion of ethanol into hydrogen is an energy intensive reaction, but due to the higher efficiency of fuel cells compared to ICEs an overall increase in fuel efficiency could be envisioned. Figure 2-2 shows in an energy level diagram the idea and potential of using biohydrogen opposed to bioethanol for energy applications. Combustion of ethanol releases 1277 kJ/mol but more than 75% of this energy is just released to the atmosphere as heat when combusted in an ICE. With ESR 174 kJ/mol ethanol is used in converting ethanol and steam into CO\(_2\) and hydrogen. This hydrogen can then be utilized in a fuel cell, where it reacts with oxygen from the atmosphere and releases 1451 kJ/mol with less than 50% energy loss to the surroundings. Theoretically, the total efficiency could then be raised by about 70% with the given energy efficiencies, or even higher when considering distillation issues and use of waste heat.57

Figure 2-2 Energy level diagram comparing combustion of ethanol with transformation of ethanol to hydrogen and use in a fuel cell.

The catalytic SR of ethanol has in recent years been reviewed by several groups.58,59,60,61 The conversion of ethanol to hydrogen and CO/CO\(_2\) is possible with many different catalysts, but especially Rh and Ni catalysts have shown promising results.58,62,63,64,65
Fierro *et al.*[^62] found that Rh and Ru catalysts gave the highest hydrogen selectivity among different noble metals for oxidative SR. Moreover they found that addition of Cu to Ni catalysts enhanced the lifetime of the catalyst by lowering the coke depositions. Aupretre *et al.*[^63] showed that Ni and Rh catalysts were very active for non-oxidative SR, and later that especially a combination with Rh on a Ni$_{1-x}$Mg$_x$Al$_2$O$_4$ support gave very promising results[^64]. Frusteri *et al.*[^65] reported that Ni catalysts have the highest selectivity towards hydrogen and Rh catalysts to be almost as selective but far more resistant to carbon formations. In another paper[^66], they describe how doping a Ni catalyst with an alkali metal can improve the catalyst performance with regard to ethanol conversion. Furthermore, it was claimed that carbon formation is significantly lowered by using a basic support instead of an acidic support[^66]. Liguras *et al.*[^67] described how the acidity of the support influences the carbon formation on the catalyst, mainly because acidic supports lead to the formation of ethylene, which is known as a carbon forming species in SR reactions[^52,68].

A Ru and a Ni catalyst was prepared on a non-acidic support (MgAl$_2$O$_4$) and tested for the SR of ethanol. Moreover, nickel catalysts doped with small amounts of potassium and silver were prepared to analyze the effect of promoters on carbon formation rate at the catalyst surface.

### 2.2.1 Reaction mechanism

Steam reforming of ethanol is thought to proceed through two separate routes; either by dehydrogenation to acetaldehyde (2.5) or by dehydration forming ethylene (2.6).

\[
\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CHO} + \text{H}_2 \quad (\Delta H^\circ = 68 \text{ kJ/mol}) \tag{2.5}
\]

\[
\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O} \quad (\Delta H^\circ = 45 \text{ kJ/mol}) \tag{2.6}
\]

These two intermediates can then be decomposed and steam reformed to an equilibrium mixture of methane, carbon dioxide, carbon monoxide, hydrogen and water (2.7-2.9). Furthermore, ethylene is known to polymerize into pyrolytic coke on metal surfaces (2.10)[^52], and it is assumed that it is mostly ethylene that is responsible for the carbon formation on the catalyst in this reaction although other carbon-forming

[^62]: Fierro *et al.*[^62]
[^63]: Aupretre *et al.*[^63]
[^64]: Frusteri *et al.*[^64]
[^65]: Liguras *et al.*[^65]
reactions might also be important,\textsuperscript{52} cf. section 2.3. Equilibrium among the gasses is achieved through the methane SR reaction (2.1) and the water gas shift reaction (2.3). The suggested mechanism is also illustrated schematically in Figure 2-3.

\begin{align*}
CH_3CHO & \rightarrow CH_4 + CO \quad (\Delta H^\circ = -19 \text{ kJ/mol}) \quad (2.7) \\
CH_3CHO + H_2O & \rightarrow 3H_2 + 2CO \quad (\Delta H^\circ = 187 \text{ kJ/mol}) \quad (2.8) \\
C_2H_4 + 2H_2O & \rightarrow 4H_2 + 2CO \quad (\Delta H^\circ = 210 \text{ kJ/mol}) \quad (2.9) \\
C_2H_4 & \rightarrow \text{coke} \quad (2.10)
\end{align*}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig2-3}
\caption{Ethanol reaction pathways. Ethanol can be directly dehydrogenated to acetaldehyde or dehydrated to ethylene. Both of these species can in multiple steps be further converted to a syngas mixture, equilibrated by ordinary SR and WGS reactions.}
\end{figure}

\section*{2.3 Carbon study}

The most crucial concern in ESR is the deactivation of the catalyst due to carbon formation.\textsuperscript{58,69} Accordingly, cautious investigations of carbon formation on different nickel- and ruthenium-based catalysts were performed.

Carbon is formed through several well known reactions, but in particular ethylene is an important precursor for carbon formation\textsuperscript{58} as illustrated in Figure 2-3. Rostrup-Nielsen \textit{et al.}\textsuperscript{52,68} have previously described the different reaction paths for carbon formation and the types of carbon formed on the catalysts during the SR of hydrocarbons, as summarized in Table 2-1. From the table, it is clear that many different parameters influence the carbon formation. Some of the most important are temperature and steam/carbon ratio, but the catalytic metal, the support material, the exact process conditions, the surface structure of the catalytic metal, the presence of promoters, \textit{etc.}, are also central parameters for the formation of carbon on the catalysts.
Table 2-1  Carbon-forming reactions and the nature of the coke deposits.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>No.</th>
<th>Carbon type</th>
<th>Consequence</th>
<th>Critical Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2\text{CO} \rightarrow \text{C} + \text{CO}_2$</td>
<td>(2.11)</td>
<td></td>
<td></td>
<td>Low $\text{H}_2\text{O}/\text{C}$ ratio, high temperature, presence of olefins and aromatics</td>
</tr>
<tr>
<td>$\text{CO} + \text{H}_2 \rightarrow \text{C} + \text{H}_2\text{O}$</td>
<td>(2.12)</td>
<td>Whisker carbon</td>
<td>Break-up of catalyst pellets</td>
<td></td>
</tr>
<tr>
<td>$\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$</td>
<td>(2.13)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{C}_n\text{H}_m \rightarrow \text{nC} + \text{m/2H}_2$</td>
<td>(2.14)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{C}_n\text{H}_m \rightarrow$ olefins $\rightarrow$ coke</td>
<td>(2.15)</td>
<td>Pyrolytic coke</td>
<td>Encapsulation of catalyst pellet, deposits on tube wall</td>
<td>High temperature, residence time, presence of olefins</td>
</tr>
<tr>
<td>$\text{C}_n\text{H}_m \rightarrow (\text{CH}_2)_n \rightarrow$ gum</td>
<td>(2.16)</td>
<td>Gum</td>
<td>Blocking of metal surface</td>
<td>Low $\text{H}_2\text{O}/\text{C}$ ratio, low temperature, presence of olefins and aromatics, absence of $\text{H}_2$</td>
</tr>
</tbody>
</table>

An attempt to lower the carbon formation rate on the catalysts could be to promote them with another metal that blocks the step sites on the active metal, since these sites usually are the most reactive in the coke formation.\textsuperscript{70} It has been proved for a Ni catalyst doped with Ag that the silver blocks the step sites, whereby the catalytic bond breaking selectivity in for instance ethane hydrogenolysis could be somewhat controlled.\textsuperscript{71} For SR it could be envisaged that blocking of these sites on the nickel crystals would have a far more pronounced effect on the rate of coke formation than on the rate of reforming.\textsuperscript{52,62} Besenbacher \textit{et al.}\textsuperscript{72} designed a Au/Ni surface alloy catalyst for SR with gold blocking the most reactive sites. Hereby, a slightly less active but far more robust catalyst was achieved compared to an unpromoted nickel catalyst.\textsuperscript{72} Thus, in a similar manner nickel catalysts doped with silver and potassium were prepared. In addition to possible step-site blocking, potassium is also expected to increase the steam adsorption on the catalyst and thereby lower the formation of coke on the catalyst.\textsuperscript{68} A high steam pressure is known to decrease carbon formation,\textsuperscript{68} and therefore a high water to ethanol ratio should also decrease coking problems.

Another way of diminishing the carbon formation issue is doing a partial oxidation or an autothermal reforming.\textsuperscript{73} Due to the oxygen available less carbon is formed on the catalyst. Autothermal reforming also has the advantage that it is slightly exothermic but the drawback is that less hydrogen is formed from the reaction, \textit{cf.} equation 2.17.

$$\text{CH}_3\text{CH}_2\text{OH} + 2\text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \rightarrow 2\text{CO}_2 + 5\text{H}_2 \quad (\Delta H^\circ = -69 \text{ kJ/mol}) \quad (2.17)$$
2.3.1 Experimental

2.3.1.1 Catalyst synthesis
A 10 wt% Ni/MgAl$_2$O$_4$ and two similar catalysts promoted with 1 wt% K and 1 wt% Ag were prepared by the incipient wetness impregnation technique. An industrial high surface area spinel (MgAl$_2$O$_4$) with a pore volume of 427 mL/kg and a specific surface area of 72 m$^2$/g received from Haldor Topsøe A/S was used as support material. The spinel tablets were crushed to a size fraction of 300-710 µm and dried for 1 h at 100 °C. The solutions for the impregnations were prepared by dissolving the desired amount of the different metal compounds, as nitrate salts, in water under moderate heating. After impregnation, the catalysts were dried at 100 °C for 2 h and finally calcined at 500 °C for 4 h. A 2 wt% Ru/MgAl$_2$O$_4$ catalyst was prepared similarly from an aqueous solution of the ruthenium nitrosyl nitrate [Ru(NO)(NO$_3$)$_3$], leaving out the calcination step to prevent any formation of the volatile and hazardous RuO$_4$ as well as to avoid a decrease in reactivity of the catalyst due to metal sintering. The different catalysts investigated in this study are listed in Table 2-2.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>10 wt% Ni/MgAl$_2$O$_4$</td>
</tr>
<tr>
<td>Ag/Ni</td>
<td>1 wt% Ag - 10 wt% Ni/MgAl$_2$O$_4$</td>
</tr>
<tr>
<td>K/Ni</td>
<td>1 wt% K - 10 wt% Ni/MgAl$_2$O$_4$</td>
</tr>
<tr>
<td>Ru</td>
<td>2 wt% Ru/MgAl$_2$O$_4$</td>
</tr>
</tbody>
</table>

2.3.1.2 Catalyst characterization
All catalysts were characterized by BET (Brunauer, Emmett and Teller) surface area measurements and hydrogen pulse chemisorptions to determine the total surface area, metallic surface area, metal dispersion and metal particle size. The hydrogen pulse chemisorptions were made at 50 °C for the nickel-based catalysts and at 150 °C for the ruthenium catalyst. Before the actual pulse chemisorptions, the catalysts were reduced and activated in situ according to the catalytic experiments described in the next paragraph. After reduction, the catalyst was kept at the reduction temperature for 1 h in a nitrogen flow of 50 mL/min to remove adsorbed hydrogen.
2.3.1.3 Catalytic measurements

The experimental setup used in the catalytic investigation is schematically illustrated in Figure 2-4. Catalytic experiments were performed in a tubular fixed bed quartz reactor with an inner diameter of 6 mm. For each test, 200 mg of catalyst material was loaded into the reactor and secured by quartz wool. The reactor was placed in an electrically heated oven. Before each run, the loaded catalyst was reduced and activated by heating with a rate of 5 °C/min to 500 °C for 2 h in a gas flow of 100 mL/min of Formier gas (10 % hydrogen in nitrogen) (the Ru catalyst was reduced at 600 °C).

![Figure 2-4 Schematic drawing of the experimental setup for the catalytic measurements.](image)

SR experiments, at 400-600 °C, were conducted with an inert (He or N₂) gas flow of 80 mL/min and an ethanol/water liquid flow of 0.04 mL/min. The liquid was pumped by a Knauer K-120 HPLC pump and vaporized by heating tape at 150-200 °C. The ethanol/water solution was prepared to contain approximately 25 vol% ethanol, which gave a total molar gas flow ratio to the catalyst bed of ethanol-water-helium of about 1:10:20 corresponding to a GHSV (gas hourly space velocity) of 8 s⁻¹ or a WHSV (weight hourly space velocity) of 2.4 h⁻¹. An Agilent GC 6890N equipped with a CP Poraplot Q-HT capillary column to the FID detector and an advanced packed column system consisting of Porapak N column and a Molsieve column to the TCD detector was used for analyzing the reaction stream. Furthermore, a Rosemount BINOS 100 was continuously measuring the CO and CO₂ contents in the exit gas after condensation of any liquids in an ice bath.
2.3.1.4 Temperature programmed oxidation (TPO)

The experimental setup used for activity measurements (Figure 2-4) was also used for analyzing the amount of carbon formed on the catalysts during SR. The TPO experiments were carried out by heating the oven to 600 °C at 10 °C/min in a gas flow of 20 mL/min consisting of a mixture of 5 % oxygen in helium. By this method, the carbon deposits were completely oxidized to CO and CO$_2$, thus facilitating accurate measurements with the BINOS detector.

2.3.1.5 Transmission electron microscopy (TEM)

High resolution TEM images were obtained from selected catalysts after reaction in order to characterize the morphology and structure of the carbon deposits. The pictures were recorded with a Philips CM200 FEG transmission electron microscope operating with a primary electron energy of 200 kV and a point resolution of 1.9 Å. About thirty pictures were taken for each catalyst at varying magnifications to get reasonable trends about particle size distribution and carbon formations.

2.3.2 Results and discussion

2.3.2.1 Catalyst characterization experiments

The results from the BET physisorption experiments and hydrogen pulse chemisorption experiments are shown in Table 2-3.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET surface area (m$^2$/g)</th>
<th>Metal surface area (m$^2$/g metal)</th>
<th>Metal dispersion (%)</th>
<th>Metal particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>72</td>
<td>66</td>
<td>9.9</td>
<td>10</td>
</tr>
<tr>
<td>K/Ni</td>
<td>74</td>
<td>40</td>
<td>6.0</td>
<td>17</td>
</tr>
<tr>
<td>Ag/Ni</td>
<td>70</td>
<td>28</td>
<td>4.2</td>
<td>24</td>
</tr>
<tr>
<td>Ru</td>
<td>92</td>
<td>265</td>
<td>84</td>
<td>1.9</td>
</tr>
</tbody>
</table>

All the nickel based catalysts have a BET surface area similar to the support material of around 72 m$^2$/g. From the TEM images (cf. section 2.3.2.4) it is observed that all the nickel crystals have a particle diameter around 10 nm, which fits very well for hydrogen
pulse chemisorption experiments of the Ni catalyst but not the K/Ni and the Ag/Ni. This is possibly because the silver or potassium is partly covering the surface of the nickel particles. Also the K/Ni catalyst formed some very large particles (see paragraph 2.3.2.4), which should increase the mean particle size observed by $H_2$ chemisorption and decrease the metal dispersion. The ruthenium catalyst formed very small particles of around 2 nm. The large surface area of the Ru particles apparently also increased the BET surface area of the whole catalyst slightly.

2.3.2.2 Ethanol steam reforming experiments
Experiments performed under the chosen conditions (200 mg catalyst material, a molar mixture of ethanol/water/helium of 1:10:20, temperatures from 400-600 °C and a gas flow to the catalyst bed of 120 mL/min) all reached steady state after 10-15 minutes run time. At steady state the reactions were at equilibrium which always was the case during the first 6 hours run time. Hereafter carbon formation and following catalyst deactivation influenced the ethanol conversion and product distribution for some of the catalysts. Figure 2-5 shows the theoretical equilibrium composition, under the experimental conditions. At equilibrium the ethanol conversion is 100 %, and selectivities shown in Figure 2-5 are in complete agreement with the actual results for all the catalysts, as long as no deactivation was observed. Thereby the amount of hydrogen produced was simply a matter of the operating temperature. Water is being condensed out of the exit-gas on an ice bath before entering the BINOS, and has therefore been removed from the equilibrium calculations in Figure 2-5 to simulate the actual exit-gas composition entering the BINOS.

From the BINOS, which continuously measured the CO and CO$_2$ concentrations in the effluent gas, and the GC measurements a total carbon balance was achieved. Hydrogen was not measured directly, but knowing all other species from the reaction and calculating backwards gives a fairly accurate measurement of the amount of hydrogen – in particular when equilibrium is reached.
Significant amounts of carbon formations were detected on all the nickel based catalysts for the SR experiments performed at 400 °C. This was a contrast to the ruthenium catalyst, which barely had any carbon deposited. The signals from the BINOS for these experiments are shown in Figure 2-6. The deactivation patterns on the different catalysts are rather dissimilar in the timeframe of the experiment. The deactivation results in the appearance of unconverted ethanol in the effluent, and, which is probably more convenient to monitor, by a drop in the CO\textsubscript{2}-concentration and a rise in the CO-concentration. Figure 2-6 illustrates these patterns for the Ni-based catalysts. The Ag promoted Ni catalyst shows a rapid deactivation after ca. 7 h and the pure Ni catalyst deactivates less rapidly after ca. 10 h, whereas the K/Ni catalyst barely deactivates during the first 16 h run time. The Ru catalyst does not seem to deactivate at all. The indications of time for deactivation are only suitable for a fast comparison of the different nickel based catalysts. By this comparison it can already now be concluded that promotion of nickel with potassium extend the catalyst lifetime, whereas silver promotion apparently decreases the catalyst lifetime.
The combined analytical experiments show (for the silver promoted nickel catalyst) that the first thing that happens during deactivation is a decrease in the CO$_2$-concentration and a simultaneous increase in the CO-concentration. Thereafter the ethanol conversion starts decreasing and so does the production of methane whereas acetaldehyde and trace amounts of ethylene start to appear in the effluent gas stream, before all the products go toward zero. Since acetaldehyde is much more abundant than ethylene in the gas stream during the deactivation, it seems likely that the main reaction path for ethanol is through acetaldehyde. However, both reaction paths are possible and less ethylene is expected in the exit gas due to its higher affinity for coking the catalyst, cf. Figure 2-3.

Deactivation appears with a profile down through the catalyst bed as shown in Figure 2-7. At start of run the gas is equilibrated in the first part of the bed and this is also where the carbon is deposited. Along with carbon depositions formed on the catalyst
the equilibration part is shifted down the bed. This proceeds until all of the catalyst is partly covered with coke and equilibration of the gas stream therefore no longer is possible, or until the upstream part of the bed is totally clogged by carbon. At 600 °C all catalysts reached equilibrium and none of them seemed to deactivate. Even after 6 days run time there was no observed deactivation of the Ni/MgAl$_2$O$_4$ catalyst.

2.3.2.3 TPO experiments

The results of the TPO experiments performed on the used catalysts from the SR experiments illustrated in Figure 2-6 are given in Table 2-4. The TPO experiments show that there actually are less carbon deposits on the Ag/Ni catalyst than on the pure Ni catalyst even though the Ag/Ni catalyst deactivated faster. This might be explained by the rapid deactivation, when carbon is formed on the catalyst and less ethanol is converted, then less carbon will most likely be produced on the catalyst. It can, however, also be due to differences in the carbon formations on the two catalysts, cf. section 2.3.2.4. Table 2-4 also confirms the positive effect of promoting the catalyst with potassium, which only had about one third the amounts of carbon deposits compared to the pure nickel catalyst. But, as expected from Figure 2-6, the Ru catalyst was even more carbon resistant and less than 2 mg carbon was formed during the 16 h run.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>TPO (mg C)</th>
<th>TPO (mg C/h)</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>73.5</td>
<td>4.6</td>
<td>Deactivation</td>
</tr>
<tr>
<td>Ag/Ni</td>
<td>66.2</td>
<td>4.1</td>
<td>Rapid deactivation</td>
</tr>
<tr>
<td>K/Ni</td>
<td>26.9</td>
<td>1.7</td>
<td>Slow deactivation</td>
</tr>
<tr>
<td>Ru</td>
<td>1.70</td>
<td>0.1</td>
<td>No deactivation</td>
</tr>
</tbody>
</table>

**Figure 2-7** The carbon profile is moving down through the catalyst bed as deactivation occurs.
In Figure 2-8 the effect of the reaction temperature on the amount of carbon deposited on the catalysts is illustrated. There is a clear trend in the explored temperature interval that higher temperatures lead to less carbon deposits on all the catalysts. At 600 °C hardly any carbon was formed and no deactivation was observed on any of the catalysts even after running for a week. These results are somewhat surprising since methane decomposition on supported nickel catalysts usually leads to increasing carbon formation with increasing temperature.\textsuperscript{52} They are however in full agreement with other groups’ observations on ESR.\textsuperscript{75} The explanation of the lower amount of carbon deposits at high temperatures may lie in diffusion limitations at these temperatures. Since the ethanol conversion is very fast at the catalyst surface there might be an ethanol gradient toward the catalyst, and thereby diffusion limitations. This means that the ethanol concentration on the catalyst surface is always very low, and therefore the carbon formation rate will be low under such circumstances, too.

Figure 2-8 clearly illustrates the positive effect of promoting the nickel catalyst with potassium, as significantly fewer carbon deposits occur at all temperatures. Also the SR experiments showed that the K/Ni catalyst had a longer lifetime than the Ni catalyst. The silver promoted catalyst is not included in the diagram because the rapid deactivation gives incomparable results regarding hourly normalized carbon formation. The Ru catalyst was by far the best of the tested catalysts, especially at lower temperatures around 400 °C.
2.3.2.4 TEM experiments
Looking at the results from the TPO and SR experiments it could be logical to assume that the different deactivation patterns and carbon formation rates are the result of differences in carbon growth on various catalysts. To examine this hypothesis a couple of TEM experiments were performed on selected catalysts after SR runs. For each of the examined catalysts around thirty pictures were taken at various magnifications to achieve fair trends of the catalyst’s metal particle size and the carbon deposits. Examples of these pictures with the most interesting and illustrating observations are shown in Figure 2-9.

Figure 2-9d shows the pure Ni catalysts and the general observation is that the nickel particles are around 10 nm in diameter. A mixture of amorphous carbon, whisker carbon and gum was formed on all the nickel catalysts. Apparently, the gum formation is more predominant on the Ag/Ni catalyst than on any of the other catalysts where whisker carbon formation seems to dominate. According to Rostrup-Nielsen et al.\textsuperscript{52,68} gum formations will lead to rapid catalyst deactivation caused by carbon encapsulation of the metal on the catalyst pellets (cf. Table 2-1). This can perhaps explain why the Ag/Ni catalyst deactivates more rapidly than the other catalysts, since many Ni particles like the one shown in Figure 2-9b were found to be encapsulated in graphite layers. On the other Ni catalysts where whisker carbon dominates, less deactivation should be observed due to the fact that whisker carbon does not immediately lead to deactivation of the catalyst.\textsuperscript{52} Whisker carbon or carbon nanotubes are a result of adsorbed carbon atoms, which dissolve in a Ni-particle, diffuse through it and nucleate into a carbon fiber. During this process small fragments of the nickel particle are left in the whisker and at the end the catalyst pellet will be physically destroyed as described by the reaction schemes in Table 2-1. This might happen without a beforehand pronounced deactivation of the catalyst.\textsuperscript{52}

The K/Ni catalyst was special in the way that several large particles (around 100 nm) were present resulting in carbon formed in so-called “octopus” structure, where several fibers are growing from one nickel crystal (cf. Figure 2-9c).\textsuperscript{76} These large particles create a kind of whisker carbon formation, which perhaps partly can explain the barely existing
deactivation observed on the K promoted catalyst. Another important observation is, of course, the fact that far less carbon is formed on the K/Ni catalyst, which most likely could be the reason for the very slow deactivation. The explanation why less carbon is formed on the K/Ni catalyst is probably ascribed to a better steam adsorption as mentioned above.68

Figure 2-9 TEM images of typical carbon formations on the different catalysts: (a) Ru catalyst. The image shows an ensemble of supported Ru particles without carbon deposits. (b) Ag/Ni catalyst. The image shows a Ni particle encapsulated by gum (graphite layers). (c) K/Ni catalyst. The image shows an “octopus” carbon nanofiber formed around a Ni particle. (d) Ni catalyst. The image shows numerous carbon nanofibers with Ni particles located at their tip apexes.
Essentially no carbon was observed on the ruthenium catalyst, which is in agreement with earlier published work on methane SR.\textsuperscript{77} As seen in Figure 2-9a the Ru particles are distributed quite uniformly on the spinel support with a particle size of ca. 1-2 nm which is in agreement with the results from the hydrogen pulse chemisorption experiments described in paragraph 2.3.2.1.

### 2.3.3 Conclusions

Bioethanol is becoming more and more important as a fuel or fuel additive to gasoline. Yet, a conversion of ethanol to hydrogen could increase the energy efficiency of the fuel significantly by utilizing hydrogen in fuel cells with much higher energy efficiencies than in conventional combustion engines. One possible way to convert bioethanol to biohydrogen is by steam reforming, whereby an optimal six hydrogen molecules are formed from every molecule of ethanol.

Some industrially important heterogeneous catalysts based on ruthenium and nickel show interesting potential for the SR of ethanol, though some challenges still remain \textit{e.g.} in reducing carbon depositions on the catalysts. A major factor in limiting carbon formations is the operating temperature. Higher temperatures decrease the carbon formation significantly. Since the activities of the catalysts are high at the temperatures used in SR, the most important parameter to optimize is the catalyst lifetime. Promoting the nickel catalyst with 1 wt\% potassium significantly decreased carbon formations and improved the catalyst lifetime. The much more expensive ruthenium catalyst was, however, even more carbon resistant resulting in an even longer catalyst lifetime. An economical evaluation should therefore be made for industrial use of these catalysts to decide whether it would make better sense to use the cheap nickel based catalyst and then replace it more often.
2.4 Technical bioethanol
One of the key economical parameters in using bioethanol for chemicals is to avoid the expensive distillation needed for fuel grade ethanol. However, the less distilled the bioethanol is the more contaminants from the fermentation process will be present in the feed. It is therefore of vital importance to analyze the effect of these contaminants on catalyst life time, selectivity, etc. for the possible reactions.

Thus, an investigation of technical second generation bioethanol produced from wheat straw was started. Earlier a couple of publications have come out in the area using first generation bioethanol. The use of diverse feedstocks for the production of bioethanol can pose different challenges in a subsequent steam reforming process, due to the variety of contaminants, and hence it is crucial to have good experimental data with different feeds. Consequently, three different distillation fractions of a technical second generation bioethanol produced from wheat straw were analyzed and tested in the SR process.

The Danish company Inbicon, a subsidiary of DONG Energy A/S, has for the last 4 years operated a pilot plant, able to convert straw into ethanol using the so-called IBUS (Integrated Biomass Utilization System) process. The demonstration plant is located in Skærbæk, Denmark, and has a capacity up to 1000 kg of straw per hour. The bioethanol examined here was received from this pilot plant.

2.4.1 Experimental

2.4.1.1 Production and characterization of technical bioethanol
Three different purities of bioethanol were received from Inbicon. The produced fractions were based on a run of 50 kg/h of Danish wheat straw. The straw was heated with steam for 5 to 15 minutes between 180 and 220 °C. The dry-matter concentration of the pretreated straw was approximately 26 %. To the pretreated straw yeast and enzymes supplied by Novozymes AS were added. The mixture of heated straw, enzymes and yeast were fermented for 5 days in an 11 m³ fermenter, which resulted in an ethanol concentration of around 5-6 %. This fibre beer was distilled in a traditional
A distillation column, with modified trays in the stripper section. The column has a capacity of 1000 kg fibre beer per hour, and is operated under vacuum at around 0.1 bar. A complete description of the Inbicon process has been published recently. Three different fractions of bioethanol were examined. The first fraction was the fibre beer, which contained 5.7 vol% ethanol in water together with some biomass residues. The other two fractions were taken at different locations in the distillation process. Fraction 2 and fraction 3 had an ethanol concentration of 42 and 72 vol % respectively, and both contained greatly reduced amounts of impurities. The fractions were analyzed by GC-MS (Agilent 6850 GC equipped with a capillary HP-5MS column and FID detector and Agilent 5975C MSD) and GC (Agilent 6890N equipped with a capillary HP-5 column and FID detector), and the fibre beer was also analyzed by HPLC (Dionex Ultimate 3000 HPLC equipped with a Phenomenex Rezex RH-Sepharose H+ 8% Column) to determine detectable components and the amounts in which they are presented. The analytical results are shown in Table 2-5.

<table>
<thead>
<tr>
<th>Fraction 1</th>
<th>Vol %</th>
<th>Fraction 2</th>
<th>Mol %</th>
<th>Fraction 3</th>
<th>Mol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Major constituents</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethanol</td>
<td>5.7</td>
<td>Ethanol</td>
<td>18</td>
<td>Ethanol</td>
<td>44</td>
</tr>
<tr>
<td>Xylose</td>
<td>1.2</td>
<td>3-methyl-1-butanol</td>
<td>0.7</td>
<td>Ethyl acetate</td>
<td>0.5</td>
</tr>
<tr>
<td>Glucose</td>
<td>1.1</td>
<td>2-methyl-1-propanol</td>
<td>0.3</td>
<td>1,1-diethoxyethane</td>
<td>0.2</td>
</tr>
<tr>
<td>Lactate</td>
<td>0.5</td>
<td>2-methyl-1-butanol</td>
<td>0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetate</td>
<td>0.5</td>
<td>Propanol</td>
<td>0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glycerol</td>
<td>0.4</td>
<td>Cyclopentanone</td>
<td>0.05</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trace constituents</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td></td>
<td>Furfural</td>
<td></td>
<td>Propanol</td>
<td></td>
</tr>
<tr>
<td>Acetic acid</td>
<td></td>
<td>4-hexen-1-ol</td>
<td></td>
<td>2-methyl-1-propanol</td>
<td></td>
</tr>
<tr>
<td>Others</td>
<td></td>
<td>1,1-diethoxyethane</td>
<td></td>
<td>3-methyl-1-butanol</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2-methyl-1-butanol</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Cyclopentanone</td>
<td></td>
</tr>
</tbody>
</table>

2.4.1.2 Catalyst preparation, characterization and testing
For an accurate comparison between the technical bioethanol and the commonly used ethanol/water mixtures, the same catalysts (Ni, K/Ni and Ru cf. Table 2-2) as those previously investigated in the carbon study (section 2.3) were tested. The catalyst synthesis, characterization and experimental setup are all described in section 2.3.1 above.
2.4.2 Results and discussion

The unpurified fibre beer fraction is a dark mixture of many different compounds (cf. Table 2-5) and some sort of purification is needed before it can be used in any process. If the solids are disregarded, the main contaminants are different sugars and higher alcohols. Several methods were investigated for cleaning this crude bioethanol with the best results obtained by using activated carbon under reflux at 80 °C for 16h. After filtration, a clear ethanol solution was obtained but it still contained considerable amounts of sugars, which caramelize as soon as vaporization of the solution is attempted. No easy and inexpensive method was found for removing these sugars except distillation. Hence, this fraction was not studied further in the SR reaction.

Although the different sugars in the beer have to be removed, there is no need to distill to fuel grade ethanol; for SR purposes, a simple flash distillation will probably be sufficient. This will remove the parts of the feed that are not easily vaporized, whereas most of the fusel oils and other low boiling contaminants will remain in the ethanol solution. Such contaminants will not necessarily pose any problems since they most likely also can be steam reformed over the same catalyst. In the previous studies of Arkande et al.\textsuperscript{80,81} they used first generation bioethanol from fermentation of crops where the main contaminants were lactic acid and glycerol. What they saw was exactly that these contaminants could also be reformed in agreement with other studies of glycerol steam reforming (GSR).\textsuperscript{83,84} Lactic acid and glycerol are, however, not represented as contaminants in the second generation bioethanol (fraction 2 or fraction 3, cf. Table 2-5), instead several different mono-alcohols dominate. This also demonstrates the diversity in using biomass. The composition of contaminants in various grades of bioethanol is dependent on the used feedstock as well as on the refinery process, which differs between first and second generation plants and depends on the actual fermentation technology used.

To achieve the overall best economical scenario, it is required to keep the purification of the feedstock at a minimum. Therefore SR of the less pure fraction 2 would be preferred over fraction 3, or perhaps even better a fraction that matches the stoichiometry of the ESR reaction with an ethanol/water ratio of 1:3. This is, however, assuming that the
various higher alcohols found as contaminants are not detrimental to the SR catalysts. That just leaves the question whether such a fraction of bioethanol will perform comparably to a pure ethanol/water feed, or the reduction in the cost of feedstock will be consumed by faster catalyst deactivation.

Table 2-6 Average carbon formation rate on the different catalysts as a function of reaction temperature using either a 25 vol% ethanol in water solution or bioethanol (fraction 3 diluted to 25 vol% ethanol) as feedstock. Compositions of the catalysts are in accordance to Table 2-2.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Ni (mg/h)</th>
<th>K/Ni (mg/h)</th>
<th>Ru (mg/h)</th>
<th>Ni-bio (mg/h)</th>
<th>K/Ni-bio (mg/h)</th>
<th>Ru-bio (mg/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>4.86</td>
<td>1.53</td>
<td>0.11</td>
<td>4.55</td>
<td>2.37</td>
<td>0.15</td>
</tr>
<tr>
<td>450</td>
<td>0.62</td>
<td>0.44</td>
<td>0.014</td>
<td>0.38</td>
<td>0.31</td>
<td>0.026</td>
</tr>
<tr>
<td>500</td>
<td>0.15</td>
<td>0.082</td>
<td>0.008</td>
<td>0.12</td>
<td>0.094</td>
<td>0.027</td>
</tr>
<tr>
<td>600</td>
<td>0.02</td>
<td>0.011</td>
<td></td>
<td>0.05</td>
<td>0.041</td>
<td>0.021</td>
</tr>
</tbody>
</table>

For an accurate comparison between the technical bioethanol and the previously used ethanol/water mixtures, the bioethanol of fraction 3 was diluted to approximately 25 vol% ethanol. From Figure 2-10 and Table 2-6, it can be seen that the rate of carbon formation shows the same trends in the runs with technical bioethanol as in the previous ones with a pure ethanol/water mixture. However, the rate of carbon formation is generally slightly higher for fraction 3 than for the pure ethanol/water mixture, which perhaps can be explained by the slightly higher concentration of carbon-containing compounds in the feed.

Figure 2-10 Carbon formation rate on the different catalysts as a function of reaction temperature using a: 25 vol% ethanol in water and b: bioethanol (Fraction 3 diluted to 25 vol% ethanol) as feedstock. Composition of the catalysts is according to Table 2-2.

Another observation from the comparison between Figure 2-10a and Figure 2-10b is the apparent significantly lower rate of carbon formation on the nickel based catalysts for SR
with pure ethanol/water at 600 °C. These runs were maintained over a week compared to 16-18 hours for the experiments with technical bioethanol. It is anticipated that the rate of carbon formation is highest in the start of the reaction and therefore the apparent rate of carbon formation will be slightly lower for these two long runs.

With the Ru catalyst a comparative study with the more contaminated bioethanol of fraction 2 was made, since this catalyst had higher activity and longer life time at lower temperatures. Fraction 2 was also diluted to 25 vol% and used as feed in the reaction at 400 °C and 500 °C. The exit gas composition as measured on the BINOS at 400 °C is shown in Figure 2-11. From this figure the same deactivation pattern can be observed: the yield of CO₂ decreases whereas the yield of CO increases after approximately 12 h for fraction 2. For the run using fraction 3 as feedstock neither the CO nor the CO₂ concentration changes during the duration of the run (approximately 18 h). For the run at higher temperature, 500 °C, no deactivation is seen for any of the fractions during the duration of the run.

![Figure 2-11 Exit gas composition over time, as measured by the BINOS, for runs at 400 °C over the Ru/MgAl₂O₃ catalyst using bioethanol fraction 2 and fraction 3 as feedstock.](image)
From Figure 2-11 it is also seen that the CO$_2$ concentration at equilibrium is higher for fraction 2 than for fraction 3. This is probably a consequence of the increased amount of steam reformable material in fraction 2. The extra contaminants in fraction 2 correspond to about a 10% increase in the carbon content, in comparison to fraction 3, which is in good agreement with the results.

The faster deactivation of the catalysts while using fraction 2 at 400 °C can either be caused simply by the increased carbon concentration at the catalyst surface or result from the more complex larger oxygenated compounds present in the feed, or perhaps a combination of both. An increased carbon concentration at the catalyst surface would lead to a higher rate of carbon formation, resulting in a faster catalyst deactivation. It is likely, though, that the more complex nature of the contaminants contributes to the faster deactivation of the catalyst. Through GC-analysis it is evident for all the experiments that full conversion of ethanol leads to something close to the equilibrium gas-mixture as shown in Figure 2-5. Moreover, all the contaminants in fraction 2 and 3 are also reformed as they do not appear in the GC-analysis. Only when the catalysts deactivate do, ethanol, acetaldehyde, ethylene, ethane and traces of the contaminants start to appear in the exit gas. This is observed simultaneously with a decrease in methane and CO$_2$ and an increase in the CO concentration; the same deactivation patterns as have been noticed with all of the used ethanol/water mixtures.

As mentioned in the carbon study section 2.3 an alternative to the ordinary SR process could be to do oxidative/autothermal reforming. This would probably negate some of the problems with carbon formation as caused by, for instance, higher alcohols present in fraction 2, but at the expense of a lower H$_2$ yield.\textsuperscript{73}

2.4.3 Conclusions
Here, it is indicated what some of the challenges will be to implement the bioethanol steam reforming process into industrial applications. When using technical bioethanol of lower purity the lifetime of the catalyst decreases as a consequence of the increased amount and character of the carbon containing compounds; this deactivation must be addressed in the design of the process. As long as the deactivation issues are accounted
for, it is apparent that the use of fuel grade ethanol is not required; a simple flash distillation of the fibre beer to remove the sugars and other non-volatile substances from the feedstock seems to be sufficient. Therefore, the economics in a biorefinery can be improved by minimizing the process heat (steam) for the energy intensive distillation along with the capital costs of the distillation equipment.

### 2.5 Glycerol steam reforming

Glycerol could be another possible renewable feedstock for hydrogen production. It has already been shown by several groups that, it is possible to produce hydrogen from glycerol.\textsuperscript{83,84} To investigate whether the catalysts used in the ESR studies would also be active for glycerol steam reforming (GSR), a 50 wt% glycerol solution was prepared by mixing 99.5 % glycerol with DI (de-ionized) water.

Glycerol (with a boiling point of 290 °C) and other chemicals with high boiling points are not suitable for reactions in the previously used continuous flow equipment, because it is not possible to vaporize the glycerol in the tubing before entering the reactor. Therefore, another continuous flow experimental setup was built, which accounted for this problem by feeding the liquid directly into the reactor upstream of the catalyst bed. At this position a fast vaporization and mixing with carrier gas will be possible at the temperatures normally used for gas phase reactions like SR.

![Figure 2-12](image.png)

**Figure 2-12** Schematic drawing of the continuous flow experimental pressure setup for catalytic measurements.
The setup is illustrated in Figure 2-12. In general it works similarly to the other setup (Figure 2-4) except that the condensation is happening before the GC measurements. This, however, should not be important for the SR process since the products are light gasses; in fact it is an advantage that the GC columns are not exposed to all the water in the effluent stream. Another possibility with this setup is that it can be pressurized to around 20 bar; perhaps not really interesting for SR applications but for many other reactions run at higher pressures such as Fischer-Tropsch (FT) synthesis or methanol to gasoline (MTG) process.

A couple of GSR experiments were performed at 500 °C over 500 mg of the 2%Ru/MgAl_2O_4 catalyst. The 50 wt% aqueous glycerol solution was pumped with a feed rate of 0.04 mL/min and a flow of 80 mL/min of helium was used as carrier gas. The experiments were mainly used as test reactions for the setup. The results showed that glycerol was reformed to hydrogen, methane, carbon dioxide and carbon monoxide, though after 20 h reaction time particularly the methane selectivity had decreased and glycerol, acetol and glycidol were found in the condensate. TPO experiments also showed a relatively high rate of carbon formation on the catalyst with more than 3 mg/h.

### 2.6 Conclusion

Hydrogen is one of the most important molecules in the chemical industry and has been proclaimed to be the central energy carrier in a possibly hydrogen society. Hydrogen has potential as energy carrier for use in fuel cells which generally are more energy efficient than combustion engines. Moreover, hydrogen (produced from a renewable feedstock) does not make any pollution when utilized either by combustion or in fuel cells producing water as the only exhaust.

In this chapter it has been illustrated how different renewable alcohols can be steam reformed to produce hydrogen as an alternative to its production from fossil resources, which generate GHG leading to global warming.
Steam reforming of renewable alcohols over ruthenium and nickel-based catalysts shows interesting industrial potential. Apparently the most crucial issue is catalyst lifetime, which primarily depends on the carbon formation rate on the catalysts. From the ethanol steam reforming it can be concluded that running at high temperatures and high steam concentrations decreases carbon formation. Contaminants in the feed when using crude bioethanol, on the other hand, increase the carbon formation rate. There is, however, no need to distill the ethanol to fuel grade to use it for steam reforming where a simple flash distillation to some 50 wt% seems sufficient.

One possible way of using bioethanol in a more fuel efficient manner could be to SR it to hydrogen and use it in fuel cells. In this way the expensive fuel grade distillation will also be avoided and the cost of ethanol lowered.
3 Synthesis gas

The manufacture of synthesis gas (syngas) is often very similar to the production of hydrogen. The main difference lies in the amount of CO present, which is mainly controlled by the water gas shift (WGS) reaction (3.1). When producing hydrogen it is very important to remove all CO from the gas especially for low temperature fuel cells where even small amounts of CO poison and deactivate the Pt catalysts used on the electrodes. For syngas on the other hand a high CO concentration is often preferred because of its potential for further processing in for instance methanol synthesis (3.2) or Fischer-Tropsch (FT) synthesis (3.3).

\[
CO + H_2O \rightarrow CO_2 + H_2 \quad (\Delta H^\circ = -41 \text{ kJ/mol}) \quad (3.1)
\]

\[
CO + 2H_2 \rightarrow CH_3OH \quad (\Delta H^\circ = -90 \text{ kJ/mol}) \quad (3.2)
\]

\[
nCO + (2n + 1)H_2 \rightarrow C_nH_{2n+2} + nH_2O \quad (\Delta H^\circ < 0) \quad (3.3)
\]

When biomass is reformed all the way to hydrogen, carbon dioxide is formed as well, which is not really useful but fairly harmless (except for global warming when fossil resources are used), and is therefore released to the atmosphere. Avoiding the WGS reaction will on the other hand mean that CO is the main product next to hydrogen. Carbon monoxide is a very harmful and even deadly gas to humans and should be handled with care. However, it is also a very interesting and useful chemical for the synthesis of other important chemicals or fuel.

In this chapter it is investigated how glycerol can be converted into syngas with a controlled WGS activity. The project was carried out in the group of Prof. James A. Dumesic in cooperation with Dante A. Simonetti and Edward L. Kunkes at University of Wisconsin in Madison, USA.
3.1 Syngas from glycerol

During the production of biodiesel about 10 wt% glycerol is formed as a byproduct/waste product. A way to optimize the process could be to use the glycerol directly at the biodiesel plant to produce even more biodiesel. For that reason it was studied how glycerol can be converted to synthesis gas with a H₂/CO ratio close to 2, which is suitable for Fischer-Tropsch synthesis\textsuperscript{85} and thereby the production of liquid hydrocarbons\textsuperscript{86} (reaction 3.3).

Figure 3-1 Schematic illustration of liquid fuel and chemical production via catalytic processing of glycerol.

In Figure 3-1 a schematic of glycerol processing is illustrated. Glycerol is as mentioned available from the transesterification of vegetable oils and animal fats in an around 85 wt% aqueous solution\textsuperscript{87} but it can also be made from fermentation of biomass \textit{e.g.} glucose in a 25-30 wt% aqueous solution\textsuperscript{88}. The latter would be an interesting alternative to the fermentation process to ethanol where a 5-10 wt% solution is generated. The higher concentration of glycerol may make it a more energy efficient alternative to the bioethanol production in situations where water has to be completely or partly removed from the feed. The aqueous glycerol feed can be converted to syngas by low...
temperature processing, which in one aspect could be used in methanol synthesis,\(^9\)
which again can be used for other chemicals or in the transesterification step in the
biodiesel production. Another alternative would be to use the syngas for FT synthesis of
liquid hydrocarbon fuel, possibly via a controlled WGS for achieving a suitable \(\text{H}_2/\text{CO}\) ratio.

The conversion of glycerol into hydrogen and carbon monoxide is reported to take place
according to the endothermic reaction in equation 3.4:\(^9\)

\[
C_3H_8O_3 \rightarrow 3CO + 4H_2 \ (\Delta H^\circ = 349 \text{ kJ/mol}) \tag{3.4}
\]

The energy corresponds to about 24 % of the lower heating value of glycerol, which is
merely the energy of combustion of glycerol to carbon dioxide and water vapor, equation 3.5.

\[
C_3H_8O_3 + 3.5O_2 \rightarrow 3CO_2 + 4H_2O \ (\Delta H^\circ = -1480 \text{ kJ/mol}) \tag{3.5}
\]

This means that for producing syngas alone around one fifth of the glycerol should be
burned to obtain the necessary heat for the reaction. However, combining glycerol
processing with the exothermic FT synthesis, as illustrated in Table 3-1, would result in
an overall slightly exothermic reaction (3.9), thus increasing the energy efficiency in the
combined process. The reactions are calculated with octane as the model hydrocarbon
compound and comprise: FT reaction to octene (3.6), hydrogenation of octene to octane
(3.7) and WGS (3.8) to obtain the needed \(\text{H}_2/\text{CO}\) ratio to balance the reactions.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>No.</th>
<th>Heat (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycerol to syngas</td>
<td></td>
<td>349</td>
</tr>
<tr>
<td>(C_3H_8O_3 \rightarrow 3CO + 4H_2)</td>
<td>(3.4)</td>
<td></td>
</tr>
<tr>
<td>Fischer-Tropsch reaction to octene</td>
<td></td>
<td>-340</td>
</tr>
<tr>
<td>(\frac{112}{25}H_2 + \frac{54}{25}CO \rightarrow \frac{7}{25}C_8H_{16} + \frac{54}{25}H_2O)</td>
<td>(3.6)</td>
<td></td>
</tr>
<tr>
<td>Hydrogenation of octene to octane</td>
<td></td>
<td>-40.5</td>
</tr>
<tr>
<td>(\frac{7}{25}H_2 + \frac{7}{25}C_8H_{16} \rightarrow \frac{7}{25}C_8H_{18})</td>
<td>(3.7)</td>
<td></td>
</tr>
<tr>
<td>Water-gas shift</td>
<td></td>
<td>-30.7</td>
</tr>
<tr>
<td>(\frac{19}{25}H_2O + \frac{19}{25}CO \rightarrow \frac{19}{25}CO_2 + \frac{19}{25}H_2)</td>
<td>(3.8)</td>
<td></td>
</tr>
<tr>
<td>Overall</td>
<td></td>
<td>-62.9</td>
</tr>
<tr>
<td>(C_3H_8O_3 \rightarrow \frac{2}{25}C_8H_{18} + \frac{19}{25}CO_2 + \frac{37}{25}H_2O)</td>
<td>(3.9)</td>
<td></td>
</tr>
</tbody>
</table>
Previously in the group of Dumesic it was investigated which catalyst would be the best for converting a 30-50 wt% glycerol-water solution into syngas. Different platinum catalysts were examined due to platinum’s ability to cleave C-C bonds opposed to C-O bonds. It was found that a 5 wt% Pt/C catalyst had a high catalytic activity and a superior lifetime among other platinum supported catalysts, Pt/(MgO-ZrO$_2$, Al$_2$O$_3$, ZrO$_2$, CeO$_2$-ZrO$_2$). The experiments were performed at 350 °C and ambient pressure. The idea of the project was to combine the glycerol to syngas process with Fischer-Tropsch synthesis as illustrated in Figure 3-1. However, looking into FT it is seen that the optimal process conditions are low temperature (200-300 °C) and high pressure (10-60 bar), while glycerol conversion to syngas is optimal at high temperatures and atmospheric pressure. Therefore it is challenging to try to achieve high glycerol conversion at lower temperatures. By analyzing DFT (density functional theory) calculations on different near-surface metal alloys bimetallic catalysts were suggested as an optimal solution. The DFT studies predicted that alloys between platinum and ruthenium or platinum and rhenium could minimize the coverage of CO on the surface by lowering the CO binding energy to the metal. Reducing catalyst poisoning from surface coverage of CO should increase the reactivity of the Pt-catalyst and thereby make it possible to decrease the temperature. The results showed indeed that these metal alloys were more reactive at lower temperatures, and with a 5 wt% Pt-Re(1:1)/C the temperature was decreased to as low as 275 °C which is suitable for FT synthesis.

### 3.2 Integrated glycerol processing and Fischer-Tropsch synthesis

To analyze the integrated glycerol reforming and FT synthesis, two separate analyses for optimizing each process were performed. Moreover, a study was made to explore the effect of the main contaminants in the syngas gas, from the glycerol reforming, on the FT catalyst and the product distribution. Finally the two processes were investigated in a combined run.
3.2.1 Experimental

For the glycerol processing a 10 wt% Pt-Re/C (atomic Pt:Re ratio 1:1) catalyst was prepared by incipient wetness impregnation of carbon black with an aqueous solution of H$_2$PtCl$_6$-6H$_2$O and HReO$_4$. For the FT synthesis 1 wt% and 2.9 wt% Ru/TiO$_2$ catalysts were prepared also by incipient wetness impregnation and according to the methods described by Iglesia et al.$^{97}$ Further details about the catalyst preparation and characterization can be found elsewhere.$^{98}$

The reaction kinetics were measured in two different but similar continues flow systems. The experimental setups for the glycerol processing and FT synthesis were analogous to the apparatus schematically shown in Figure 2-12 and they worked principally identically. Catalyst was loaded into a ½-inch outer diameter tubular stainless steel reactor. The catalyst bed was contained between an end plug of quartz wool and fused SiO$_2$ granules which aid in vaporization of the liquid feed. The Pt-Re/C catalyst powder was mixed with an equal volume of SiO$_2$ granules to decrease the pressure drop across the catalyst bed. Prior to activity measurements the catalyst was reduced in a flow of H$_2$ (140 mL/min) at 450 °C for 2 h with a ramp of 0.5 °C/min. An HPLC pump was used to introduce the aqueous feed solution into the liquid injection unit above the reactor. The needle extends into the reactor just above the fused SiO$_2$ granules. The effluent from the reactor was water-cooled and liquids were condensed out in the gas-liquid condenser. The effluent liquid was drained periodically for GC analysis to detect the presence of glycerol and other liquid byproducts. The effluent gas stream passed through a back-pressure regulator, which controlled the system pressure and was further analyzed by GC to achieve a total carbon balance. All feed solutions were prepared by mixing glycerol (99.5%) with DI water.

The apparatus for the FT experiments was similar to the glycerol reforming except that the downstream line was heated to 100 °C. The Ru/TiO$_2$ catalysts were reduced in situ using a procedure similar to the Pt-Re/C catalyst. The ruthenium catalyst was mixed with equal volume of crushed SiO$_2$ to dissipate the heat generated by the exothermic FT synthesis. The effluent gasses and liquids were analyzed by different GC’s and occasionally by GC-MS. High purity H$_2$ and CO gasses were mixed to give a gas mixture of
H$_2$:CO close to two. Aqueous solutions of acetone, ethanol and acetol were introduced into the reactor as described above.

For the combined run the Ru/TiO$_2$ mixed with SiO$_2$ was inserted downstream of the Pt-Re/C catalyst. Weight hourly space velocities (WHSV) for the glycerol conversion are calculated from the mass flowrate of glycerol into the reactor and the total mass of catalyst. The gas hourly space velocities (GHSV) used for the FT experiments are calculated from the total volumetric flowrate of gas, at STP (standard temperature and pressure), to the reactor and the total volume of the bed, which has catalyst density around 0.175 g/mL for Ru/TiO$_2$ mixed with SiO$_2$.

### 3.2.2 Results and discussion

#### 3.2.2.1 Glycerol processing

A stability test of the Pt-Re/C catalyst was made with a 30 wt% aqueous glycerol feed pumped at 0.08 mL/min over 520 mg catalyst (WHSV = 3.0 h$^{-1}$) at 275 °C and 8.3 bar. The catalyst had an induction period for about 60 h where conversion of glycerol to gas phase products decreased from 68 % to 57 %. Thereafter the catalyst showed excellent stability for at least another 60 h time on stream.$^{98}$ A similar experiment at 5 bar showed 80 % conversion to gas phase products (H$_2$, CO, CO$_2$ and light alkanes) and about 15 % conversion to the aqueous liquid effluent. These products were oxygenated hydrocarbons with ethanol, methanol, acetone and acetol as the most abundant.

To combine the experiments with FT it is necessary to expose the FT catalyst to water and oxygenates from the aqueous effluent. Iglesia has shown that small amounts of water could have a positive effect on Co-based FT catalysts$^{99}$, but the highest examined water partial pressure was 3 times the CO partial pressure, whereas the 30 wt % glycerol solution results in a partial water pressure 8 times the CO partial pressure. It was therefore chosen to look at less diluted glycerol solutions and a 50 wt% and 80 wt% were prepared. These solutions were tested (cf. Table 3-2) at pressures from 1-11 bar, 275 °C, 1.0 g catalyst and a liquid flow of 0.04 mL/min corresponding to WHSV between 1.4 and 1.7 h$^{-1}$. 

54
Table 3-2 Performance of Pt–Re/C for conversion of concentrated solutions of glycerol in water to synthesis gas at various pressures. Reaction carried out over 1.0 g of catalyst at 275 °C using 0.04 mL/min of feed (WHSV between 1.4 and 1.7 h⁻¹). Conversion to gas phase products is calculated as carbon atoms in gas phase product stream/total carbon into reactor as feed.

<table>
<thead>
<tr>
<th>Feed concentration (wt%)</th>
<th>Pressure (bar)</th>
<th>Conversion to gas phase products (%)</th>
<th>( \frac{\text{H}_2}{\text{CO}} )</th>
<th>( \text{CO}/\text{CO}_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>1</td>
<td>86</td>
<td>1.4</td>
<td>28</td>
</tr>
<tr>
<td>80</td>
<td>5</td>
<td>56</td>
<td>1.2</td>
<td>13</td>
</tr>
<tr>
<td>80</td>
<td>11</td>
<td>44</td>
<td>1.0</td>
<td>4.7</td>
</tr>
<tr>
<td>50</td>
<td>11</td>
<td>55</td>
<td>1.4</td>
<td>2.7</td>
</tr>
<tr>
<td>50</td>
<td>5</td>
<td>76</td>
<td>1.5</td>
<td>7.8</td>
</tr>
</tbody>
</table>

From Table 3-2 it is seen that the conversion to gas phase products decreases with increasing pressure and increases with decreasing glycerol concentration. The WGS activity increases with increasing pressure as can be seen in the decreased \( \text{CO}/\text{CO}_2 \) ratio. Lower glycerol concentration also leads to an increase in the WGS activity due to the higher steam partial pressure. These experiments were all carried out above the dew point of glycerol feed solutions. Another experiment was carried out with the 80 wt% solution at 17 bar with incomplete vaporization of the feed. The catalyst showed the same stability for this experiment and the conversion was similar to the experiment at 11 bar, though due to higher pressure increased WGS activity was observed. In all the experiments complete conversion of glycerol was achieved with 6-30 wt% oxygenated hydrocarbons in the liquid phase (whenever the conversion to gas phase products was below 90 %) The largest amounts of oxygenated hydrocarbons in the liquid phase were found at high pressures and high glycerol feed concentrations.

3.2.2.2 Fischer-Tropsch synthesis

To accomplish energy integration between the endothermic reforming of glycerol and the exothermic FT reaction it is important to have the temperature for the FT higher or equal to the temperature for the upstream glycerol processing, to let the generated energy dissipate from the FT bed to the reforming bed. It will also be most suitable to use the same pressure for both reactions to minimize compression costs. And finally it is important that the FT catalyst is stable, and preferably active in converting the
oxygenated molecules from the glycerol processing, where they will possibly participate in the FT chain growth.

For testing the equipment for conducting FT experiments different catalysts based on ruthenium and cobalt were tested and a pressure study was performed with a 1 wt% Ru/TiO$_2$ at 275 °C. In a typical experiment 2 g of catalyst was mixed with an equal volume of crushed SiO$_2$ and a flow of H$_2$/CO with ratio of 1.8 was used resulting in a GHSV of 500 h$^{-1}$.

![Figure 3-2](image_url) The influence of pressure on FT reaction (♦ CO conversion, ● methane selectivity and ■ C$_5$+ selectivity). Experiments performed with 2 g of 1 wt% Ru/TiO$_2$ mixed with an equal volume crushed SiO$_2$ at 275 °C with a H$_2$/CO ratio of 1.8 and a GHSV of 500 h$^{-1}$.

The results of the pressure study confirm the already known facts that the CO conversion increases with increasing pressure and that the selectivity to C$_5$+ species increases in the same manner while the CH$_4$ selectivity decreases with increasing pressure. The ruthenium catalysts were finally chosen for all the FT experiments because they all exhibited excellent properties for the FT synthesis, which was the main criteria for this study.

To analyze the effect of oxygenates from the glycerol conversion in the feed to the FT bed, solutions with 30 wt% ethanol, acetone and acetol were prepared since they were
the main by-products. Also an experiment was made to analyze the effect of water alone. Table 3-3 shows the results from FT experiments performed over 4 g of 2.9 wt% Ru/TiO$_2$ catalyst mixed with an equal volume of crushed SiO$_2$ at 275 °C and a gas flow of 150 mL/min with a H$_2$/CO ratio around 2. The experiments were carried out by keeping the partial pressure of carbon monoxide and hydrogen constant and then adding the liquids with 0.06 mL/min resulting in increased total pressure.

<table>
<thead>
<tr>
<th>Oxygenated Feed</th>
<th>P$_{CO}$ (bar)</th>
<th>P$_{H2}$ (bar)</th>
<th>P$_{H2O}$ (bar)</th>
<th>P$_{oxy}$ (bar)</th>
<th>P$_{tot}$ (bar)</th>
<th>GHSV$^a$ (h$^{-1}$)</th>
<th>X$_{CO}$$^b$ (%)</th>
<th>S$_{C5+}$$^c$</th>
<th>S$_{CH4}$$^c$</th>
<th>S$_{C2-C4}$$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>1.7</td>
<td>3.3</td>
<td>--</td>
<td>5.0</td>
<td>410</td>
<td>53</td>
<td>0.30</td>
<td>0.39</td>
<td>0.29</td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>1.7</td>
<td>3.5</td>
<td>2.9</td>
<td>8.1</td>
<td>630</td>
<td>55</td>
<td>0.32</td>
<td>0.41</td>
<td>0.29</td>
<td></td>
</tr>
<tr>
<td>Acetone/H$_2$O</td>
<td>1.9</td>
<td>3.8</td>
<td>2.1</td>
<td>0.3</td>
<td>8.1</td>
<td>570</td>
<td>0.37</td>
<td>0.41</td>
<td>0.23</td>
<td></td>
</tr>
<tr>
<td>Ethanol/H$_2$O</td>
<td>1.9</td>
<td>3.7</td>
<td>2.2</td>
<td>0.3</td>
<td>8.1</td>
<td>590</td>
<td>0.38</td>
<td>0.39</td>
<td>0.23</td>
<td></td>
</tr>
<tr>
<td>Acetol/H$_2$O</td>
<td>1.8</td>
<td>3.5</td>
<td>2.6</td>
<td>0.2</td>
<td>8.1</td>
<td>630</td>
<td>0.60</td>
<td>0.24</td>
<td>0.17</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ GHSV calculated as total volumetric flowrate into the reactor divided by total volume of the catalyst bed.

$^b$ CO conversion is calculated as $\frac{(F_{CO})_{in}-(F_{CO})_{out}}{(F_{CO})_{in}}$, where $F$ is the molar flowrate.

$^c$ Selectivities calculated as $S_{C_nH_x} = \frac{nF_{C_nH_x}}{F_{tot}}$, where $n$ is the number of carbons in $C_nH_x$, $F_{C_nH_x}$ is the molar flowrate of $C_nH_x$, and $F_{tot}$ is the total molar flowrate of carbon in all Fischer-Tropsch hydrocarbon products. The selectivities are calculated on a CO$_2$ and oxygenated hydrocarbon free basis.

From Table 3-3 it is seen that the reference experiment with no liquid flow had 53% CO conversion and selectivity to C$_{5+}$ species of 30%. These numbers did hardly change by addition of water, and it can be concluded that water is not detrimental to the FT catalyst and does not seem to influence selectivities much. Adding 30 wt% aqueous solutions of different oxygenates, on the other hand, resulted in a decrease of the CO conversion to around 30%. But where ethanol and acetone only changed the selectivities marginally, the acetol co-feed doubled the C$_{5+}$ selectivity with a simultaneous decrease in the methane and C$_2$-C$_4$ selectivity. This indicates that opposite to ethanol and acetone the acetol seems to participate to some extent in the hydrocarbon chain growth. And indeed by looking a bit more carefully at the products from the runs almost all the ethanol and acetone went through the system unreacted and were recovered in the gaseous or aqueous liquid effluent. Acetol, however, was completely converted with 40% being converted to acetone, methanol and ethanol in the aqueous liquid phase or the gas phase and 20% being converted to oxygenated
species in the organic liquid phase mainly as pentanones, hexanones and heptanones. The resulting 40% of acetol seemed to have participated in the FT chain growth and was converted to hydrocarbons.

3.2.2.3 Combined run

For the combined run a two-bed catalyst system was employed with 1.0 g of a 10 wt% Pt-Re (1:1)/C upstream of 1.7 g of 1.0 wt% Ru/TiO₂, both mixed with an equal volume of SiO₂. The used process conditions were pressures between 5 and 17 bar, a temperature of 275 °C and 0.04 mL/min of an aqueous feed of 80 wt% glycerol.

Table 3-4 Results from experiments for glycerol conversion combined with Fischer-Tropsch synthesis a 275 °C and 0.04 mL/min of an 80 wt% aqueous glycerol feed.

<table>
<thead>
<tr>
<th>P_{tot} (bar)</th>
<th>S_{C5} a (%)</th>
<th>S_{CH4} a (%)</th>
<th>S_{C2-C4} a (%)</th>
<th>S_{Alkanes} b (%)</th>
<th>S_{CO2} b (%)</th>
<th>S_{CO} b (%)</th>
<th>S_{org-oxy} b (%)</th>
<th>S_{aqu-oxy} b (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.63</td>
<td>0.15</td>
<td>0.21</td>
<td>31.9</td>
<td>15.2</td>
<td>37.3</td>
<td>1.7</td>
<td>13.9</td>
</tr>
<tr>
<td>11</td>
<td>0.75</td>
<td>0.10</td>
<td>0.15</td>
<td>44.1</td>
<td>16.5</td>
<td>17.5</td>
<td>7.4</td>
<td>14.6</td>
</tr>
<tr>
<td>17</td>
<td>0.70</td>
<td>0.12</td>
<td>0.18</td>
<td>55.2</td>
<td>23.1</td>
<td>1.3</td>
<td>9.1</td>
<td>11.2</td>
</tr>
</tbody>
</table>

a Selectivities calculated as in Table 3-3.

b Total carbon selectivities, calculated as S_i = F_i/F_{tot}, where F_i is the total flowrate of carbon in product i, and F_{tot} is the total flowrate of carbon in all products.

The experiments all had a complete conversion of glycerol. Results shown in Table 3-4 indicate an increase in the C₅⁺ selectivity when the pressure is increased from 5 to 11 bars in accordance to the single FT experiments described above. Increasing the pressure further to incomplete vaporization of the glycerol feed decreases only the C₅⁺ selectivity slightly. In general it is seen how the selectivity to alkanes increases with increasing pressure as a direct consequence of a simultaneous decrease in the CO selectivity. The same trend is observed for the oxygenated hydrocarbon products (acetone, pentanones, hexanones and heptanones) in the organic liquid phase, and the resulting effluent is similar in composition to FT experiment with an acetol co-feed. At 17 bar the selectivity to CO decreases followed by an increased selectivity to alkanes and CO₂, but a decreased C₅⁺ selectivity. Therefore it is possible to conclude that under these
conditions the WGS reaction is more pronounced (as mentioned earlier) and the carbon distribution is shifted towards lighter alkanes.

It is noticeable that the $\text{H}_2/\text{CO}$ ratio in these experiments typically varies from 1.0-1.5 as shown in the glycerol conversion experiments, cf. Table 3-2. These ratios are below the optimal ratio of 2:1 but high selectivity of $\text{C}_{5+}$ hydrocarbons is still achieved.

### 3.2.3 Conclusion

![Figure 3-3](image)

**Figure 3-3** Process pathway for production of liquid fuel from biomass by integration of glycerol conversion to synthesis gas and Fischer-Tropsch synthesis.

Figure 3-3 summarizes how liquid hydrocarbons can be produced from biomass via an integrated process for converting glycerol to synthesis gas and subsequent FT synthesis. Aqueous solutions of glycerol are produced from vegetable oils and animal fats by transesterification as by-product in the production of biodiesel. It can also be produced by fermentation of carbohydrates. These aqueous glycerol solutions can by the integrated process, using a Pt-Re/C catalyst for syngas production and a Ru/TiO$_2$ catalyst
for FT synthesis, be converted to a mixture of liquid hydrocarbons, gaseous hydrocarbons and aqueous solutions containing oxygenated hydrocarbons.

Gaseous alkanes could eventually be reformed to synthesis gas and fed to the integrated process or they could be combusted to produce electricity and/or heat. Several possibilities exist for the aqueous solution containing acetone, methanol, ethanol and some other oxygenated hydrocarbons. One possibility would be to make a distillation and produce chemicals or solvents. Alternatively the solutions could be used in an aqueous phase reforming to make hydrogen. Most valuable product is the liquid hydrocarbons which can further be upgraded to premium fuels.

Importantly, the integrated process poses synergies between the operations thereby avoiding the highly endothermic and exothermic reaction steps resulting from separate operation. Additionally, combined run eliminates the need to condense water and other byproducts between the catalyst beds. Finally the end products can all be utilized leading to a minimal amount of waste from the process. Thus the integrated process has both environmental and economical interesting potentials.
4 Acetic acid

One of the many interesting alternatives to use ethanol as fuel is to produce acetic acid. Acetic acid is produced in around 10 million MT/y and it is sold at a value more than twice that of fuel grade ethanol. These numbers point out the potential in converting the production of acetic acid from a fossil based one to a renewable via bioethanol. If aqueous solutions of ethanol can be cheaply oxidized to acetic acid, all acetic acid could be produced from bioethanol at a lower price and in a more environmental friendly way than by its present production from fossil resources.

Today acetic acid is mainly produced by the Monsanto process or the similar Cativa process, wherein carbonylation of methanol, according to equation 4.1, is catalyzed over a rhodium or iridium complex, respectively. The processes are run at 150-200 °C and pressures around 30-60 bar.\textsuperscript{100}

\[ \text{CH}_3\text{OH} + \text{CO} \rightarrow \text{CH}_3\text{COOH} \ (\Delta H^\circ = -135 \text{ kJ/mol}) \] \hspace{1cm} (4.1)

The oxidation of ethanol to acetic acid, equation 4.2, is an interesting alternative to the methanol carbonylation reactions. The reaction has been known for almost two centuries where it was discovered by Döbereiner\textsuperscript{101}, but it has never been implemented for industrial large scale acetic acid production.

\[ \text{CH}_3\text{CH}_2\text{OH} + \text{O}_2 \rightarrow \text{CH}_3\text{COOH} + \text{H}_2\text{O} \ (\Delta H^\circ = -493 \text{ kJ/mol}) \] \hspace{1cm} (4.2)

In heterogeneous catalysis Pd and Pt have often been the preferred catalytic metals for oxidation catalysis.\textsuperscript{102} The last 20 years, however, it has been proved that the previously considered inert gold has excellent properties as an oxidation catalyst.\textsuperscript{103,104} This is only true, though, if the gold catalysts are prepared in a manner where the gold exists as very small nanoparticles.\textsuperscript{103} The potential of Au catalysts have been demonstrated in several oxidation reactions e.g. for CO oxidation,\textsuperscript{103,105} or oxidation of alcohols with air.\textsuperscript{106}

The oxidation of ethanol with air is in several ways an environmentally friendly alternative to the carbonylation process. First of all, the use of air as oxidation medium is
probably the most “green” and environmentally friendly oxidation medium available. Secondly, methanol is produced from syngas, equation 4.3, which again is available from the energy consuming steam reforming of methane, equation 4.4. About one third of the methane is used as heating source in the endothermic steam reforming reaction. Therefore, for every mol of acetic acid produced by the carbonylation of methanol one mol of CO$_2$ is released to the atmosphere, resulting in a C-factor of 0.7 for the process.

\[
2H_2 + CO \rightarrow CH_3OH \quad (\Delta H^\circ = -90 \text{ kJ/mol}) \quad (4.3)
\]

\[
CH_4 + H_2O \rightarrow CO + 3H_2 \quad (\Delta H^\circ = 206 \text{ kJ/mol}) \quad (4.4)
\]

As a result of both the economical and environmental prospects it was decided to look carefully into formation of acetic acid by aqueous-phase oxidation of ethanol with air in the presence of a heterogeneous gold catalyst.

### 4.1 Experimental

#### 4.1.1 Catalyst preparation

1 wt% Au/MgAl$_2$O$_4$ catalysts were prepared by deposition-precipitation of HAuCl$_4$∙3H$_2$O on HSA (high surface area) spinel similarly to the procedure described by Haruta.$^{103}$ 51.3 mL of an aqueous solution of HAuCl$_4$ [0.01 M] is adjusted to a pH-value between 8 and 10 by addition of an aqueous solution of Na$_2$CO$_3$. 10.0 g of MgAl$_2$O$_4$-support$^{107}$ (tabletized, crushed and sieved to a particle size of 100-250 µm) is added to the solution and the mixture is aged for an hour at 50 °C. The suspension is filtered, and the catalyst is washed until the filtrate is free of chloride, tested with addition of AgNO$_3$ to the used washing water. The gold is now deposited on the support as Au(OH)$_3$. Following, the catalyst is dried in an oven at 110 °C, and finally it is calcined at 500 °C for 2 h. For comparative experiments catalysts containing 1 wt% Pd and Pt supported on MgAl$_2$O$_4$ were prepared by incipient wetness impregnation of hydrochloric acid solutions of PdCl$_2$ and PtCl$_6$, respectively. The catalysts were calcined in the same way as the gold catalyst.
4.1.2 Activity measurements

In a typical experiment, 150 mg of catalyst and 10 ml of aqueous 5 wt% ethanol are placed in a 50 mL stirred Parr autoclave. After closing the autoclave a technical air (20% O_{2}, 80% N_{2}) pressure of 30-50 bar is added and the autoclave is sealed. Afterwards the autoclave is heated to a temperature between 90 °C and 200 °C. When the set point is reached the autoclave is kept under stirring for 4-45 h, while pressure and temperature are monitored. Next, the autoclave is cooled to 5 °C and the gas is collected in a gasbag for gas chromatography analysis (GC). 1 ml of the liquid is removed and used for GC analysis (the GC was equipped with both FID and TCD detectors) and the remaining liquid including the catalyst is transferred quantitatively with water to a beaker. The used catalyst and the remaining liquid are titrated with NaOH to determine the concentration of acetic acid, and compared with the results from GC and GC-MS experiments. Also the content of Al, Mg and Au in solution after each run was measured occasionally by ICP-MS (inductively coupled plasma mass spectrometry).

4.2 Results and discussion

The fermentation broth from conversion of different types of biomass typically consists of around 5 wt% ethanol. To prevent any further expensive cleanup of this solution it was decided to analyze a simulated bioethanol also consisting of a 5 wt% aqueous solution. The support, MgAl_{2}O_{4}, was chosen due to its stability at high water pressures and because it can be considered completely inactive in redox processes. The catalytic effect can thereby be expected to be due to catalytic activity of the metals and not to a synergistic effect with the support.

As a starting point it was investigated whether the prepared gold catalyst would be active for the aqueous phase oxidation of ethanol into acetic acid, and the results were compared to similar experiments performed over Pt and Pd catalysts. The results are shown in Table 4-1. Au was significantly more active and selective towards acetic acid than the Pt catalyst but also more selective than the Pd catalyst. The Au catalyst only seemed slightly more active than the Pd catalyst, which however had almost twice the molar concentration. Another difference between the metals is that Au has CO_{2} as the
main byproduct whereas Pd and Pt have acetaldehyde. Clearly the Au catalyst has shown some interesting potential for the reaction and additional experiments were further performed to find optimal process conditions.

<table>
<thead>
<tr>
<th>1 wt% metal on MgAl₂O₄</th>
<th>Temperature (°C)</th>
<th>Air pressure (bar)</th>
<th>Time (h)</th>
<th>Conversion (%)</th>
<th>Yield (%)</th>
<th>STY [a] (mol∙h⁻¹∙L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>180</td>
<td>30</td>
<td>4</td>
<td>97</td>
<td>83</td>
<td>0.21</td>
</tr>
<tr>
<td>Pt</td>
<td>180</td>
<td>30</td>
<td>4</td>
<td>82</td>
<td>16</td>
<td>0.047</td>
</tr>
<tr>
<td>Pd</td>
<td>180</td>
<td>30</td>
<td>4</td>
<td>93</td>
<td>60</td>
<td>0.15</td>
</tr>
</tbody>
</table>

[a] Space time yield calculated as mol product divided by volume solution and reaction time.

In Figure 4-1 the temperature and pressure dependencies are investigated under the same conditions as in the previous experiments. From the temperature study it is seen that increased temperature leads to increased ethanol conversion and higher acetic acid yield. However, above 170 °C the conversion is more than 90 % and a further increase in temperature has only little effect. The pressure study shows that the pressure has little or no effect on the conversion and selectivity to acetic acid. The slightly increasing yield of acetic acid at higher pressures is probably due to more oxygen available. At high ethanol conversions the oxygen is almost completely consumed, an increased partial pressure of oxygen under these reaction conditions will therefore probably lead to a slight increase in reactivity/selectivity.

![Figure 4-1](image)

**Figure 4-1** Ethanol conversion (filled circles) and acetic acid yield (empty circles) with 10 mL of 5 wt% aqueous ethanol after 4 hours reaction using 150 mg of 1 wt% Au/MgAl₂O₄ catalyst. Left: temperatures in the range of 90-200 °C and an air pressure of 30 bar. Right: pressures in the range of 30-45 bar and a temperature of 150 °C.
A study of the reaction evolution with time was made at 150 °C, 30 bar air pressure, 10 mL 5 wt% aqueous ethanol solution and 150 mg of 1 wt% Au/MgAl₂O₄. Figure 4-2 indicates rapid increase in conversion of ethanol and yield of acetic acid the first 4-5 h, hereafter it levels off and gets close to 100 % conversion and 80 % yield. An increased yield is possible by tuning the reaction a bit, in particular increasing the available amount of oxygen. A yield of 92% was for instance achieved after 8 h run at 180 °C and 35 bar air pressure.

Figure 4-2 Performance of 150 mg of 1 wt% Au/MgAl₂O₄ catalyst in the oxidation of 10 mL aqueous 5 wt% ethanol with air at 150 °C and 30 bar (filled circles: ethanol conversion; empty circles: acetic acid yield).

The reaction mixtures were also analyzed by ICP-MS to examine the stability of the catalyst in the solution. Less than 1 % of the MgAl₂O₄ was found to be lost with these experiments. In another experiment the catalyst was filtered off and reused three times after which it had lost most of its activity. The GC measurements were occasionally compared with titration experiments, where an aqueous solution of sodium hydroxide was used to determine the acetic acid concentration. The experiments always gave identical results within the experimental uncertainties.
4.3 Conclusion

In this chapter it is shown how an aqueous solution of ethanol could be efficiently oxidized to acetic acid over a gold catalyst. The reaction has the possibility to significantly increase the value of the feed since the acetic acid is much more valuable than ethanol. As an additional benefit this would also lower the CO$_2$ released to the atmosphere by around 700 kg per ton acetic acid produced.

This project was the initial project in the area of catalytic oxidation reactions over gold catalysts. The area has later turned into one of Center for Sustainable and Green Chemistry’s core areas with several publications on oxidation of alcohols, polyols, aldehydes and amines.
5 Ethanol dehydration on solid acid catalysts

Dehydration and cracking reactions over solid acid catalysts are examples of processes, which already have found industrial use but still contain an unexploited potential. Zeolites, for example, are used in the FCC (fluid catalytic cracking) process for cracking of heavy petroleum feeds to lighter hydrocarbons like gasoline. Solid acid catalysts are very active dehydration and cracking catalysts and have as such found use in dehydrating ethanol to ethylene and converting methanol into hydrocarbons. These processes are, however, not in operation anymore due to the competition from the oil industry, but in the present situation, with high oil prices, an increased environmental concern and with possible improvements in the technology and catalyst development, these processes could once again gain significant importance.

5.1 Low temperature dehydration

Dehydration of ethanol to ethylene can potentially be a very important reaction in a renewable chemical industry. Ethylene is the world’s largest scale chemical with a yearly production of more than 110 million MT in 2005 with an expected growth rate of around 4 % per year. The main uses of ethylene are the production of ethylene oxide, ethylene dichloride and polyethylene, which again primarily are used for the manufacture of various plastics.

Around 95 % of all ethylene is produced from steam cracking of petroleum hydrocarbons. This is a very energy intensive reaction that requires temperatures from 500-850 °C. In fact only around 20 % of the energy input is used on the actual conversion to olefinic products whereas the rest is used to control pumps, turbines etc. Also, the overall economy of the process is best using light hydrocarbon feeds, but along with the depletion of the fossil resources a feed shift towards naphtha and heavier petroleum feeds is seen, which again leads to a lower efficiency and higher expenses.
The climate impact of the ethylene manufacture is also quite high under present conditions. The C-factor from production of ethylene from ethane has been calculated to 0.65\textsuperscript{118}. However, with the change to a heavier feedstock the energy consumption goes up and so does the CO\textsubscript{2} released to the atmosphere. Actually, the energy consumption increases with almost 50% going from an ethane feed to naphtha feed\textsuperscript{117}.

One of the most promising alternatives to steam cracking of fossil resources for the manufacture of ethylene is the dehydration of bioethanol over a heterogeneous acid catalyst. The process has been demonstrated on industrial scale over activated or supported alumina or phosphoric acid at temperatures above 300 °C\textsuperscript{119}. This, however, happened before the steam cracking process took over due to the previously very low oil prices. Many catalyst studies have been made for this reaction, and above all solid acid catalysts and mostly different types of zeolites have received attention\textsuperscript{120,121}.

Ethylene from bioethanol is perhaps one of the most interesting possibilities in introducing sustainability into the chemical industry. The depletion of oil and natural gas with its increasing prices together with a rise in CO\textsubscript{2} release due to the use of heavier petroleum feeds, leads to a situation where other processes can compete in both an environmental and economical manner. At the same time the production of bioethanol increases rapidly and it is manufactured at a relatively low cost of around half that of ethylene. One of the advantages of using bioethanol is that the ethanol does not have to be distilled to fuel grade ethanol, but also that the product is easily isolated from the feed simply by condensing out water. Moreover, the process is executed at fairly low temperatures of less than 200 °C on the most acidic solid acid catalysts.

\textbf{5.1.1 Experimental}

The experiments with ethanol dehydration were performed in a continuous flow fixed bed reactor with a 25 vol% ethanol/water solution added through a HPLC pump, evaporated by heating tape at 150-200 °C and carried through the catalyst bed with a 40 mL/min flow of helium. The WHSV for the experiments was 2.8 h\textsuperscript{-1}. The effluent stream
was analyzed by an Agilent 6890 GC equipped with a Varian PoraPlot Q-HT column to the FID detector. A complete description of the setup can be found in section 2.3.1.3.

5.1.2 Results

Several solid acid catalysts were tested for the reaction and compared to the old industrialized catalyst. Some of the most promising are shown in Figure 5-1, where it is seen that a standard zeolite like HZSM-5 is significantly more active than the activated alumina catalyst and similar to a sulfated zirconia. Most efficient, however, were triflic acid (trifluoromethanesulfonic acid, CF$_3$SO$_2$H) impregnated on ZSM-5 and a heteropoly acid like the one shown in Figure 5-1 (H$_3$PW$_{12}$O$_{40}$ on SiO$_2$), which gave almost identical temperature/ethylene yield curves.

The results from Figure 5-1 indicate that the acidic strength of the solid acids used is of major importance to the actual temperature needed for a full conversion of ethanol to ethylene. However the very acidic catalysts also seem to deactivate faster. As an example two different HZSM-5 catalysts can be mentioned, one with a Si/Al ratio of 20 and one with 40. The most acidic had a significant and continuous deactivation...
throughout a 5 day run, whereas the HZSM-5 with a Si/Al ratio of 40 had a short initial
deactivation and then was completely stable throughout a 4 day run.

Ethylene is not the only product found under dehydration of ethanol. In general the first
dehydration step is a dehydration of two ethanol molecules into diethyl ether and water
(5.1), which is subsequently dehydrated into two molecules of ethylene (5.2), or
decomposed to an ethylene and ethanol molecule (5.3). It is illustrated in Figure 5-2 on
the example of a $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2$ heteropoly acid sample but the same trend was seen
for all the tested catalysts. It looks like a classical example of a reaction with three
components where $\text{A} \rightarrow \text{B} \rightarrow \text{C}$, though it is expected that a direct dehydration of
ethanol to ethylene (5.4) is also possible.$^{122}$

$$
2\text{CH}_3\text{CH}_2\text{OH} \rightarrow (\text{CH}_3\text{CH}_2)_2\text{O} + \text{H}_2\text{O} \quad (\Delta H^\circ = -24 \text{ kJ/mol}) \\
(\text{CH}_3\text{CH}_2)_2\text{O} \rightarrow 2\text{CH}_2\text{CH}_2 + \text{H}_2\text{O} \quad (\Delta H^\circ = 115 \text{ kJ/mol}) \tag{5.2}
$$

$$
(\text{CH}_3\text{CH}_2)_2\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{CH}_2\text{CH}_2 \quad (\Delta H^\circ = 69 \text{ kJ/mol}) \tag{5.3}
$$

$$
\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_2\text{CH}_2 + \text{H}_2\text{O} \quad (\Delta H^\circ = 45 \text{ kJ/mol}) \tag{5.4}
$$

Figure 5-2 Ethanol conversion and selectivity to products illustrated as the carbon percentage yield of
each specie for the run with the heteropoly acid ($\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2$), (♦ unconverted ethanol, ■ ethylene
yield. ▲ diethyl ether yield). Process conditions were 0.04 mL/min 25 vol% ethanol/water, 200 mg
catalyst, 40 mL/min He flow, ambient pressure and a WHSV of 2.8 h$^{-1}$. 

70
5.1.3 Conclusion

Ethanol can effectively be converted into diethyl ether or ethylene at low temperatures over solid acid catalysts and thereby decrease the energy input for the reaction compared to previously used activated alumina catalysts. At present oil prices it seems economically viable to produce ethylene from bioethanol rather than from petroleum feeds, though with current bioethanol production it is not possible to manufacture the same amounts. Besides the economical potential there will be an environmental benefit from using bioethanol with a significant decrease in the emission of CO$_2$.

5.2 High temperature dehydration

At higher temperatures (300-500 °C) the same type of dehydration experiments gives a completely different product distribution with many types of aliphatic, olefinic and aromatic products. The process is well described in the literature for converting methanol into olefins (MTO) or gasoline (MTG) or in more general terms into hydrocarbons (MTH). The MTG reaction was first discovered in the 1970s, and commercialized by Mobil in the 1980s. The plant situated in New Zealand combined the production of methanol from natural gas with the MTG process and had a capacity of 600,000 ton gasoline per year. However, due to the low oil prices the MTG part was closed down in the 1990s and only the methanol synthesis was kept in production.

Several new large methanol plants, including a 5000 MT per day plant in Saudi Arabia and a 1500 MT per day plant in Russia, have recently been established in corporation with Haldor Topsøe A/S. With these and other new large methanol plants, and a subsequent expected increase in methanol available, a potential reestablishment of MTH plants could easily be imagined. Already the process is projected at some plants for producing small olefins like ethylene and propylene with the probably largest plant being built in Nigeria with a yearly production of 1.3 million MT.

Dehydrating ethanol under similar conditions is another possibility and could be a potential way of converting crude bioethanol into something more valuable. One possibility could be to co-feed bioethanol with methanol and thereby avoid the intensive
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distillation to fuel grade ethanol. Importantly, analyzing the ethanol to gasoline (ETG) process (or ethanol to hydrocarbons (ETH) and ethanol to olefins (ETO)) could give insight into the reaction mechanism of the analogous reaction with methanol. Thus, ETG and MTG (and mixtures with and without water) experiments were performed and compared, both with regard to their product distribution but most importantly concerning the retained material in the zeolite catalyst pores, to gain knowledge of the possible reaction mechanism.

5.2.1 Hydrocarbon pool model

The MTG process has been intensively studied by many groups and a plausible reaction mechanism has been suggested via the hydrocarbon pool model.\textsuperscript{130,131} The idea behind the hydrocarbon pool mechanism is that the actual catalytic sites should be found as organic-inorganic hybrids consisting of a cyclic organic species contained within the zeolite framework. The different organic species inside the zeolite pores acts as the hydrocarbon pool from which smaller products are formed by cracking reactions. The idea is illustrated in a very simplified manner in Figure 5-3 with a xylene molecule in the hydrocarbon pool working as the actual catalyst via integration in the zeolite framework. The aromatic compound combines with the zeolite and methanol add up to give some type of organic-inorganic compound which cracks down to give for instance an olefin and regenerates the aromatic compound.

![Figure 5-3](image-url) A simplified reaction scheme showing the principle behind the hydrocarbon pool model in the MTG reaction. Methanol reacts with hydrocarbons trapped inside the zeolite giving a charged organic-inorganic hybrid that then loses a smaller fragment giving back the same or a similar hydrocarbon.
The proposed hydrocarbon pool model relies primarily on the work by Kolboe et al., who have made extensive studies on the retained material in the zeolite pores after MTG reactions over several zeolite types like H-beta, SAPO-34 and HZSM-5. It has been suggested that the ETG reaction gives similar products as the MTG reaction. However, the retained material in the ETG reaction has not previously been explored, but with the similarities between the two reactions the retained material for the ETG process could perhaps give important insight into the MTG reaction.

5.2.2 Experimental

5.2.2.1 Catalytic tests
The catalyst used in this study was HZSM-5 (Si/Al = 11.5), supplied by Zeolyst International and fractionized to 300-700 µm. The same experimental setups as previously described in section 2.3.1.3 and 2.5 were used for the present study. Examination of the catalysts was performed at temperatures from 400-450 °C, at ambient or 10 bar pressure, a WHSV of 6-9 h\(^{-1}\), and reaction times varying from 15 min to 24 h.

5.2.2.2 Analysis of retained material
For determining the retained material in the zeolites a replication of the method employed by Guisnet et al. was made in order to gain insight into the ethanol to gasoline reaction. In a closed Teflon vial 100 mg of used catalyst was dissolved in 3 ml of 20 wt% hydrofluoric acid. The mixture was shaken and allowed to stand overnight. When the zeolite was completely dissolved, the retained material was extracted with 1 ml of dichloromethane with added chlorobenzene as an internal standard. The organic phase was filtered and most of the dichloromethane was allowed to evaporate; Arstad et al. have shown that this should not have any effect on the product distribution in the sample. The concentrated samples were then analyzed on GC-MS (Agilent 6850 GC fitted with a quadruple mass spectrometer detector 5975C).
5.2.3 Results

For a comparison between the ETG and MTG processes similar experiments were performed at 1 bar and 10 bar with an aqueous 96 % ethanol or methanol solution. The gaseous product distribution was almost identical for the two experiments as shown in Figure 5-4 and also the condensed liquid organic phase had a very comparable product distribution, cf. Figure 5-5. These product patterns were collected from experiments conducted at ambient pressure after 2 h run time over 300 mg HZSM-5. At 10 bar product distribution shifts toward liquid hydrocarbon products but ETG and MTG processes still give very similar product distributions. The main differences in the product distribution between the MTG and the ETG runs are found in the organic liquid phase, where small amounts of tri- and tetra-methyl benzene are found in the MTG reaction but not in the ETG reaction. In contrast some ethyl- and ethyl methyl benzenes are found in the ETG but not in the MTG effluent organic phase.

![Figure 5-4](image)

**Figure 5-4** Comparison of the gaseous product distribution from ETG and MTG runs at 400 °C, ambient pressure and a WHSV of 6 h⁻¹. The chromatograms are obtained after 2 h run on stream over 300 mg of HZSM-5, using FID detector.
Ethanol dehydration

Figure 5-5 Comparison of product distribution for the organic liquid phase from ETG and MTG processes at 400 °C, ambient pressure and a WHSV of 6 h\(^{-1}\). The chromatograms are showing the product distribution in the collected organic phase obtained after 2 h reaction over 300 mg HZSM-5.

With the almost identical product distributions of the MTG and ETG processes it could be expected that the retained material in the zeolite pores would also be the same for the two reactions but that was surprisingly not the case. Figure 5-6 shows the most abundant species found in the retained material after dissolving the zeolites. The retained material for the MTG runs contained only different methyl benzenes, whereas the retained material from the ETG runs primarily consisted of ethyl benzenes and some ethyl methyl benzenes. According to the product distribution reflected in Figure 5-5 and Figure 5-6 it is seen that the truly retained material consists of pentamethyl benzene and hexamethyl benzene for the MTG run and the two lowest rows in Figure 5-6b for the ETG run, whereas the remaining species apparently are able to escape through the zeolite pores as they are also seen in the liquid organic phase.
For a more thorough analysis of the retained material in the HZSM-5 catalyst the changes in the product distribution of the retained material over time have been investigated. For this analysis the reactor was operated at 450 °C and after 15, 60 or 120 minutes, the reactor was quench cooled by being immediately moved to another oven where the catalyst was flushed with helium for 5 minutes at around 50 °C to remove small molecules not trapped inside the zeolite pores. Results from the GC-MS analysis of the retained material are shown in Figure 5-7. The results indicate an increase in the amount of triethyl methyl benzene and tetraethyl benzene over time with a simultaneous decrease in the other ethyl methyl benzenes. This implies that the methyl benzenes are reacting faster than the ethyl benzenes and that especially triethyl methyl benzene and tetraethyl benzene are reacting so slowly that they might be considered “dead ends” from which no further reaction occurs. Hexamethyl benzene was also found by Bjørgen et al. to be such a dead end for the MTG reaction over HZSM-5 zeolite.
Considering that the most reactive species of the hydrocarbon pool are the same for both MTG and ETG processes it is likely that an almost identical product distribution appears in both gaseous and liquid products. It could be argued that the true reaction mechanism in the zeolite is a reaction between either dimethylether (DME) for the MTG and ethylene for the ETG since both of these are formed instantaneously by dehydration over the acid catalyst under these temperatures. Consequently what actually happens with the effluent stream during deactivation is an increase in DME and ethylene for the
MTG and ETG processes, respectively, no methanol, or ethanol, is seen in the effluent stream. It seems like the catalyst used for the ETG runs deactivates faster than for the MTG runs. Two possible ways of deactivation of the zeolites can be imagined, one is the formation of coke, which occurs especially on the catalyst with a long time on stream. Secondly the formation of the very slowly reacting (or dead end) molecules like tetraethyl benzene, which are increasing over time, appears to deactivate the catalyst by occupying the acidic sites within the zeolite framework. The reason why catalysts in ETG runs deactivates faster than in the case of MTG runs could perhaps be related to the formation of species like triethyl benzene and tetraethyl benzene which can react further into aromatic coke, and thereby act as deactivation precursor in both of the suggested deactivation scenarios.

The effect of water was also investigated for both ethanol and methanol runs as well as mixtures thereof. Water has a negligible effect on the product distribution but might prolong the catalyst’s life time slightly. Mixing ethanol and methanol in different ratios gave almost identical effluent products, though interestingly, ethyl benzenes were only observed for runs with more than 50 % ethanol (on a carbon basis) in the feed. This indicates that when relatively small amounts of ethanol are present, the reaction mechanism goes entirely via the MTG hydrocarbon pool, possibly because the reaction rates are faster for these species than for the ones containing ethyl benzenes. Or put in another way at low ethanol partial pressures the ethylene (ethanol) entering the zeolites appears to be completely reacted via the MTG hydrocarbon pool, but at high ethanol partial pressures the resulting increased amount of ethylene available leads to the formation of ethyl benzenes.

5.2.4 Conclusion

It is reasonable that the ETG and MTG processes give almost identical product distributions since the products originate from the same type of retained species via the hydrocarbon pool model. The main difference in the liquid products is some small amounts of different ethyl and methyl substituted benzenes, which are not completely retained in the zeolite framework. Accordingly the formation of ethyl benzenes has only
minor effect on the products formed, but are possibly leading to a faster catalyst deactivation. However, mixing ethanol in a methanol rich stream does not lead to ethyl benzenes and thus should not decrease the life time of the catalyst. Also it was found that water in the feed had almost no effect neither on the product distribution nor the catalyst life time. One way of adding value to crude bioethanol, available in places located close to large methanol plants, could therefore be simply adding it to the methanol stream of a possible MTG plant for the production of olefins or high octane gasoline.
6 Conclusion and outlook

It is at present not known what the future will look like in terms of energy, fuel and chemicals, although, one thing is sure: The fossil resources used today will not last forever, and now it seems to be the right time for a gradual conversion towards sustainability by switching to renewable resources. Whether the future will be built on a hydrogen society, nuclear fusion power, electricity from solar cells or perhaps biomass and waste utilization is not possible to say. Most likely the best solution will be a combination of various options. The important challenge for scientists and engineers is careful research and development of all the different possibilities, so that society can make wise decisions for a sustainable future based on these results.

The chemical industry is facing a change from being completely based on fossil resources. In the future chemical industry renewable resources could be the primary feedstock. In this thesis it has been suggested how a number of chemicals can be produced from renewable resources. In particular there is potential in primary renewable building blocks, which by simple catalytic reactions can be converted into some of the most important chemicals used in the petrochemical industry today. This strategy might be the most straightforward way of moving towards a renewable chemical industry, though in the long perspective a production of chemicals with similar properties as commodity chemicals used today might be advantageous by more efficiently utilizing the biomass or waste in the manufacture of chemicals.

The contemporary chemical industry has been effectively optimized during the last century and it is therefore not easy to develop new routes for producing chemicals which can economically compete with those produced from fossil resources. However, along with depletion and the simultaneously rising costs of fossil resources, the competitive potential of chemicals produced from biomass is increasing. The routes from renewable resources also have the advantage of being more environmentally friendly.
In the present study it is shown how two important renewable alcohols, ethanol and glycerol, can be converted to syngas which can be further used in methanol synthesis or in a Fischer-Tropsch process to produce synthetic fuel. Alternatively they can be converted to hydrogen for use in fuel cells in a possible hydrogen society or for the manufacture of other industrial chemicals. Additionally the conversion of ethanol to acetic acid by oxidation over a gold catalyst and the dehydration to ethylene over solid acid catalysts have been examined. Both reactions show very promising potential and can directly substitute similar important petrochemical reactions. It should be emphasized that these reactions seem to have the potential to outcompete the routes based on fossil resources, not only on the environmental level but also economically.

This area of chemical research has an unexploited potential, and hopefully this thesis will inspire other scientists and engineers to continue the development of new routes towards a renewable chemical industry.
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74. Equilibrium calculations are performed with the program *HSC Chemistry 5.1* by Outokumpu Research Oy, Finland
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Further details about the catalysts are available from the supporting material to reference [90] on http://www.angewandte.org


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