Impact of chemical reactions in the gas phase on the in-situ combustion process: an experimental study

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Abstract

In-Situ Combustion (ISC) is a thermal enhanced oil recovery method. Therefore, air or oxygen-enriched air is injected in the reservoir. The oxygen reacts with part of the hydrocarbon forming heat and combustion products. The released heat increases the temperature locally in the reservoir and lowers the viscosity of the oil. Formed gaseous products additionally enhance the oil production due to miscible and immiscible gas drive.

Although worldwide the application of ISC is limited, research on the underlying processes is extensive. In particular, discussions focus on the question whether it is better to describe oil recovery by ISC as thermal recovery method with minimal description of the occurring chemical reaction or if it is crucial to include more detailed descriptions of the occurring chemical reactions. Most ISC research focuses on the description of reaction kinetics and lacks the description of other phenomena involved, e.g. gas phase reactions, the influence of porous media and the effect of flow. The focus of this experimental study is to determine the relevance of chemical reactions in the gas phase for the success of ISC and to get a better understanding of the temperature influence on ISC.

For the experiment a vertically-positioned stainless steel tube filled with a mixture of sand and oil was heated to a desired temperature. From below air was injected, oil and exhaust gases are produced from the top of the tube. The outlet gas was analysed with the help of a gas chromatograph. Liquid produced from the tube was collected and characterized with the help of refractive index analysis. The sand was retrieved after the experiment and categorized based on visual observations. Additionally, the organic content in the sand after the experiment was determined by weight loss by heating the sand gradually to 500°C. Thermal Gravity Analysis under nitrogen and air atmosphere of oil, sand and oil+sand samples was performed. The determined weight loss as function of the temperature together with the analysis of the outlet gas helped to identify the occurring chemical reactions.

The experiments showed that gas phase reactions should be incorporated in the description of ISC processes. The actual gas phase combustion could not be proven unambiguously, typical ISC temperature profiles were not seen and the reactions were not self-sustaining. It was shown that reactions occur in the gas phase. For a pure component oil cracking and recombination in combination with combustion was behaving similar as the crude oil in ISC, although the temperature range for these reactions are wider for the crude oil. Initial low oil saturations have no impact on the general chemical combustion behaviour; the position of oxidation products depends on the initial saturation. At low temperature the formation of solid components was due to oxygenation and not to anaerobic cracking. Still a number of underlying processes occurring during ISC are not completely understood. In particular, the effect of pressure on the chemical reactions, on the occurrence of a gas phase and the resulting outlet gas need further investigation.
## Table of Contents

Abstract ........................................................................................................................................... 3

1. Introduction ............................................................................................................................... 6
   1.1 In-Situ Combustion (ISC) .................................................................................................... 6
   1.2 Objective ............................................................................................................................. 7
   1.3 Outline ................................................................................................................................ 7

2. Theory ......................................................................................................................................... 8
   2.1 Chemical Reactions ................................................................................................................ 8
      2.1.1 Low-Temperature Oxidation ......................................................................................... 8
      2.1.2 Cracking ......................................................................................................................... 8
      2.1.3 Combustion .................................................................................................................... 8
      2.1.4 Reaction Kinetics .......................................................................................................... 9
   2.2 Phase Behaviour ..................................................................................................................... 11
      2.2.1 Gas-liquid Phase Distribution ....................................................................................... 11
      2.2.2 Kelvin Equation ............................................................................................................. 11
   2.3 Theoretical Outline for Experiment ....................................................................................... 12

3. Experiment ................................................................................................................................. 13
   3.1 Materials ............................................................................................................................... 13
   3.2 Experimental Apparatus ....................................................................................................... 13
   3.3 Experimental Procedures ..................................................................................................... 15
   3.4 Experimental Lay-out .......................................................................................................... 16
   3.5 Further Used Apparatus ....................................................................................................... 17
      3.5.1 Weight-loss determination ............................................................................................. 17
      3.5.2 Thermal Gravimetric Analysis ...................................................................................... 17
      3.5.3 Refractive Index .......................................................................................................... 17
      3.5.4 Microscopy .................................................................................................................. 17
   3.6 Error Analysis ....................................................................................................................... 18
      3.6.1 Temperature distribution .............................................................................................. 18
      3.6.2 Output Gas Analysis ..................................................................................................... 19
      3.6.3 Ideal Gas Behaviour ..................................................................................................... 20

4. Results & Discussion ..................................................................................................................... 22
   4.1 Oil Saturation ......................................................................................................................... 22
      4.1.1 Temperature and Outlet Gas analysis ............................................................................ 22
      4.1.2 Liquid Production ......................................................................................................... 24
      4.1.3 Sand Analysis ................................................................................................................. 25
      4.1.4 Summary of Saturation Experiments .......................................................................... 28
4.2 Nitrogen Injection ........................................................................................................... 28
  4.2.1 Temperature and Outlet Gas Analysis ........................................................................ 28
  4.2.2 Liquid Production .................................................................................................... 30
  4.2.3 Sand Analysis .......................................................................................................... 32
  4.2.4 Summary Nitrogen Injection Experiments ............................................................... 33
4.3 Rotterdam Field Oil ....................................................................................................... 33
  4.3.1 Temperature and Outlet Gas Analysis ....................................................................... 34
  4.3.2 Liquid Production .................................................................................................... 37
  4.3.3 Sand Analysis .......................................................................................................... 38
  4.3.4 ISC of Rotterdam Field Oil ..................................................................................... 40
4.4 TGA Results .................................................................................................................. 40
  4.4.1 TGA of Hexadecane ............................................................................................... 40
  4.4.2 TGA of Rotterdam Field Oil ................................................................................... 42
4.5 Combining Results and Discussion .............................................................................. 43
5. Conclusions ...................................................................................................................... 45
6. Recommendations .......................................................................................................... 46
Acknowledgements ............................................................................................................. 47
References ............................................................................................................................ 48
Additional Figures ............................................................................................................... 49
Appendix A .......................................................................................................................... 52
Appendix B .......................................................................................................................... 57
Appendix C .......................................................................................................................... 58
1. Introduction

In this chapter the subject of this thesis is introduced. The need for this study is explained, after which the objective is presented. With this the complete framework of thesis is given.

1.1 In-Situ Combustion (ISC)

Some oil fields contain very viscous oils with complex chemical composition, often called heavy oils. One method to produce these heavy oils is enhancing their mobility, this can be done by solvent injection for de-asphalting or for dilution, by heat injection for thermal cracking and oxidation or by catalytic upgrading (Yang and Gates, 2009b). Steam injection is the most applied thermal recovery method (Manrique et al., 2010). However, the generation of steam requires large amounts of energy. Additionally, the necessary upgrading to maintain steam quality at reservoir conditions is energetic unfavourable (Yang and Gates, 2009b).

The second most common thermal recovery method is in-situ combustion (ISC). For ISC part of the oil is combusted supplying heat and gaseous solvents to increase oil mobility. In the last decade ten reports are published about ISC field projects (Manrique et al., 2010). Most of these projects report difficulties with respect to process control and HSE issues.

For ISC air (or oxygen enriched air) is injected in the reservoir, see Figure 1. The hydrocarbon present in the formation partly combusts reacts with the oxygen releasing energy. Because of the activation energy in most cases initially oil needs to be ignited to start the combustion reaction. The energy released by the exothermic reaction sustains further reactions and lowers the viscosity of the oil downstream of the combustion zone. The nitrogen and produced other gaseous components displace this oil by either miscible or immiscible flooding.

Figure 1 Schematic drawing of processes in ISC. Air is compressed, pumped into reservoir; there the oxygen reacts with the oil releasing energy. The produced heat initiates combustion of the oil or vaporizes part of the oil. Gaseous (reaction) components are condensed ahead of the combustion zone. Due to the lowered oil viscosity the oil bank partly can be produced by gas flooding. From Shell Canada Energy, M. Zatka 2009

Reactions at reservoir conditions are complex to predict. One aspect is that commonly reaction schemes are defined for oils with well-known compositions at atmospheric pressure. However, real crude oils consist of a huge number of components and their composition is often not very well defined. Further, ISC is applied at reservoir conditions so that the pressure is clearly above atmospheric pressure. Another aspect is that during in-situ combustion a number of reactions occur simultaneously influencing each other. Unfortunately, the relation between these reactions
is not fully identified, even not for well-defined model oils. As a last point, the influence of the porous medium and its constituents on the chemical reactions is not fully known.

A number of conceptual combustion models describing ISC have been formulated in the past (Alexander et al., 1962; Belgrave et al., 1993; Fassihi, 1981). Most of these models assume liquid phase combustion as the source of energy to sustain ISC. However, recent studies at the Delft University of Technology (KhoshnevisGargar et al., 2010) and other researchers (Yang and Gates, 2009a) showed that combustion also takes place in the gas phase.

In this study, the influence of gas phase combustion on ISC is investigated experimentally. This thesis is regarded as a start of a study investigating the relevance of gas phase combustion for ISC.

1.2 Objective
The objective of this thesis is best posted by a question:

What is the impact of the gas phase reactions in an ISC process?

To answer this question, first a literature study was done to identify crucial parameters. The crucial parameters to distinguish the impact were determined to be: saturation, temperature and oil type. The impact of these parameters was then tested by (combustion) tube experiments. The experimental set-up was designed and constructed. The results of the experiments for the various parameters were combined for a conclusion.

1.3 Outline
In this chapter 1 the topic of ISC is introduced and the reason for this thesis is presented. The objective of this study and the pathway to obtaining the objective is given as well.

In chapter 2 the chemical reactions obtained from literature are presented. Further comments are made with respect to phase behaviour. This will be combined to conclude for the outline of the experiments.

Chapter 3 presents the details on the experiments performed. For the combustion tube experiments the materials involved, the characteristics of the apparatus and the procedures are given. The lay-out of all experiments is presented as well for the combustion tube experiment. Other involved apparatus to gain more information on the results and materials are presented. The chapter ends with the error analysis of the temperature distribution and the exhaust gas analysis.

The results from the experiments are presented and discussed in chapter 4. First the influence of oil saturation on hexadecane combustion is presented. Then the influence of nitrogen injection on hexadecane is given to see the effect of cracking and temperature. The results of a crude oil at different temperatures with nitrogen and air injection are presented as well. To further obtain information on the liquids involved, thermal gravimetric analysis of both oils is discussed. All results will be combined at the end of the chapter, to determine common behaviour.

Chapter 5 will conclude on the work performed in this thesis. Recommendations for further research are given in chapter 6. References, additional figures and extra information are forming the end of this paper work.
2. Theory

In this chapter the theory is represented necessary to understand the choice of investigated parameters and the interpretation of the experiments. First the chemical reactions occurring during ISC are described; then other aspects which are important for ISC processes such as phase behaviour and the Kelvin equation are shortly introduced.

2.1 Chemical Reactions

Historically it is assumed that only three kinds of chemical reactions occur during ISC, namely low-temperature oxidation, cracking and combustion. According to this approach oxidation forms products which are further cracked. At high temperatures the cracking products will combust in presence of oxygen.

2.1.1 Low-Temperature Oxidation

At low temperatures hydrocarbons do not combust to carbon dioxide and water but an oxidation addition in combination with radical forming reaction might occur either forming hydroperoxide alcohols or carboxylic acids, aldehydes or ketones (Burger, 1972; Warnatz, 2000). The oxidation of an alkane to an aldehyde can be described by their chemical formulae:

I. \[ CH_3CH_3 + O_2 \rightarrow CH_3COH + H_2O \]

Analysis of bitumen mixtures showed that the released heat is lower for these low-temperature oxidation reactions than for combustions. In general, these reactions are not complete, can produce small amounts of carbon oxides and water, will often lower the viscosity and increase the density and are occurring at lower temperatures (e.g. for bitumen between 200-350°C)(Voussoughi and El-Shoubary, 1989). In ISC models these oxidation reactions are regarded as the first step of ISC.

2.1.2 Cracking

Fassihi described cracking for ISC by “the process which leaves fuel on the solid matrix as the crude oil moves forward” (Fassihi, 1981). This residue is identified as the fuel for the actual combustion reaction. In the past it was discussed whether this fuel is solid carbon deposited on the rock, or so-called coke (Fassihi, 1981). Nowadays, it is widely accepted that coke is formed from a hydrocarbon breaking up into two smaller hydrocarbon chains (Kapadia et al., 2010). This process is commonly called pyrolysis and is generally thought to occur in an oxygen-free environment. However, often there is only low oxygen content present so that the term thermolysis is often used to describe processes at which decomposition of the hydrocarbon occurs due to heating. The cracking of a hydrocarbon into two hydrocarbons can be described by a chemical formula, for instance the cracking of eicosane into octane and dodecane:

II. \[ C_{20}H_{42} \rightarrow C_8H_{16} + C_{12}H_{26} \]

2.1.3 Combustion

The actual combustion describes the reaction of oxygen with hydrocarbon to carbon oxides, water and heat. Only when the combustion is complete water and carbon dioxide are formed. However, carbon monoxide is formed as well when combustion is incomplete:
III.

\[ CH_n + \left[ \frac{2m+1}{2(1+m)} + \frac{n}{4} \right]O_2 \rightarrow \left[ \frac{1}{1+m} \right]CO + \left[ \frac{m}{1+m} \right]CO_2 + \frac{n}{2}H_2O \]

\[
m = \frac{CO_2}{CO}
\]

\[
n = \frac{H}{C}
\]

The ratio of formed \( CO_2 \) and \( CO \) is related to the availability of oxygen (Burger, 1972). According to Belgrave et al. combustion occurs at higher temperatures than LTO, e.g., above 350°C (Belgrave et al., 1993).

2.1.4 Reaction Kinetics

Chemical reactions can be described in general by:

IV.

\[ aA + bB \rightleftharpoons cC + dD \]

, where the various components \((A, B, C\) and \(D)\) react in the ratio corresponding to the stoichiometric numbers \((a, b, c\) and \(d)\). The rate of reaction describes how fast the reaction occurs and can be described by

V.

\[ \text{rate} = k (a - x)^n = -\frac{d[x]^n}{dt} \]

, where \( k \) \((\text{mol}^{-a} \cdot \text{L}^{-a} \cdot \text{s}^{-1})\) the rate constant is introduced, the order of reaction is \(n\) and the decrease of concentration of component \(x\) (concentration of reactant or product) over time is \(d[x]/dt\) \((\text{mol}^n \cdot \text{s}^{-1})\). The temperature dependence of the rate constant is commonly described by an Arrhenius-type equation (Upadhyay, 2006):

VI.

\[ k = Ae^{-E_{act}/RT} \]

, where \( A \) \((\text{mol}^{-a} \cdot \text{L}^{-a} \cdot \text{s}^{-1})\) is the so-called frequency factor or pre-exponential factor, \( E_{act} \) \((\text{J/mol})\) is the activation energy, \( R \) the gas constant and \( T \) \((\text{K})\) the absolute temperature.

A lot of focus in research on ISC is on the determination of the activation energy and the pre-exponential factor of various reactions (Kök and Pamir, 1995; Yoshiki and Phillips, 1985). Kapadia, Kallos and Gates describe 18 reactions for ISC and give their corresponding activation energy and pre-exponential factors (Kapadia et al., 2010). Some of the description of reaction is based on experiments; others are inserted on hypothesis in simulations. In Figure 2 the rate constants as function of the temperature, calculated with these parameters, are depicted. The largest reaction rate constant is found for complete methane combustion (reaction 12 indicated by triangles). See Additional Figure 1 for the reaction scheme leading to methane combustion.
Reaction rate constant for 18 ISC reactions as function of temperature. Data and description of reactions given by (Kapadia et al., 2010). The reaction rates displayed with symbols and lines are the reactions most important for this paper. Reaction 12 is the complete combustion of methane (Yang and Gates, 2009a). Reaction 10 is the LTO reaction describing asphaltene conversion to coke (Adegbesan, 1982). Reaction 2 is the thermolysis of asphaltene to coke. Reaction 4 is the thermolysis of asphaltene to methane (Hayashitani, 1978). Reaction 16F is the formation of methane from coke and hydrogen (Guntermann et al., 1982).

The large reaction rate constant for methane combustion is indicating that methane combustion is expected to be the fastest reaction at already low temperatures. Since it is assumed that methane is not present at the start of experiment, the rate of methane combustion is ultimately controlled by the reactions forming methane (reaction 4 and 16F). For temperatures up to 700°C the methane formation rate constant is higher for reaction 16F than for reaction 4. However, reaction 16F uses a coke which is formed by reaction 2 or reaction 10. In general the reaction rate of reaction 10 is the lowest for all studied reactions. Up to 300°C reaction 2 has a lower reaction constant than reaction 4 so that the faster reaction rate of reaction 16F might be compensated. Methane formation directly from cracking (reaction 4) is fastest up to 300°C, then up to 700°C methane formation from coke and hydrogen, after which direct cracking is the fastest reaction again.

Based on these reaction kinetics the finding of methane in an exhaust gas from a ISC tube experiment is unlikely, since it will be assumed that methane combustion is very rapid. Other gasses in an ISC tube experiment are likely to be present, since they have a low reaction rate constant (reaction 13). But this conclusion has to be taken with care, since the determination of the kinetics is not entirely based on experiments.
2.2 Phase Behaviour
In the previous sub-chapter chemical reactions occurring during ISC were described. This knowledge helps to couple the results of the outlet gas analysis to possible occurring chemical reactions. Unfortunately, the influence of the phase behaviour in general and in the porous medium has not been accounted for in these descriptions.

2.2.1 Gas-liquid Phase Distribution
The vapour-liquid equilibrium ratio $K_i$ describes the distribution of a component $i$ over the coexisting vapour and liquid phase at a given temperature and pressure (Chilingar et al., 1987):

\[ K_i = \frac{y_i}{x_i} \]

, where $K_i$ is the vapour-liquid equilibrium ratio for component $i$, $y_i$ is the mol fraction of the component in the vapour phase and $x_i$ the mol fraction of component in liquid phase. Assuming an ideal gas and an ideal liquid phase, the vapour-liquid equilibrium ratio is described by the ratio of the vapour pressure of component $i$ ($p_i$) at the given temperature at the total pressure ($P$):

\[ K_i = \frac{p_i}{P} \]

In general it can be stated based on equation VIII that an increase of the (system) pressure at the same temperature results in a smaller $K_i$ value, thus less of component $i$ is in the gas phase. If the temperature is increased at constant total pressure, the vapour pressure of the component $i$ increases so that consequently, the $K_i$ value increases. Most models describing the chemical kinetics do not include the gas-liquid distribution in general. In particular, the impact of the pressure on gas phase combustion experiments is of interest.

2.2.2 Kelvin Equation
In 1870 Lord Kelvin (real name is W Tomson) determined a relationship between vapour pressure of a liquid and the curvature of the gas-liquid interface. Some refinements have led to the currently well-known Kelvin Equation (Fisher and Israelachvili, 1981):

\[ \ln \left( \frac{p_i}{p_{is}} \right) = \left( \frac{M_i}{\rho_i RT} \right) \left[ \frac{\gamma}{r_m} - \left( p_i - p_{is} \right) \right] \]

, where $\rho_i$ is the density of liquid component $i$, $M_i$ the molecular weight of liquid component $i$, $p_i$ the vapour pressure at the fraction of the component $i$, $p_{is}$ the vapour pressure of pure component $i$, $\gamma$ the liquid/vapour phase interfacial tension, $r_m$ the radius of gas-liquid interface, $R$ the gas constant and $T$ the absolute temperature. It describes a linear relationship between the pressure ($\ln (p/p_{is})$) and the curvature ($1/r_m$).

In a porous medium the volume of the pore is confined, this increases the curvature of the gas-liquid interface ($r_m$ gets smaller). Thus, according to the Kelvin Equation the vapour pressure of a component $i$ is higher if it is in porous medium or in a capillary. This increase of the vapour pressure in porous medium is crucial for ISC because volatile components evaporate at higher temperatures.
2.3 Theoretical Outline for Experiment
Based on theory studied in this thesis, the effect of cracking to methane or coke should be considered. Therefore nitrogen injection plays a crucial role to observe the difference between the cracking of hydrocarbons and the combustion or oxidation of the hydrocarbons.

Further it is seen that the formation of methane is dominated by different reactions in different temperature regions. Therefore the variation of temperature is important to be allowed to change to study the effect on (gas phase) reactions.

As showed, the reactions are heavenly influenced by the confined space of the porous medium. By changing the oil saturation in the tube, it is hoped that the availability of oil in a pore space is influencing the behaviour of combustion. Hopefully a lower saturation will minimize the pressure increase and favourite gas phase reactions.

Since it is known that real crude oils have complex chemical compositions, the behaviour is best described first by pure component oil. This description can be used to understand and match crude oil combustion behaviour.

All these parameters should be checked in a real combustion tube experiment, since it allows the description of more components involved, such as heat and mass flow.


3. Experiment

In order to meet the objectives of this study, a special combustion tube was designed and constructed to allow the investigation of ISC in a vertical set-up. The main focus of the design was to allow repetition of experiments in a harsh environment with the same equipment, control parameters, data acquisition, to ensure safety during tests and to minimize experimental equipment induced errors. The complete experimental set-up allowed controlling the experiment and analysing the data. Sand and oil are added to a vertical tube, which can be closed at the bottom and top. Heating is applied to the tube from the outside. Gas is injected from the lower end while the effluent fluids are produced at the top.

More than a dozen tests were carried out using this set-up. Some smaller tests were performed to study particular characteristics of the equipment and materials involved. The results of the experiments are discussed in the chapter Results and Discussion; in this chapter the materials involved, the experimental set-up and procedures are described. Further it is clearly stated which parameters have been changed during this study. Other equipment involved in analysing the results will be presented in this chapter as well. An analysis is given to understand the errors and behaviour of some equipment.

3.1 Materials

The sand for the experiments is from the same batch and contains more than 98 vol% of quartz. The P50 grain size of sand passing the filter is 284 micrometre (see Additional Figure 2).

Two oils were used in this work, n-hexadecane and a light crude oil. The n-hexadecane is purchased from Merck Schuchardt OHG and has a purity of 99mol%. The crude oil originates from the Rotterdam Field with an asphaltene content of 4 mass%. In Table 1 the properties of hexadecane and RO are given.

Table 1 Properties of Fluids used in experiments. Properties are given for Room Conditions: 293K and 1 atm.

<table>
<thead>
<tr>
<th>Fluid</th>
<th>Property (at Room Conditions)</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexadecane</td>
<td>Density</td>
<td>770 kg/m³</td>
</tr>
<tr>
<td></td>
<td>Boiling Temperature</td>
<td>287 °C</td>
</tr>
<tr>
<td></td>
<td>Refractive Index</td>
<td>1.4325</td>
</tr>
<tr>
<td></td>
<td>Viscosity</td>
<td>3.5 cp</td>
</tr>
<tr>
<td></td>
<td>Chemical formulae</td>
<td>C16H34</td>
</tr>
<tr>
<td></td>
<td>Melting Point</td>
<td>18°C</td>
</tr>
<tr>
<td>Rotterdam Field Oil</td>
<td>Density</td>
<td>770 kg/m³</td>
</tr>
</tbody>
</table>

The injected gasses were nitrogen and air. Nitrogen was delivered by the Linde Group and had a purity of 99.995 vol%. Cleaned and compressed air was injected as oxygen source.

3.2 Experimental Apparatus

The experimental set-up is shown in Figure 3 and consists mainly of a stainless steel tube with an OD of 2.54cm (1”), a wall thickness of 1.2mm (0.049”) and a length of 25.5cm. The tube was made of steel (ASTM A269 TP316) and is placed vertically in a holder.
At the top and the bottom of the tube two Swagelok (Stainless steel 316) safety valves are installed to control in- and outflow of the tube. The pressure in the tube is monitored by a pressure gauge at the top of the tube. Six thermocouples (TC) (ThermoCoax Type K) are inserted to allow monitoring of the temperature at different locations in the tube, from the top one thermocouple and from the bottom five thermocouples (see Figure 4). An extra TC is added on the outside of the tube to monitor the temperature change induced by the heating tape. The temperature data of five thermocouples is collected every second on a computer using an in-house data acquisition system.

To heat the tube two Isopad IS-SP heating tapes are wrapped around the tube. The heating tapes are regulated with an Eurotherm temperature regulator based on the temperature determined using the two thermocouples; TC5 and TC2 (see Figure 4). The heating tapes can withstand temperatures up to 450°C. Between the tube and the heating cable, an electrical resistant tape is placed to minimize electrical leakage. The complete tube is insulated with Thermal Ceramic Superwool to prevent heat loss.

Gas is injected unheated from the bottom with the injection rate controlled by a Mass Flow Meter, Sierra Instruments Smart Track 2 Model 100 (with an accuracy of 0.005cc/min). To prevent sand falling out of the tube into the bottom valve, a filter, made of sintered stainless steel (Siperm R 316L), is placed in the bottom end of the tube. The Siperm filter has a low permeability, reducing gravity-based liquid flow out of the tube. It also has 5 small holes to allow positioning of the 5 TCs.

At the outlet a line leads the effluent fluids to a Gas Chromatograph (GC). In order to prevent clogging of the GC column by heavier components, a cooling trap made of glass is placed before the inlet port of the GC. Further, a molecular sieve is placed directly at the inlet of the GC. An Agilent Cerity Portable 3000 Mirco Gas Chromatograph is used for the analysis of the outlet gas.
The GC is prepared to analyse gas streams and can identify nitrogen, oxygen, neon, carbon monoxide, carbon dioxide, methane, ethane, ethylene, acetylene and propane. Helium is used as a carrier gas, for more details on settings of the GC please see Appendix A.

![Figure 4 Schematic drawing of the tube including thermocouples and their corresponding height measured from the bottom end.](image)

3.3 Experimental Procedures

A calculated amount of liquid (oil) is added to the tube before the sand is filled into the tube. It is made sure that there is hardly any gas included. Possible captured oxygen is replaced by injecting nitrogen. After nitrogen is injected for a couple of hours, the valves are closed and the heating of the tube is started. To minimize pressure build-up during the heating the valve at the top of the tube is opened after the pressure has reached 1 bar at the top pressure gauge. Immediately produced liquid or expelled sand are collected in the cooling trap. These liquids are transferred to a container and the weight is roughly determined.

When the desired temperature is reached at TC5 injection is started by opening the bottom valves. Every 10 minutes gaseous samples are taken and analysed with the GC. The experiment is terminated after several hours when the composition of the combustion gasses does not vary anymore or when the concentrations are too low for detection.

The total workflow for gas analysis is described in Figure 5. First the area under the GC is determined, from which the absolute amount of component is calculated. The sum of the amounts of all components measured is often lower than the sum ideally in place (as will be explained later). Therefore, the measured components are fractioned over the total amount of components that is possible in the gas phase, giving the real fraction in the gas phase. This fraction is used to calculate the rate of component in the exhaust gas.
3.4 Experimental Lay-out

In this study the influence of the oil saturation, the temperature, the injection gas (nitrogen or air) and oil type on in-situ combustion is studied. In Table 2, the experimental conditions of all conducted experiments are given.

Table 2 Table of experimental conditions of all experiments conducted for this work. In the table the number describing the test, the ambient temperature, the liquid saturation level, the gas and the injection rate, the oil type and the objective of the experiment are given.

<table>
<thead>
<tr>
<th>N</th>
<th>Temp set</th>
<th>Satura tion</th>
<th>Injection gas &amp; rate</th>
<th>Amount of Oil</th>
<th>Case</th>
</tr>
</thead>
<tbody>
<tr>
<td>1&amp;2</td>
<td>300°C</td>
<td>50%</td>
<td>Air 10cc/min</td>
<td>15.2gr Hexadecane</td>
<td>Base Case</td>
</tr>
<tr>
<td>3&amp;4</td>
<td>300°C</td>
<td>30%</td>
<td>Air 10cc/min</td>
<td>7.6 gr Hexadecane</td>
<td>Influence of saturation</td>
</tr>
<tr>
<td>5</td>
<td>300°C</td>
<td>100%</td>
<td>N2 10cc/min</td>
<td>27.6gr Hexadecane</td>
<td>Effect of Temperature on Cracking</td>
</tr>
<tr>
<td>6</td>
<td>400°C</td>
<td>100%</td>
<td>N2 10cc/min</td>
<td>25.8gr Hexadecane</td>
<td>Effect of Temperature on Cracking</td>
</tr>
<tr>
<td>7</td>
<td>150°C</td>
<td>100%</td>
<td>N2 10cc/min</td>
<td>26.3gr Hexadecane</td>
<td>Effect of Temperature on Cracking</td>
</tr>
<tr>
<td>8&amp;9</td>
<td>250°C</td>
<td>100%</td>
<td>Air 10cc/min</td>
<td>31.2gr Light Oil</td>
<td>Influence multicomponent Oil</td>
</tr>
<tr>
<td>10</td>
<td>450°C</td>
<td>100%</td>
<td>N2 10cc/min</td>
<td>23.8gr Hexadecane</td>
<td>Effect of Temperature on Cracking</td>
</tr>
<tr>
<td>11&amp;12</td>
<td>400°C</td>
<td>100%</td>
<td>Air 10cc/min</td>
<td>27.5gr Light Oil</td>
<td>Effect of Temperature</td>
</tr>
<tr>
<td>13</td>
<td>400°C</td>
<td>100%</td>
<td>N2 10cc/min</td>
<td>28.3gr Light Oil</td>
<td>Effect of Cracking</td>
</tr>
</tbody>
</table>

Additional tests were performed to understand the behaviour of hexadecane in combustion and in the stainless steel pipe combustion. The results of these additional tests were used for this thesis, but they will not be discussed. See Additional Figure 3 for information on these additional tests.
3.5 Further Used Apparatus
Results from combustion experiments are analysed directly. To get further understanding of the occurring processes additional experiments or analysis are conducted.

3.5.1 Weight-loss determination
After each experiment the sand of the tube is collected. Samples of these sand samples which still contain liquid and sometime solids residues are heated up in an oven to determine the weight loss due to evaporation. The heating is done in steps to allow rough identification of the evaporated components. For the sands of interest, a sample is taken and weighed and placed in an aluminium basket. First the oven is heated to 105°C-110°C. After an hour the weight of the sample is determined. This first weight loss is due to evaporation of water or volatile components. Then the temperature is increased in steps of 100°C up to 500°C and the weights of the samples are regularly determined after each temperature increase. The initial weight of the samples depends on the total amount of sand retrieved from the tube and varies between 1.5gr and 36gr. The scale used had an accuracy of 0.1 gr in the range up to 4000gr.

It is assumed that reactions in the reactor stop when the experiment is stopped. So it is assumed that the sands (and liquid) found in the tube after cooling to room temperature are the same sands as at the end of the experiment.

3.5.2 Thermal Gravimetric Analysis
Thermal Gravimetric Analysis (TGA) is widely used to determine the approximate composition of multicomponent and complex solutions, such as crude oils or polymer solutions. The samples are heated with a constant temperature gradient in the presence of a flowing gas (air or nitrogen). The weight of the sample is continuously determined. TGA has some shortcomings, e.g., the weight loss as function of temperature cannot be interpreted directly. Usually other analytical methods are required to get a conclusive result. TGA has also been used to determine the kinetics of ISC. However, also here the results are not conclusive and require additional experiments (Nickle et al., 1987). In this work TGA is applied to determine temperatures at which considerable weight loss occurs, determine if these weight losses can be related to cracking or combustion and to investigate the interaction between sand and oil.

Samples are analysed in a TGA SDT 2960 manufactured by TA Instruments. The temperature is increased linearly with a gradient of 5K/min. Oils analysed are hexadecane and a crude Rotterdam Field Oil. Further, samples of sand are mixed with both hexadecane and Rotterdam Oil with the same ratio as sand and oil in the combustion tube experiment.

3.5.3 Refractive Index
The liquids collected in the cooling trap are analysed by Refractive Analysis to determine if the liquid is the oil original in place or if it is a product of one of the chemical reactions. Since refractive index analysis is only possible for light transmitting liquids, samples of the Rotterdam oil could not be investigated. The instrument used is the CETI Convex optical, with a stated accuracy of 0.0005nD. Demineralized water and hexadecane are used as reference fluids.

3.5.4 Microscopy
A Leica MZ8 Microscope is used to investigate the surface of the sand grains after the experiments. With microscopy the solid phase deposited on the sand grains and in the matrix can be characterized. A camera is used to capture the images.
3.6 Error Analysis

In this chapter two possible sources for erroneous results or erroneous interpretation of the results are discussed: the temperature distribution in the tube and the analysis of the effluent gas.

3.6.1 Temperature distribution

One part of the analysis of the experiments is the temperature distribution and change during the experiment. For the interpretation of the determined temperature profiles it is vital to know how the temperature is distributed over the reactor tube even without chemical reactions occurring. The temperature distribution was determined with the tube filled with only sand and with the tube filled with water and sand and air injected from below to mimic similar conditions as for the ‘real’ experiment.

![Figure 6 Calibration of temperature in the tube. Calibration is done with sand only (left) and with sand and water (right). The TC_heattape was not installed.](image)

To establish a constant temperature in the tube, the reactor tube is wrapped with two heating tapes. The heating tapes are controlled with the help of two thermocouples, namely TC2 and TC5 (see Figure 4). The temperature was set to 300°C; thus evaporation of water occurs in the latter experiment. In Figure 6 the determined temperature profiles as observed at thermocouples TC1, TC3, TC4 and TC6 (see for positions Figure 4).

From these experiments the following conclusions can be drawn:

- The read-out of the TCs is accurate within 1K: at the temperatures employed in this experiment, this uncertainty is negligible.
- One of the heating tapes is only wrapped around the lower connector; therefore the temperature is expected here to increase slower due to the steel mass there. However, the temperature is distributed more evenly in the long run because the larger steel mass keeps the heat better contained. The second heating tape is wrapped around the steel pipe section and the top connector. The steel pipe is heated fastest, which is observed for TC1 in both cases. The top connector is heated slowest (TC6), because it contains more mass of steel and heated with the pipe heating tape.
- The effect of the heating scheme is seen in the tube filled with sand only. Between 500 and 1000 seconds the temperature seems to stabilize, but this is due to the fact that the temperature was first set to a temperature of 150 °C. So it is an effect of the heating schedule and not of the materials involved. The temperature profile of the tube filled with water and sand shows a plateau at 100°C; this is caused by the complete evaporation of water: heat needs to be added to the system to completely convert liquid water to
steam. After all the water has become steam the temperature starts increasing again. The temperature at the four thermocouples in the set-up filled with sand only is constant after the desired temperature of 300°C has been reached at TC5 and TC2. However, at the top of the tube only 270°C is reached.

- For the set-up filled with sand and water, the temperature is only constant at TC3 and TC4 after a temperature of 300°C has been reached at TC5. The temperature at TC1 and TC6 reaches almost 300°C after 1500 second, before the temperature decreases and at the end of the experiment there is a difference of 50K between the top of the tube (TC1 and TC6) and TC3. Again the temperature in the tube close to the thermocouple which is used for the temperature control is about 300°C, while at the top part the temperature is lower. The first high temperature even in the top part of the tube is due to overheated steam originating from evaporation of water.

- These temperature profiles can now be used to identify temperature effects from the chemical reactions.

3.6.2 Output Gas Analysis

The effluent gas is analysed with the help of a GC. In the GC column the different components are separated and these components are identified at the end of the GC column. Based on the area underneath the peak the amount of each component in the mixture is quantified. It should be noted that for the identification of the components one needs to know which components need to be expected. The above mentioned components which are analysed in this study are the main products as found in air, or after (in) complete combustion and cracking. The separation is due to the interactions between the components in the gas phase and the stationary phase of the column. GC columns own certain characteristics; for each column and flow rate of the carrier gas the time needed for a component to pass through the GC column is characteristic and is called retention time. The retention time is often decreasing in the run of the experiment and is slightly different for each analysis. This can be related to contamination of the column and influences the signals of components with longer retention times such as carbon dioxide, methane and acetylene.

To correlate the detected area with the absolute amount of component, a calibration needs to be conducted. For the calibration a gas consisting of the components of interest and with known composition is injected into the GC. Three calibration gasses were used for the study at hand: nitrogen gas (99.995 vol%), ‘clean’ air and the Universal Gas Calibration Standard (UGCS). The coupling of the amount of nitrogen and the peak area was determined with the nitrogen ‘calibration gas’ and ‘clean’ air. For oxygen this relation was obtained from injection of ‘clean’ air. For the other components the UGCS was used for calibration. Please see Appendix A for further details on the calibration. The following points are given to allow judgement of the accuracy of the analysis by GC:

- The area for all components of the calibration gas except of ethylene is almost the same for repetitive analysis. This proves that the variation of detection time on the total area is negligible. The deviation of area to the average area is maximum 2.5% for most gasses, except for ethylene which had a minimum area of 92.5% of the total area.

- The GC was calibrated with the UGCS before and after the experiments. In general the results of the calibration before and after the experiments were the same. However, sometimes the components were not identified such as ethane or acetylene when the calibration was done after the experiment due to a shift in the retention time.

- The peak area displaying the amount of ethylene in the calibration gas varies by a factor 3 for the different calibrations (see Figure 7). The retention times of carbon dioxide, ethane
and ethylene are very close and therefore the corresponding bases of the peaks are likely to interfere. This could not be improved by varying GC parameters such as sample volume or sampling pressure and might be an explanation for the problems to identify ethylene. The amount of some of the components in the UGCS is lower than the amount expected in the gas stream to be analysed (except from methane). This means that the calibration curve needs to be extrapolated to allow determination of the concentrations of the outlet gas. Extrapolation is an absolute error increasing process, meaning that due to this extrapolation the analysis of these components becomes very uncertain and prone for errors.

- The amount of a component present in the gas mixture is determined by assuming ideal gas law. The volume, temperature and pressure at the inlet to the columns are known, so the total amount of component can be calculated. For the analysed gases this assumption is only acceptable for low pressures (< 1 bar).

- Nitrogen is inert and flows with a constant flow so that its peak area can be used to determine a correction factor to correct for variations in the injection pressure or flow rate.

![Figure 7 Ethylene calibration determined using USCG. The peak area is plotted as function of the amount of component (mol). The red line is the linear fit between the mean of the two determined areas for the same composition and the origin.](image)

**3.6.3 Ideal Gas Behaviour**

It is assumed that the gas composition analysed by GC is correct. The following assumptions are made:

- The exhaust gas from the reactor enters the GC with a delay of 20 min due to travel through the volume between the tube exit and the GC. The gas is not interacting or reacting during the transport from the tube to the GC.
The sum of the amount of components measured in the exhaust gas in the GC can be calculated. The exhaust gas can contain more components than the GC is analysing and this should be accounted for. The amount of component based on ideal gas law is likely to differ from the amount measured. A new term is introduced to describe this behaviour the ideal gas behaviour and can be described by:

\[
\text{ideal gas behavior} = \left( \frac{\sum_{i=1}^{m} n_i^{\text{measured}}}{n_{\text{total}}^{\text{ideal gas law}}} \right), \text{where } n \text{ is the amount of component and } i \text{ is the component type, } m \text{ the number of components and } n_{\text{total}}^{\text{ideal gas law}} = \frac{PV}{RT}. \]

The ideal gas behaviour is therefore influenced by non-measured components in the exhaust gas and the validity of the ideal gas law assumption.
4. Results & Discussion

In this chapter the results of the experiments are presented and discussed. Thereby, the influence of saturation, temperature, cracking and oil type on ISC is shown. Primary results are the temperature profiles in the tube at five positions, the composition of the exhaust gas and the cumulative amount of produced liquid. Secondary results are the analysis of sand after the experiments and of the produced liquid. TGA is conducted to further support the interpretation of the results obtained from the tube combustion tests.

4.1 Oil Saturation
The first four experiments performed are determining the influence of oil saturation, for saturation of 30% and 50% (see Table 2). All these experiments were performed in duplo to show the reproducibility (see also Appendix C).

4.1.1 Temperature and Outlet Gas analysis
In Figure 8 the temperature profiles for the experiments with 30 and 50% oil saturation are given. The temperature registered by the TCs for the 30% saturation level shows an initial increase during the heating period before it stabilizes after around 2 hours, see the left profile in Figure 8. The scattering of the signals for TC1 and TC3 is not a result of the experiment but due to the equipment. The experiment with 50% oil saturation results in a strongly fluctuating temperature profile (see Figure 8 at the rhs). It is believed that the strong fluctuations are related to electrical leakage, influencing the signal and control. However, a closer observation of the experiment in Appendix C indicates that both experiments show fluctuating behaviour, but for the second experiment the signal becomes constant after several hours. Therefore the fluctuating behaviour is related to temperature control (TC2), where temperature seems to decrease rapidly, which is why the heating tape starts heating. And the effect of heating by the tape is observed in the other TCs.

In general, for the 30% and 50% oil saturation experiments the same temperature profiles are found. Close to the TCs used for temperature control the temperature is about the set
temperature. The temperatures at the top (TC6 and TC1) are the lowest. This is also in agreement with the temperature profiles determined with tubes filled only with sand or with sand and water (see Figure 6). Only for the temperature at TC3 and TC4 a peak is observed immediately at the start of the injection. This temperature peak is related to combustion. This can also be seen in the analysis of the outlet gas (see Figure 9). With some delay an increase in carbon monoxide and dioxide is seen. This delay is caused by the fact that the gas needs to be transported through the lines to the GC. The signal for TC6 is increasing over the first 7 hours, but this is a result of heat conduction and convection and not of combustion because the temperature stays for all times clearly below 300°C. The same behaviour has been observed when the temperature profiles were determined (see Figure 6).

Comparing Figure 8a and Figure 8b it can be seen that the temperature increases to slightly higher temperatures for the experiment with the higher oil saturation. Interestingly, in total the temperature decreases then more than for the experiment with 30% oil saturation. Even though the temperature increases more, some smaller temperature increases can be seen after 8, 10 and 16 hours. These temperature fluctuations are also visible in the gas composition of the outlet gas where slight increases of carbon monoxide and dioxide are observed. The fact that the temperature neither at TC3 nor at TC4 reaches a constant value indicates that the process is not completed.

![Figure 9 Exhaust gas composition analysed with the help of a GC. Experiments were conducted at 300°C and with injecting air. At the right hand side the results are depicted for an initial 30% hexadecane saturation and at the left hand side for 50% hexadecane saturation. The production rate of nitrogen is assumed to be constant at 3.2*10^-4 mol/min.](image)

For these two experiments the results of the combustion gas analysis can be summarized as:

- The total amount of carbon dioxide, carbon monoxide and cracking products such as acetylene, methane and propane formed is very low.
- The experiment with 30% saturation shows an increase of oxygen after 12hr, up to oxygen levels normal for air. This indicates that after 12hr the oxygen consuming reactions recede and at the end of the experiment they have almost stopped. This is not seen for the 50% saturation case: the oxygen consuming reactions are still occurring.
- For both cases carbon dioxide and carbon monoxide are produced indicating that indeed combustion occurs. The maximum amount of carbon dioxide produced is slightly higher for the 50% saturation case. The maximum amount of carbon dioxide found in the exhaust gas occurs about one hour later for the 30% oil saturation experiment.
Only a small amount of the hexadecane has been combusted, a calculation is given in Appendix B. This can be concluded from the fact that the temperature hardly changes as well after carbon dioxide and carbon monoxide have been found in the exhaust gas (see Figure 8).

The fact that there is always oxygen in the outlet gas even if carbon mono and dioxide are formed indicates that the process is not limited by oxygen.

The production rate of carbon monoxide is the same for both experiments and fairly constant. The profile of the carbon monoxide in the exhaust gas is not showing any change when the carbon dioxide has its peak. This indicates that often assumed relation between carbon dioxide and monoxide, based on the completeness of combustion, is hard to establish.

Very small amounts of cracking products such as methane, ethylene and ethane are found in the exhaust gas after the amount of carbon dioxide in the gas has decreased. Together with the fact that there is no lack of oxygen, it can be concluded that either these cracking products are formed after combustion, or that they are formed simultaneously but immediately converted into carbon dioxide.

The non-ideal behaviour of the exhaust gas (as defined in 3.6 Error Analysis) for the 50% saturation case is maximum 8.5%, observed from Figure 10. All combustion experiments with changing hexadecane saturation have a minimum sum of the amount of components measured at a peak of carbon dioxide. This indicates that the non-ideal behaviour is not caused by the occurrence of heavy components in the gas phase (since there was no indication of cracking products analysed in the GC), but by non-ideal behaviour of the carbon dioxide gas. For combustion of hexadecane with 50% saturation the gas analysed is less ideal than for the same experiments with 30% saturation.

Figure 10 Ideal behaviour of exhaust gas of 50% hexadecane saturation air injection. Fraction of sum of the amount of measureable components in GC over the total amount based on ideal gas law depicted on the vertical axis. Hexadecane combustion experiment performed with 50%saturation at temperature of 300°C and air injection.

### 4.1.2 Liquid Production

During the experiment liquid was collected from the tube leading from the reactor to the GC. To enhance the liquid drop out, a cooling trap cooled with water was used. The cooling trap was emptied regularly and the temperature at TC2 and the weight of the sample were recorded. In Figure 11 the cumulative weight of liquid is plotted against the registered temperature. It should be noted that these data should be treated with care. Retrieving the liquid from the cooling trap was not straight forward so that some the liquid might have got lost. In particular for the experiments with air injection where only relative small amounts of liquid were collected, this
might have a huge impact. For most samples the liquids were obtained during heating, at injection or at the end of the experiment. This means that liquid production from the reactions in the experiment is hard to observe and the largest contribution is comes often from the heating stage. Refractive Index analysis concluded that all liquids were neither pure water (index of 1.3312) nor hexadecane (index of 1.4325).

Figure 11 Cumulative liquid production curves as function of temperature for hexadecane experiments and the corresponding refractive index. The cumulative weight of the experiments with hexadecane at an ultimate temperature of 300°C is plotted. The corresponding refractive index measured for each sample is also indicated in the labels.

4.1.3 Sand Analysis
The sand was retrieved from the combustion tube after the experiments with 30% and 50% hexadecane saturation and air injection (experiments number 1 to 4). The characteristics of the sand are shown in Figure 12.

Figure 12 Schematic pictures of the sand found in the tube after experiments with Hexadecane and injection of air at a set tube temperature of 300°C. a) 50% oil saturation; b) 30% oil saturation
At the end of the experiment with 30% saturation the sand in the tube is dry and clean except of a small zone in which sintered sand is found (see Figure 12b). In this sintered sand the sand grains are ‘baked together’ by a black or brownish substance (see Figure 13). This substance seems to be a product of the combustion reactions, since it is not found in experiments with nitrogen injection (which will be presented in the next sub-chapter). The fact that at the end of this experiment there is either dry sand and dry sintered sand left in the tube indicates that the oil production and the combustion reactions have been completed, as is concluded from GC analysis of the outlet gas (see 4.1.1 Temperature and Outlet Gas analysis). Looking at the sand of the experiment with 50% hexadecane saturation, one can see that there are zones of wet, dry and sintered sand. This clearly shows that not all oil has been produced and that the combustion reactions have not been completed, as was concluded before. The difference in the extent of reaction is indicated by colour in the sintered sand as well (see Figure 13).

The start of the bottom of the sintered sand in the tube is at the same height as TC2. This indicates that fluctuating behaviour of the temperature can be related to reactions in the sintered sand. These reactions seem to consume large amounts of energy, either through a high activation energy or endothermic reaction.

As explained earlier samples of the different zones of sand were taken and dried in the oven (see 3.5.1 Weight-loss determination). In Figure 14 the determined weight loss of the sand from the tube after the experiment is depicted. The contribution of each heating stage to the overall weight loss can also be observed.

- All sampled sand in the oven from the first experiment at 50% saturation lost weight in the heating to 105°C and for heating from 300°C to 400°C. The loss of weight in this last heating stage is not determined for samples from sands of the second test at 50% saturation.
- The samples of the sands from the first experiment at 30% saturation show all weight losses after heating to 500°C. For the second sample set at this saturation this was not observed.
Figure 14 Determined mass after drying process in the oven of sands taken from the tube after experiment. The numbers mentioned first refer to the experiment; (1) and (2) hexadecane saturation of 50%, air injection at a set tube temperature of 300°C, (3) and (4) hexadecane saturation of 30%, air injection at a set tube temperature of 300°C. The left hand axis gives the weight loss as fraction of total weight; at the right hand axis the absolute weight in gram is given. The weight loss for each heating stage is indicated by the different bar colours.

The following was observed concerning the sand weight losses of the samples from the experiments with the same saturation:

- The total relative weight loss is equal (16% and 15%) for both experiments at 50% saturation.
- The relative weight loss of the 30% saturation is strongly influenced by the small amount of the top wet sample. But the absolute amounts inserted are comparable for this saturation, and so is the absolute weight loss.

Comparing the results from the sands with the different saturations leads to the following statements:

- Sintered sands all show weight losses at higher temperatures (above 300°C) for both saturation levels; ultimately they all lost their colour after heating to 500°C.
- Low absolute weight losses are shown for the bottom dry part, assuming contamination of the bottom by some wet sand parts. This indicates that combustion or sweep from of the bottom is very efficient.
- Sintered sand and top wet sands for 50% saturation lose larger amounts of weight during heating than the lower saturation level. This strengthens the conclusion that the reaction has not yet been completed when the experiment was stopped. The weight loss of the sintered sand in the lowest heating stage of 50% saturation is not observed in the same stage at lower saturation in the sintered sand. This indicates that the sintered sand is binding volatile components during formation or during cooling. These volatile components could be water or volatile hydrocarbons.
4.1.4 Summary of Saturation Experiments
The combination of the results of the experiments at different saturation levels can help to understand ISC of hexadecane and the influence of saturation:

- Ignition during the experiment or a moving front is not observed for the experiments as can be seen in the temperature profiles. For the lower saturation the temperature increase at the top and the simultaneous increase of carbon dioxide in the outlet gas indicate that combustion of material is responsible for the heating of the top part of the tube.
- The occurrence of hard sintered sand at the end of the experiment can be related to reactions in the presence of oxygen and volatile components. The sintered sand contains heavy components, which form the hard ‘cement’ keeping the grains together.
- From the outlet gas analysis, the temperature profiles and the position of the sintered sand after the experiment, one can conclude that for the low saturation the behaviour is more like the burning of a flame in the bulk. One observes radical formation in the gas phase which are responsible for the recombination of smaller hydrocarbon chains to heavy hydrocarbons if not enough oxygen is present as for example in the top of the tube (Warnatz, 2000). For the higher saturation the behaviour is more dictated by the porous medium and the distribution of liquid and gas phase in the porous medium. The flow is more restricted, less radicals are formed which recombine to heavy hydrocarbons in lower parts of the tube.

4.2 Nitrogen Injection
To study solely the influence of temperature nitrogen instead of air was injected into the combustion tube. These experiments were conducted with a hexadecane saturation of 100%. The temperature was set to 150, 300, 400 and 450°C (see Table 1 experiments 5-7 and 10). To ensure that there is no oxygen in the tube, the sand–hexadecane mixture was flashed with nitrogen.

4.2.1 Temperature and Outlet Gas Analysis
In Figure 15 the temperature profiles and in Figure 16 the outlet gas compositions for the experiments with nitrogen injection and 100% hexadecane saturation are given. The initial relative temperature larger than one for all the experiments is due to oxidation as can be seen from the composition of the outlet gas which contains small amounts of carbon dioxide and carbon monoxide (see Figure 16). The combustion uses oxygen which was not completely removed from the oil+sand mixture by the nitrogen flushing prior to the start of the experiment. However, after this short period of initial oxidation there is no further oxygen available and the results can solely be assigned to the effect of temperature. For the experiments at 150, 300 and 400°C the temperature after the initial high temperature stabilizes at a constant temperature comparable to the experiments with air injection. However, differently than for the experiments with air injection there is no carbon dioxide or carbon monoxide in the outlet gas indicating combustion. Very small, almost not analysable amounts of cracking components such as methane, ethane and ethane are found instead. Thus the constant temperature in this thesis is due to the heating with the heating tape. The final temperature distribution is in general the same trend as found for the air injection experiments.
Figure 15 Temperature profiles of hexadecane cracking experiments. The temperatures recorded for the injection of nitrogen in a tube filled with sand and 100% hexadecane saturation: top left) set tube temperature is 150°C; top right) set tube temperature is 300°C; bottom left) set tube temperature is 400°C; bottom right) set tube temperature is 450°C.

The temperature profiles at 400 and 450°C show some interesting behaviour. At 400°C the temperature is decreasing from the top after injection: in the upper part of the tube (TC1 and TC6) show a first decrease in temperature for TC6 and then TC1 more slightly. The increase in temperature for TC6 before injection is as steep as the decline right after injection. This indicates that vapour is transported from the bottom before injection to the top. After opening the top gauge to prevent pressure build-up, the vapour is produced. The temperature increase of the heating tape is minimal during this period, indicating that temperature rise is caused within the tube at the top. The temperature decline is more pronounced than for the experiments at the lower temperatures and also more than at the thermocouples in the lower part of the tube (see Figure 15). Interestingly, the temperature increases again slightly at TC3 (and TC4) after the first high temperature and a short decline. This all happens only at the beginning of the experiment.

After this the outlet gas consists almost of pure nitrogen only and the temperature in the tube as stable and distributed according to the temperature distribution profile determined earlier. From this three things can be concluded:

1) Only initially chemical reactions occur. These reactions are initiated by the slow amount of oxygen present. Only after this some cracking reactions occur as can be seen by the small amounts of ethylene and methane present in the outlet gas.
2) Close to TC3 an exothermic reaction occurs resulting in the rise of the temperature.
3) In the upper part of the tube (TC1 and TC6), the temperature drops because the energy provided by the heating tape is constant due to constant temperature at TC2, but also because an endothermic reaction occurs.
About the same holds for the experiment at 450°C. However, here one observes a temperature increase at TC1 and TC6 after the first temperature decrease. This difference in the behaviour might be explained by the fact, that for this experiment more oxygen has been in the system and consequently more CO2 and CO have been formed by exothermic reactions. This exothermic reaction and the higher set temperature provide sufficient energy to start the cracking reaction, most likely in the upper part. Here you see a temperature decline initially. This hypothesis is also supported by the somewhat higher amounts of cracking products formed (compared to the experiment at 400°C). The temperature increase after around 0.5 h at TC1 and TC6 is most likely caused by hydrocarbon vapour reaching the top of the tube or ending cracking reactions. The formation of more cracking products is also supported by the analysis of the sand retrieved from the tube after the experiment (See Figure 19).

![Figure 16](image16.png)  
Figure 16 Exhaust gas from cracking analysed with the help of a GC. Component production rate for nitrogen injection of hexadecane (100% saturation) for 400°C (left) and 450°C (right). The production rate of nitrogen is assumed to be constant at 4.0*10^-4 mol/min.

### 4.2.2 Liquid Production

Especially interesting is the amount of liquids produced during the experiments with nitrogen injection. In Figure 17 the liquid production is given as function of the temperature. It should be noted that liquid is mainly produced during the heating of the tube. For all experiments the same total amount of hexadecane was added, but for the different experiments different percentages of the oil initially in place has been produced. The cumulative liquid production of the experiment at 300°C is clearly lower than for the experiments performed at higher temperatures. The total weight of the liquids produced at higher temperatures is close to the total weight inserted.

The collected liquid is characterized by its refractive index, also showed in Figure 17 for the corresponding samples. All samples show higher refractive index values than the refractive index of pure hexadecane. A higher refractive index is found for hydrocarbons with longer chains or aromatic components (Zhang et al., 1997). Even though the liquid cannot be uniquely identified using the refractive index, it can be concluded that the liquid is a mixture of a number of components; these components might also be aromatic components or hydrocarbons with double bonds. The latter indicates that cracking and recombination has occurred and thus the liquid is not only condensed hexadecane vapour.
The liquids in the cooling trap could originate either from condensed components of the gas phase or liquid expelled from the reactor tube by thermal expansion or gas lift. From the results it can be concluded that cracking and liquid production is more pronounced for the experiments conducted at higher temperatures as also was already seen in the results of the outlet gas analysis.

Guozong Wu determined with a bulk experiment the cracking behaviour of hexadecane in either the liquid or the gas phase at temperatures above the boiling points of hexadecane (by increasing pressure in the liquid phase experiment) (Wu et al., 1996). In Figure 18 the products of the cracking reactions as found by Wu are given. In the bulk the hexadecane forms more cracking products in the gas phase than in the liquid phase. In particular, smaller hydrocarbons are formed in the gas phase. Based on these results the occurrence of methane, ethylene and ethane in the experiments of this work can be identified as cracking products. That the cracking seems not to occur at temperatures between 300 and 400°C and that more methane is produced than found by Wu, might be explained by the fact that the hexadecane is present in porous medium. The higher methane production might be explained by catalytic effect of the sand. The occurrence of cracking products only at higher temperatures can be explained by the pore sizes. The principle here is then the same as for boiling of a pure component in porous medium; the component in porous medium boils at higher temperatures than in the bulk phase. This behaviour is described by the so-called Kelvin equation and is assigned to the higher curvature of the vapour-liquid interface, see 2.2.2 Kelvin Equation.
4.2.3 Sand Analysis

In Figure 19, the characteristics of the sand retrieved after the experiments with nitrogen injection are given. As already mentioned before, the sands of the different experiment show different characteristics. In general, it can be stated that the sands are ‘drier’ as the temperature during the experiment was higher. The sands after the experiments with 400 and 450°C were both dry at the end of the experiment. However, the sand of the 450°C experiment has become darker (greyer). This dark colour is caused by a thin layer on the sand grains of heavier components; this was also expected based on the exhaust gas analysis. The solid state was present on the individual grains, but was not cementing the grains together. The sands were not analysed in the oven because there was no solid residue, as found for the air injection experiments, present in the sand.
4.2.4 Summary Nitrogen Injection Experiments

The results and discussion of the experiments with nitrogen injection can be summarised as:

- Cracking and recombination of hexadecane is occurring at temperatures of 300°C and higher. For higher temperatures more volatile gasses are found in the gas outlet. These gasses could serve as a reactant for combustion. This cracking and recombination ultimately led to a solid state reaction product formed at 450°C positioned on the individual grains.
- The recombination and cracking is a fast reaction, but once products are formed, the reaction is stopped due to required high activation energy to further crack the formed products. Some combustion has occurred during nitrogen experiments, these indicate that combustion is at least as fast as cracking.
- Produced liquids show an increase in refractive index compared to hexadecane, this indicates that longer chain components or aromatics are present in the liquid. The recombination in the liquid phase will increase the boiling point of the liquid: liquids are still present above the boiling point of hexadecane.

4.3 Rotterdam Field Oil

The most experiments conducted for this work had been done with hexadecane to understand the underlying processes. Additionally, some experiments have been conducted with a real medium—heavy crude oil, a Rotterdam Field Oil (RO). For this experiment the temperature in the tube was set to either 250 or 400°C and either air or nitrogen was injected. The oil saturation for this experiment was always 100%. The corresponding numbers of the experiment are according to the notation in Table 1. The first experiment of Rotterdam Field Oil combustion at 400°C (experiment 11) was terminated after some hours, because of safety reasons.
4.3.1 Temperature and Outlet Gas Analysis

A) Experiments at 250 °C

The temperature profiles for the experiments with RO at 250°C with air injection and an oil saturation of 100% are given in Figure 20. In the two graphs the results of two experiments at the same conditions are given. In particular in the figure at the lhs it can be seen that shortly after the start of the experiment a temperature increase is seen in the lower part of the tube. This temperature increase coincides with the short increase of carbon dioxide and oxygen in the outlet gas, see Figure 21. The temperature at TC3 (lhs Figure 20) is slightly elevated for approximately the first 6 hours. Then the temperature declines to a temperature 1.03 times the set temperature, no change in set temperature is observed. The temperature in the top of the tube is lower than the set temperature, but this is within the accuracy. For the second experiment (figure at the rhs) comparable behaviour is seen. However, the (slight) temperature increase is found now after 15.5 hours (for the first experiment it is after about 6 hours). Also here the temperature increase coincides with a slight increase of carbon monoxide and carbon dioxide in the outlet gas.

The composition of the outlet gas as function of time is given in Figure 21. In general it can be seen that the decline of the oxygen coincides with the increase of carbon dioxide and carbon monoxide. Further, the amount of cracking products is quite low. Only methane is formed noticeably. Nevertheless, the amount of these components is at least by a factor 10 smaller than the three most predominant. This indicates that cracking is occurring, but probably on a lower level than combustion.

The temperature increases seen for TC6 in experiments 8 and 9, coincide with the decline of the oxygen concentration in the outlet gas (see Figure 21). Combustion occurs before the temperature increase, which is proven by the increase in the carbon oxide concentration in the outlet gas. The still relatively high oxygen concentration in the outlet gas during combustion indicates either that oxygen is abundant present or that due to the heterogeneity of the porous medium (sand) oxygen bypasses reaction zones. This last was not observed when analysing the sand retrieve from the tube at the end of the experiment. Nevertheless, even though combustion occurs, as seen from the increased amount of carbon monoxide and dioxide in the outlet gas, there is no clear temperature increase in the tube observed. This is due to the low amount of burnt oil.
Figure 21 Exhaust gas analysis of RO experiments at lower temperatures with air injection by the help of a GC. In these experiments air was injected in a tube with a set tube temperature of 250°C and the sand was 100% Rotterdam Field Oil saturated. Experiment 8 left and experiment 9 right. The production rate of nitrogen is assumed to be constant at 3.1*10^-4 mol/min.

The ideal behaviour of the gas is 93% for experiment 9, as indicated by Figure 22. The decline to 93% cannot be related to gas phase composition or the temperature profile. The fluctuations between 9 and 12 hours are introduced by the computational analysis. The sharply changing exhaust gas content at 15.5hrs has no effect on the ideal behaviour.

Figure 22 Ideal gas behaviour of exhaust gas in experiment 9. The fluctuations are due to the computational analysis of the behaviour. No changes are seen at 15.5hrs as a result of dropping oxygen content.

B) Experiments at 400°C

The temperature profiles for the experiments with Rotterdam Oil with either air or nitrogen injection at 400°C (experiments 12 and 13) are given in Figure 23, the composition of the outlet gas in Figure 24. It is important to note that the sharp temperature decrease after 2.5 hours during the experiment with air injection is caused by emptying the cooling trap without closing the top valve. This can also be seen in Figure 24 by a sudden but short increase of the oxygen content in the outlet gas.
The general temperature distribution is the same as found for the earlier experiments; at the top one encounters lower temperatures than at the bottom. The increase of the temperature for the experiments with air injection (Figure 23 lhs) in the first hour after air injection observed for all thermocouples is significant. This temperature increase is accompanied with an increase of carbon dioxide, carbon monoxide, ethylene, methane, acetylene and ethane in the outlet gas (Figure 24). Differently than for the experiment at lower temperature, clearly also cracking occurs at this higher temperature. From the temperature increase and the fact that carbon dioxide and carbon monoxide as well cracking products are found in the outlet gas, it can be concluded that cracking and combustion occur simultaneously. However, combustion is the dominating process as can be recognized by the continuous increase of the CO2 content in the outlet gas while the content of the cracking products decreases.

**Figure 23** Temperature profiles of the experiments with 100% Rotterdam Field Oil saturation with a set tube temperature of 400°C with air injection (left figure) or nitrogen injection (right figure). Injection starts at t=0; at negative times the effect of heating can be observed. The decrease after 2.5 hours at the rhs figure is caused by opening the oil trap for emptying the liquids produced; hence, the top valve was not closed.

**Figure 24** Exhaust gas analysis for experiment 12 and 13 by a GC. For air injection (left) and nitrogen injection (right) cracking products are observed, after an increase of oxides. The two small increases in oxygen at 2.5hrs for air injection and 3.5hrs for nitrogen are caused by opening the oil trap. The production rate of nitrogen is assumed to be constant at \(3.2 \times 10^{-4}\) mol/min for air injection and for nitrogen injection at \(4.0 \times 10^{-4}\) mol/min.
At the rhs of Figure 23 and Figure 24 the temperature profile and the outlet gas composition of the experiment with nitrogen are given. The temperature profile shows a temperature rise for the first 40min for all TCs, see Figure 23. At the bottom the temperature drops after the rise to a constant level; temperatures stay fairly constant at the top after the rise. This could mean that processes at the bottom are starting to consume some energy. The emptying of the cooling trap after 3.5 hours is not accompanied by a sudden temperature change but only by a slight increase of oxygen in the outlet gas (see Figure 24).

The ideal behaviour of both experiments at 400°C is calculated and shown in Figure 25. Both show a sharp drop to 85% from the start, for experiment 13 this drop is even steeper. After this drop the ideal behaviour of experiment 13 increases slowly to 98%. The ideal behaviour of experiment 12 is almost constant or slightly increasing to 88%. This difference is best related to non-ideal behaviour of carbon dioxide for experiment 12. The sharp drop at the start is probably a result of non-ideal behaviour of the gas itself and the occurrence of cracking components which are non-analysed.

![Figure 25 Ideal behaviour of gas analysed for experiment 12 and 13. The amount of component measured is compared with the amount expected ideal behaviour. For experiment 12 (left) the ideal behaviour is 85%. The ideal behaviour for experiment 13 (right) is 86%. The conditions are the same and differences are related to cracking or combustion.](image)

### 4.3.2 Liquid Production

During the experiments with RO more liquid weight is produced during the initial heating of the tube than for the hexadecane experiments, but this is most likely a result of a higher density of the RO. The mobility of the oil is increased by the lowering of the viscosity due to the temperature increase; this is also observed by the eye by shaking the tube containing the sample. Unfortunately, the amount of the individual liquid samples was too small to determine the viscosity. The colour of the collected liquid turned from black to brown in the run of the experiment. The dark colour made it impossible to determine the refractive index. Even after letting settle the liquid samples no phase separation of, e.g., oil and aqueous phase, was observed.

The liquids produced for these experiments at different temperatures show different total weight of the liquids obtained, see Figure 26. The liquid production is higher for higher temperatures, were the lower weights obtained for experiment 11 (RotOil 400degC air1) can be explained by the early termination. For lower temperatures the liquid is remaining in the sand as is observed from sand analysis. The liquid production is continuing after the temperature has reached its high set temperature, this was not observed before. The difference between liquids from experiment 12 and 13 is small, but it hard to conclude on this because of the uncertainty in obtaining the liquids.
During heating produced liquid weights were measured and the maximum temperature at production was recorded.

### 4.3.3 Sand Analysis

In Figure 27 the characteristics of the sand retrieved after the experiments is shown. For both air injection experiments the bottom sand contains a heavy sticking material, called ‘oil sand’. Especially the sands from experiments at 250°C (experiment 8 and 9) contain large amounts of very viscous, dark heavy residue of crude oil. The sand at the bottom of the air injection experiment at 400°C is lighter of colour and the residue is less viscous. The dark sands observed in the nitrogen experiment reach a higher height in the tube. However the majority of this height (a guess is 17cm) is made up by dry grey coloured loose sand. On top of this loose sand a hard black sand was found. The film around these grains is relatively thin but keeps the grains together. On top of this hard sand wet sand is observed. Wet sand was also seen on top of the heavy oil sand for the experiments at 250°C (experiment 8 and 9). From this it can be concluded that the oil sand is a product of combustion reactions, and not of cracking as would be expected.

![Figure 27 Sand distributions in the tube after experiments with Rotterdam Field Oil. A: Experiment 8&9 air injection and 250°C; B: Experiment 11&12 air injection and 400°C; C: Experiment 13 nitrogen injection and 400°C. For both experiments with air injection sand is found containing very heavy oil, the height of this sand is almost similar. The oil sand from lower temperatures is more viscous than the oil sand from higher temperatures with air injection. Wet sand is found for 6 cm at the top of the sands from nitrogen injection. Below this sand a small hard band of sand is found and the largest part of the tube is filled with black-grey lose sand.](image-url)
Figure 28. Mass loss of sand retrieved after experiments with 100% RO saturation determined by warming up samples in oven. The sand + oil mixtures were taken from the different sand sections of the tube after the tube experiments. The relative weight losses are shown for each heating stage. The total weight in the oven and the absolute weight loss is shown on the second y-axis. The number at the beginning of the name gives the number of the experiment (see Table 1).

Microscopic pictures of the oil sands and the hard sand are given in Additional Figure 4.

For further evaluation of the residue sand, samples of the different sections of the sand were dried in an oven by stepwise increasing the temperature. The results are depicted in Figure 28. The ‘oil sands’ found at the bottom of tube after experiment with 250°C (experiments 8 and 9) lose a lot of weight when heated. The weight loss of the bottom sands from experiments at 400°C is less, especially for the sands from the nitrogen-injection experiments. This is already expected because of the colour and stickiness: as temperature is increased heavy components are forming lighter components in an oxygen environment. The biggest weight loss for these bottom sands is observed in the temperature range between 350 and 500°C. Also the black residue disappeared when the oven was heated to 500°C and some of it even caught flame at that temperature.

The differences in the weight losses between the two experiments conducted at 400°C with air injection (experiment 11 and 12) are related to the short time experiment 11 was performed. This indicates that the composition of the sand is also a function of time: the product is not directly formed at the start.
4.3.4 ISC of Rotterdam Field Oil
The findings of the experiments with the Rotterdam Field Oil can be summarized as:

- The oil sands are formed in presence of oxygen. These residues were not found in the sands of the experiments with nitrogen injection. This means that long hydrocarbon chains are reacting with oxygen. The formed oxidized hydrocarbons are more viscous than the original RO. Increasing temperature to 400°C will result in a less viscous oil sand. Combustion of the residue was observed at 500°C.
- By increasing the temperature, the hydrocarbon chains are cut into shorter chains and other cracking products. The carbon dioxide content in the outlet gas increases while the content of cracking products decreases. The maximum content of cracking products in the outlet gas coincides with maximum temperature: this indicates that the activation energy for cracking is lower than oxidation or (partial) combustion at 400°C.
- The weight of produced liquids for nitrogen and air experiments is similar at higher temperatures. ISC seems less important at 400°C than miscible gas flow effects for the total produced liquid weight. The temperature increase resulted in a larger amount and less viscous produced liquids.

4.4 TGA Results
In order to better understand the weight losses of the sand analysis and the processes occurring in the tube during the experiments, samples of hexadecane, Rotterdam Field Oil, sand and hexadecane-sand mixtures and RO-sand mixtures were analysed with the help of TGA.

4.4.1 TGA of Hexadecane
In Figure 29, the results of the TGA are given in terms of the relative weight loss as function of the temperature. The samples of sand were added to see if the sand contains some organic components which would also add to weight loss. The sample with hexadecane has lost its weight completely at 200°C. Seeing that the boiling point of hexadecane is 287°C, it is surprising to see that the hexadecane sample has lost its complete weight at 200°C. Interestingly, the auto-ignition point of hexadecane is 201°C. This could mean that the hexadecane would combust. However, usually combustion is accompanied by strong scattering of the TGA results. This is not seen here. Further, it is interesting that the results in nitrogen and oxygen surroundings give exactly the same results. The sand–hexadecane mixtures show the same behaviour as the pure hexadecane samples; the major weight loss is at 200°C. Because the sample is made of hexadecane and sand, the weight at the end of the TGA is not zero but equal to the weight of the sand.

The very small weight loss observed for the sand-hexadecane samples between 200°C and 800°C might be explained by the fact that some material is caught between the sand grains and only escapes at higher temperatures. It could also be an effect of the sand constituents, most likely the absorption of liquid phase on the grain.
Figure 29 Results of TGA analysis of hexadecane, sand and hexadecane+sand. The analysis is done either in the surrounding of air or nitrogen. Hexadecane+sand has same mixing ratio as 100%saturation experiments.

To determine the weight loss of hexadecane in the sand the next equation is used to investigate the influence of a porous medium. The mixing ratio for sand with oil used in the tubing filling experiment is applied to correct the TGA weight of sand.

\[
\text{X. relative hexadecane weight loss in mixture} = \frac{\left( \text{Weight}^{\text{TGA \, sand+oil}} - \text{Weight}^{\text{TGA \, sand}} \right)_{T=T}}{\left( \text{Weight}^{\text{TGA \, sand+oil}} - \text{Weight}^{\text{TGA \, sand}} \right)_{T=25^\circ C}}
\]

In Figure 30 the difference between weight loss from pure hexadecane and from hexadecane in a sand mixture is shown for air and nitrogen surroundings. It is seen that hexadecane in a mixture is losing weight at lower temperatures than pure hexadecane. But the weight loss for the pure component measurement is completed at 200°C, whereas some weight seems to remain in the mixture. Further the difference between nitrogen and air surrounding for the weight loss in the mixture is different, this indicates that especially cracking of hexadecane is influenced by a catalytic effect of the sand or a porous volume.
4.4.2 TGA of Rotterdam Field Oil

Samples of Rotterdam Field Oil, sand and a mixture of sand and RO were also analysed with TGA, see Figure 31. The analysis for sand shows hardly any weight loss in either surrounding. The weight loss for the other samples is about the same when conducted in nitrogen or air surroundings. Only above temperatures of 400°C, there is clear difference between the TGA results of RO in air and in nitrogen.
For the sample in air, there is seen that at around 400°C, 450°C and above 600°C there is some unsteady weight change. For the sample in nitrogen one sees an continuous steady decrease up to around 450°C, after this the weight keeps decreasing but with a much lower rate. The data of the sand-RO mixtures seem to be similar. However, just as for the samples with RO in air and nitrogen there are slight changes at around 400, 450 and above 650°C. Because of the lower oil content in the oil + sand mixture these slight differences are difficult to see.

The same equation, X, is used to determine the influence of the porous medium on liquid weight loss, Figure 32. The weight loss of RO from the mixture in air is following perfectly the trend of the measured RO weight loss in air. The weight loss of RO in nitrogen surrounding is less perfect but for this purpose very good, especially the change of slope at 450°C. This indicates that RO is behaving in TGA similar in the mixture as in the bulk. It also proves that the method used is good, up to 600°C (where nitrogen sand analysis is influencing the result to much).

![Figure 32 Relative RO weight loss from TGA data. The relative weight loss of RO in a sand mixture can be compared to the relative weight loss of pure RO. Air and nitrogen environments are also indicated. After 600°C the influence of the sand weight loss is observed.](image)

**4.5 Combining Results and Discussion**

The objective of this study was to identify if gas phase combustion occurs during ISC and what its importance is. Therefore, experiments were conducted isothermally in a vertical reactor tube filled with a sand+oil mixture. The reactor tube was heated from the outside by heating tapes and either air or nitrogen was injected at various set temperatures. For the experiments either hexadecane or a crude oil from the Rotterdam Field were used. Hexadecane was applied because it allows identification of the occurring chemical reactions, the crude oil to compare the results to the results of the hexadecane experiments and to relate the results from the hexadecane experiments to real fields.

TGA data proved that the cracking of hexadecane is influenced by the sand mixture. For the Rotterdam oil there was no such difference seen in the bulk phase and the porous medium behaviour. For hexadecane weight losses were observed about 20 K below its auto-ignition point (in bulk and porous medium) at around 190°C. From this it can concluded that during the
combustion tube experiments gas phase reactions should occur. However, wet sands were encountered after the experiment with hexadecane at 300°C. Thus, differently than for the TGA not all hexadecane has gone into the gas phase. This might be due to the fact that for TGA the samples are much smaller than for the combustion tube experiment. The amount of liquid produced and captured in the cooling trap increased while heating up the tube and reaches its maximum at around 300°C. The collected liquid differs from the hexadecane and seems to become heavier. This indicates that solely TGA is insufficient to determine phase transitions and chemical reactions for ISC processes.

The experiments conducted with hexadecane helped to identify the chemical reactions of cracking and combustion. It showed that cracking occurs at higher temperatures. At these temperatures combustion is very limited and not self-sustaining. For lower temperatures combustion is almost not occurring. A sticky residue at the end of experiments with 30% and 50% saturation is a result of oxidation; these residues are not found in the tube after nitrogen injection experiments. The sticky residue was expected to be formed at higher temperatures than applied in these experiments. At higher temperatures and nitrogen gas injection a solid product was formed which covered the sand grains. The oxygen/fuel ratio and also contact of injected air and oil influences the deposition of the sticky residue. Produced liquids showed that in the heating process hexadecane is recombining resulting in a liquid with a higher refractive index.

Experiments with Rotterdam Field Oil show in general similar behaviour as hexadecane experiments. Reactions tend to occur over a wider temperature range, due to the composition of RO. Therefore some combustion is already observed at 250°C and at higher temperature (400°C) pronounced cracking and combustion is seen. Combustion is dominating over cracking, due to a decrease in cracking products in the exhaust gas over time. The combustion reactions were not self-sustaining and are kept running by the isothermal experimental conditions, as the case for hexadecane experiments. At higher temperatures the viscosity of the produced liquids reduces.

The occurrence of gas phase combustion was proven before at higher temperatures (maximum 900°C) (KhoshnevisGargar et al., 2010). Based on the TGA of hexadecane, hexadecane and sand, RO and RO and sand it can be assumed that a gas phase forms already at 200°C. From this and the results of the experiments with 30 and 50% oil saturation it can be concluded that chemical reactions including cracking, combustion and recombination occur in the gas phase. The amount and times at which oxygen and cracking products, especially methane, are identified in the gas phase indicate that the reaction rates of the gas phase reactions are different than those given in literature (Kapadia et al., 2010).
5. Conclusions

1. The experimental set-up designed and constructed proved to allow ISC experiments at isothermal conditions. Primary results are outlet gas compositional analysis, temperature profiles and rough estimation of the liquid production. Secondary results are characterization of sand retrieved from the tube after the experiment. Other secondary results are TGA, microscopy, rough characterization of produced liquid by refractive index and characterization by determining weight losses in an oven at various temperature stages. The isothermal set-up gives insight in the self-sustaining behaviour of the chemical reactions occurring during ISC; the reactions proved not to be self-sustaining and the typical temperature profile for ISC was not seen.

2. The actual gas phase combustion could not be proven unambiguous at the low temperatures. However, chemical reactions including cracking, combustion and recombination occur in the gas phase and were proven by the analysis of the outlet gas composition and TGA results.

3. For hexadecane cracking and recombination in combination with combustion is behaving similar as the crude oil in ISC. However, the temperature range in which products of cracking, recombination and combustion are found is wider than for hexadecane. This can be explained by the fact that the crude oil is a multicomponent solution while hexadecane is a pure component. Volatile components of the crude oil transfer into the gas phase already at lower temperatures.

4. Initial low oil saturations have no impact on the general chemical combustion behaviour; the position of oxidation products depends on the initial saturation.

5. At low temperature the formation of solid components is due to oxygenation and not due to anaerobic cracking.
6. Recommendations

Several recommendations are made for further research:

1. The gas phase compositional analysis needs to be improved. This will allow better quantification of the non-measurable components.
2. A mass flow meter determining the exhaust gas flow should be installed; in this way the real gas (nitrogen) flow rate can be determined and used for the analysis.
3. Another cooling trap is needed to collect the produced liquid; the volume of the trap still needs to be small to minimize gas phase mixing. The easiest would be a tap which allows collecting the liquid from the trap without opening the set-up and possible contaminating the gas flow.
4. More research is needed concerning the position and the chemical components forming the sintered sand from hexadecane combustion.
5. For further research on gas phase combustion, the top part of the tube should not be filled with sand (or liquid). Hereby, the effect of the lower part where more reactions are occurring can be isolated and this will help to improve the determination of the effect of gas and the porous media.
6. Further research should also include combustion of heavier crudes, the use of a horizontal set-up and experiments at high pressure, to fully understand the impact of gas phase combustion.
7. Sophisticated analysis of the produced liquids and sands is needed for qualification, characterization and quantification.
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Additional Figures

**Additional Figure 1** Reaction scheme of methane combustion from bitumen.

**Additional Figure 2** Experimental Sand passing the filters.

P10 = 0.215mm, P50 = 0.284mm, P90 = 0.398mm
<table>
<thead>
<tr>
<th>Type tube</th>
<th>Tset (°C)</th>
<th>gas injected</th>
<th>Sand and Liquid</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vert RVS tube ISC</td>
<td>250</td>
<td>5cc air/min</td>
<td>100% saturation of hexadecane in sand</td>
<td>Wet sands, no indication of combustion by exhaust gas analysis, 3.8gr produced liquids</td>
</tr>
<tr>
<td>Vert RVS tube ISC</td>
<td>250</td>
<td>10cc air/min</td>
<td>100% saturation of hexadecane in sand</td>
<td>Terminated after 2hrs, wet sands, no indication of combustion by exhaust gas analysis, 3.6 gr produced liquids</td>
</tr>
<tr>
<td>Vert RVS tube ISC</td>
<td>300</td>
<td>10cc air/min</td>
<td>100% saturation of hexadecane in sand</td>
<td>Combustion products in gas, sintered sand found at 5cm from top, &gt;8.3gr produced liquids</td>
</tr>
<tr>
<td>Horizontal glass tube</td>
<td>250</td>
<td>5cc air/min</td>
<td>2.7gr hexadecane, 8.0gr sand</td>
<td>Some produced liquids, orange brown residue on sand and glass</td>
</tr>
<tr>
<td>Horizontal glass tube</td>
<td>130</td>
<td>5cc air/min</td>
<td>3gr hexadecane</td>
<td>A sample of hexadecane was subjected to an increasing temperature, at Temp &gt;160°C combustion products were seen</td>
</tr>
<tr>
<td>Horizontal glass tube</td>
<td>250</td>
<td>5cc air/min</td>
<td>1.6gr hexadecane</td>
<td>Some produced liquids, orange brown residue on glass</td>
</tr>
</tbody>
</table>

Additional Figure 3 Overview of additional tests performed for identification and schematic drawing of horizontal glass tube configuration. This included injection in a glass tube, depicted below, where a small sample was placed; this is done to understand behaviour of hexadecane and sand. The tests performed in the stainless steel (RVS) had no good result for discussion or some parameters were changed during the experiment to gain information of the behaviour.
Additional Figure 4 Photos of RO sand taken with a Leitz MZ8 microscope. A) The oil sand sample of RO at 250°C tube temperature and air injection; B) The oil sand sample of RO at 400°C tube temperature and air injection; C) The hard sand sample of RO at 400°C tube temperature and nitrogen injection. The residue left on the grains is heaviest for A, as indicated by the dark colours which makes the observation of the individual grains hard. B is already indicating some lighter oils around the grains. For C some grains are not covered with oil.

The green bars indicate a length of 1mm. and the red bar a length of 500µm.
Appendix A

This appendix presents the settings and the calibration of the GC. The settings of the GC used given by the method are given in Table A-1

<table>
<thead>
<tr>
<th>Table A-1 GC Settings</th>
</tr>
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<tbody>
<tr>
<td><strong>Column 1</strong></td>
</tr>
<tr>
<td>Sample Inlet Temperature (degC)</td>
</tr>
<tr>
<td>Injector Inlet Temperature (degC)</td>
</tr>
<tr>
<td>Column Temperature (degC)</td>
</tr>
<tr>
<td>Sample Pump time (sec)</td>
</tr>
<tr>
<td>Injection Time (msec)</td>
</tr>
<tr>
<td>Run Time (sec)</td>
</tr>
<tr>
<td>Equilibrium Time (sec)</td>
</tr>
<tr>
<td>Column Pressure (bar)</td>
</tr>
<tr>
<td>Post Run Pressure (bar)</td>
</tr>
<tr>
<td>Detector Sensitivity</td>
</tr>
<tr>
<td>Data Rate (Hz)</td>
</tr>
<tr>
<td>Base Line (mV)</td>
</tr>
<tr>
<td>Injector type</td>
</tr>
<tr>
<td>Carrier Gas</td>
</tr>
<tr>
<td>Column Type</td>
</tr>
<tr>
<td>Detector Type</td>
</tr>
</tbody>
</table>

The detection is done based on the conductivity of the gases and the area underneath the signal peak is directly related to an absolute amount of substance. To establish a relation between area and amount of component (in absolute mol), a calibration is needed. To calculate the amount of gas taken in the columns, the ideal gas law is assumed and the volume of the sample inlet is set at 1 microliter:

\[
\frac{n_{\text{ideal gas law}}}{RT} = \frac{P/V}{RT} = \frac{(208600Pa)(1.00-10^{-9}m^3)}{(8.314J/K\cdot mol)(273K)} = 2.7878 \cdot 10^{-7} \text{mol}
\]

The following calibration gasses were used: nitrogen, ‘clean’ air and the Universal Gas Calibration Standard (UGCS). Each gas was injected for time and the specific area of each component was determined (blue bars in following figures). The areas were compared for each component and corresponding areas were picked (red bars in following figures). These picked areas were used to determine the average area of the component. For each calibration gas the absolute amount of each component was calculated. The corresponding area and absolute amount were inserted in
the method in the GC. The software of the GC determined a linear relation for area with amount and calculated the correlation of this relation. For each component the area picks and the corresponding relation can be observed from Figure A-1 to Figure A-8.

![Figure A-1 Calibration curves for nitrogen detected in this work. At the left hand side and middle the areas of nitrogen present in respectively a nitrogen gas and clean air are given, at the rhs the resulting calibration curve is shown. The blue bars are the measured areas for clean air and nitrogen. The picked areas to base averaging on are indicated by red bars.](image1)

![Figure A-2 Calibration curves for oxygen detected in this work. At the left hand side the area of oxygen present in a clean air is given, at the rhs the resulting calibration curve is shown. The blue bars are the measured areas for clean air. The picked areas to base averaging on are indicated by red bars.](image2)

![Figure A-3 Calibration curves for carbon dioxide detected in this work. At the left hand side and middle the areas of carbon dioxide present in the UGCS detected by respectively Ika and Bouwe are given, at the rhs the resulting calibration curve is shown. The blue bars are the measured areas for UGCS. The picked areas to base averaging on are indicated by red bars.](image3)
Figure A-4 Calibration curves for carbon monoxide detected in this work. At the left hand side and middle the areas of carbon monoxide present in the UGCS detected by respectively Ika and Bouwe are given, at the rhs the resulting calibration curve is shown. The blue bars are the measured areas for UGCS. The picked areas to base averaging on are indicated by red bars.

Figure A-5 Calibration curves for methane detected in this work. At the left hand side and middle the areas of methane present in the UGCS detected by respectively Ika and Bouwe are given, at the rhs the resulting calibration curve is shown. The blue bars are the measured areas for UGCS. The picked areas to base averaging on are indicated by red bars.

Figure A-6 Calibration curves for ethane detected in this work. At the left hand side the area of ethane present in the UGCS detected by Ika is given, at the rhs the resulting calibration curve is shown. The blue bars are the measured areas for UGCS. The picked areas to base averaging on are indicated by red bars.
The next table gives a good overview of the output of the calibration was based. For several components different calibration gasses were used, the correlation of the relation obtained to these calibrations is also indicated. This correlation is an indication of the error of calibration and is largest for ethylene, see Table A- 2.
Table A-2 Input for calibration of the method in GC and the corresponding correlation to linear relation. The components are listed with their corresponding average area obtained from averaging calibration gasses. Some calibrations of components are based on two calibration gasses, for these components two areas and amounts are presented. The amount of each component in the calibration gas is presented both relative and absolute. The correlation of the linear relation is indicated for each amount of component with its corresponding area.

<table>
<thead>
<tr>
<th>Component</th>
<th>Average Area</th>
<th>Amount[%]</th>
<th>Amount[mol]</th>
<th>Correlation</th>
</tr>
</thead>
<tbody>
<tr>
<td>N2</td>
<td>1423543.546</td>
<td>100.00</td>
<td>2.7877E-07</td>
<td>0.99997</td>
</tr>
<tr>
<td></td>
<td>1100733.737</td>
<td>78.13</td>
<td>2.1782E-07</td>
<td></td>
</tr>
<tr>
<td>O2</td>
<td>300137.347</td>
<td>21.02</td>
<td>5.8610E-08</td>
<td>1.00000</td>
</tr>
<tr>
<td>CO2</td>
<td>897.0719333</td>
<td>0.05</td>
<td>1.3939E-10</td>
<td>0.92414</td>
</tr>
<tr>
<td>CO2</td>
<td>1430.265306</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>1977.24124</td>
<td>0.10</td>
<td>2.7878E-10</td>
<td>0.99865</td>
</tr>
<tr>
<td></td>
<td>1861.931611</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH4</td>
<td>1608934.754</td>
<td>99.05</td>
<td>2.7613E-07</td>
<td>0.99951</td>
</tr>
<tr>
<td>CH4</td>
<td>1551733.184</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C2H6</td>
<td>1167.465886</td>
<td>0.05</td>
<td>1.3939E-10</td>
<td>1.00000</td>
</tr>
<tr>
<td>C2H4</td>
<td>886.2599984</td>
<td>0.05</td>
<td>1.3939E-10</td>
<td>0.75331</td>
</tr>
<tr>
<td></td>
<td>2687.671392</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C2H2</td>
<td>750.8048974</td>
<td>0.05</td>
<td>1.3939E-10</td>
<td>1.00000</td>
</tr>
</tbody>
</table>
Appendix B

The combustion of a hydrocarbon can be written as

\[ CH_n + \left[ \frac{2m+1}{2(1+m)} + \frac{n}{4} \right] O_2 \rightarrow \left[ \frac{1}{1+m} \right] CO + \left[ \frac{m}{1+m} \right] CO_2 + \frac{n}{2} H_2O \]

\[ m = \frac{CO_2}{CO} \]

\[ n = \frac{H}{C} \]

For hexadecane combustion \( n = \frac{34}{16} = 2.125 \). If we assume combustion at 30% hexadecane saturation, we obtain from Figure 9a at 5hrs:

<table>
<thead>
<tr>
<th>Component</th>
<th>Rate (10^{-5} Mol/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O2_exhaust</td>
<td>0.5</td>
</tr>
<tr>
<td>CO2</td>
<td>2.5</td>
</tr>
<tr>
<td>CO</td>
<td>1</td>
</tr>
<tr>
<td>O2_injected</td>
<td>8</td>
</tr>
</tbody>
</table>

Table A-3 Component exhaust gas rate at 5hrs in 30% hexadecane saturation at 300°C.

So we determine \( m = \frac{2.5}{1} = 2.5 \), this means that the stoichiometric number of O2 in the equation is 1.39. Netto 7.5 mol oxygen is consumed per minute, this would result normally in 7.5/1.39*(1/(1+2.5))=1.5 mol/min CO and 7.5/1.39*(2.5/(1+2.5))=3.9 mol/min of Carbon dioxide. The chemical reactions would therefore describe:

\[ CH_{2.125} + 1.39O_2 \rightarrow 0.29CO + 0.71CO_2 + 1.06H_2O \]

The amount of carbon monoxide and dioxide is higher than measured, if we assume all oxygen is consumed in the combustion of hexadecane:

\[ 0.34C_{16}H_{34} + 7.5O_2 \rightarrow 1.52CO + 3.85CO_2 + 5.8H_2O \]

Or the amount of oxygen consumed is lower, if we assume that the oxides are produced from only combustion:

\[ 0.215C_{16}H_{34} + 4.8O_2 \rightarrow 1CO + 2.5CO_2 + 3.7H_2O \]

It is thought that oxides are consumed by LTO reactions, therefore the lack of measured oxygen in the exhaust gas can be described. The molecular weight of hexadecane can determine the weight loss per minute at the peak: 0.215E-5mol/min*222gr/mol=4.337E-4gr/min. So for 20hrs of combustion, 0.57gr of hexadecane would have been combusted if we assume that it has the same rate as 5hrs. This is a very small amount, compared to the 7.6gr inserted.
Appendix C

This appendix gives the results to check on duplicity of the experiments involved.

30% Saturation of Hexadecane at 250degC with air injection:

Figure C-1 Gas exhaust analysis for 30% saturation of hexadecane by a GC. Experiment 3(left) and Experiment 4(right).

Figure C-2 Ideal Gas Behaviour of Gas Analysis for 30% saturation of hexadecane. Experiment 3(left) and Experiment 4(right).

Figure C-3 Relative temperature for 30% saturation of hexadecane. Experiment 3(left) and Experiment 4(right).
50% Saturation of Hexadecane at 250°C and air injection:

Figure C-4 Exhaust gas composition for 50% saturation of hexadecane. Experiment 1(left) and Experiment 2(right).

Figure C-5 Ideal gas behaviour of gas analysis for 50% saturation of hexadecane. Experiment 1(left) and Experiment 2(right).

Figure C-6 Relative temperature for 50% saturation of hexadecane. Experiment 1(left) and Experiment 2(right) have set tube temperature of 300°C. The readings for experiment 2 becomes more flattened after 11hrs, experiment1 continuous to be fluctuating. Injection starts at t=0; negative times indicate pre-heating.
100% Hexadecane saturation at 150°C (top left), 300°C (top right), 400°C (bottom left) and 450°C (bottom right):

Figure C-7 Exhaust Gas analysis by a GC of cracking of hexadecane.

Figure C-8 Temperature profiles for hexadecane cracking. Nitrogen injection started at t=0; negative times indicate pre-heating.
100% Rotterdam Field Oil Saturation at 250°C with air injection

Figure C-9 Exhaust gas analysis of RO at low temperatures with air injection. Experiment 8 (left) and 10 (right) had a sand tube filled with 100% RO saturation and air injection, heating of tube was at 250°C.

Figure C-10 Ideal behavior of RO air injection at low temperatures. Experiment 8 (left) and 10 (right) had a sand tube filled with 100% RO saturation and air injection, heating of tube was at 250°C.

Figure C-11 Temperature distribution in tube of RO with air injection at low temperatures. Experiment 8 (left) and 10 (right) had a sand tube filled with 100% RO saturation and air injection, heating of tube was at 250°C.
100% Rotterdam Field Oil Saturation at 400°C for 3 hours

Figure C-12: Exhaust gas analysis of RO air injection at high temperatures. Experiment 11 (left) and 12 (right) had a sand tube filled with 100% RO saturation and air injection, heating of tube was at 400°C.

Figure C-13: Ideal behavior of RO air injection at high temperatures. Experiment 11 (left) and 12 (right) had a sand tube filled with 100% RO saturation and air injection, heating of tube was at 400°C.

Figure C-14: Temperature distribution in tube of RO with air injection at high temperatures. Experiment 11 (left) and 12 (right) had a sand tube filled with 100% RO saturation and air injection, heating of tube was set at 400°C. At t=0 air injection starts; for negative times the effect of pre-heating is seen.