In-Situ Oil Combustion: Processes Perpendicular to the Main Gas Flow Direction

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Abstract

Since most easy oil has been produced, there is an increased interest in enhanced oil recovery methods, e.g., in-situ oil combustion. Oil combustion in its current form was first patented in 1953, by R.L. Smith and K.M. Watson. It has not seen widespread use, because controlling the process is considered very difficult, and explosion hazards and corrosion in wells made thermal oil recovery by employing steam, which was also developed in the fifties, more popular. Nevertheless, a steady stream of research continued to be done throughout the years.

Experimental and modeling work largely focused on the so-called longitudinal behavior, which describes the process in the form of a wave-train related to a propagating combustion zone. In practice, however, the override of injected air implies the existence of reactive and transport processes perpendicular to the main direction of gas flow. Therefore, this paper embarked upon an experimental study of oil combustion processes occurring below and perpendicular to the overriding gas stream.

A T-shaped quartz-reactor is used, of which the vertical part is filled with a mixture of sand and oil. An electrical resistance wire was used to heat up the interface of the overriding gas-stream and the oil-saturated sand column. The composition of the effluent gas was recorded using a gas-chromatograph. The temperature in the vertical part is recorded using thermocouples.

From the produced data, a theoretical model is suggested describing the reactions and transport phenomena occurring perpendicular to the main gas-flow direction. Both low temperature oxidation and high temperature oxidation are observed. Air is transported through the sand by thermally driven natural convection and diffusion. Coke formation is observed. From the coke formation observed when using pure hexadecane it is inferred that a mechanism exists that forms coke directly from hydrocarbon components that are in the gas-phase. An experiment using glass beads as a porous medium instead of sand proves that this mechanism also takes place in the absence of potential catalysts. The amount of coke and the amount of transport of oxygen to the combustion zone can both limit the continuation of the combustion. Which is the case depends on what oil is used.

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Introduction

Much of the world's 'easy oil' has already been produced. This has led to increasing attention for heavy oil. The Canadian Athabasca oil sands currently contain 10.7% of the world's proved oil reserves[1]. Large quantities of heavy crude are also present elsewhere, like for instance in the Orinoco belt in Venezuela. Thermal methods for enhanced oil recovery are required for unlocking the potential of these heavy oil reservoirs and oil sands. In-situ combustion is a technology very suitable for thermally enhanced production of heavy oil.

The idea of underground combustion dates back to 1888, when Mendeleev suggested injection of air into a coal seam in order to produce combustible gas from it[2]. Application of underground combustion to oil reservoirs is first described in a US patent from 1923[3]. It explains the concept of generating heat in the underground cavity at an oil well by injecting air and combustible gas, followed by the convective displacement of generated heat into the surrounding rock by injection of inert gas. The first field application dates back to 1934, when Russian engineers performed field tests employing a similar downhole combustion technique[4]. Even though difficulties with igniting the oil caused the field tests to be considered failures, they did demonstrate that combustion can occur within the porous structure of an oil-bearing sandstone. In 1947 a team of researchers from Sinclair Oil and Gas Company was assigned to investigate thermal methods for oil recovery. Their work formed the foundation of the in-situ combustion process as we know it today. This process, involving a combustion supported heat wave and a combustion wave, is first proposed in a US patent dating from June 1953[5]. Field tests and experimental work corroborated the conceptual ideas. An article[6] published in "The Oil and Gas Journal" of August 1953 by researchers from Magnolia Oil Company showed they too had been working on in-situ combustion. They arrived at similar conclusions only months after the patent had been filed, i.e., that the in-situ combustion process forms a feasible thermal recovery method. As the process was further developed and more field tests undertaken, engineering difficulties were encountered. Some of the problems encountered are explosions in the production facilities, heavy corrosion, sand production, liquid blocking and gravity segregation[7]. Because of this, steam injection is the most employed thermal recovery method nowadays. However, further development of the understanding of the underlying processes of in-situ combustion continued throughout the years, with much attention for the kinetic behavior. More recently the concept of Toe to Heel Air Injection (THAI), which combines a vertical air injection well with a horizontal producer, has been proposed and experimental results show potential for its application in bitumen- and heavy oil production[8].

On a basic level the in-situ combustion process comprises injecting air into a reservoir, igniting the oil at the injection well and propagation of the combustion front by continued air injection. What happens in the reservoir is commonly conceptualized as a sequence of propagating zones at different temperatures where different phenomena occur (Figure 1). The maximum temperature is encountered in the combustion zone where the combustion takes place. The burnt zone has been swept by the combustion wave, leaving behind mainly clean sand. Just ahead of the combustion zone high temperatures cause in-situ cracking of the oil, resulting in deposition of coke on the matrix surface.

Gaseous- and liquid hydrocarbons which now flow more easily with their viscosity thermally lowered are swept downstream of the combustion front. As the temperature in the reservoir decreases with increasing distance from the combustion front, gases will condense resulting in a zone with elevated oil saturation. Around the combustion zone, a heavy fraction separates from a lighter fraction due to distillation. Thermal cracking breaks large molecules into lighter hydrocarbons. Due to these effects, the oil in the oil bank is upgraded with respect to its original state; it will have a lower density, be less viscous and consist of relatively more saturates and aromatics, with respect to resins and asphaltenes. The water, which is originally present in the reservoir or produced by the oil combustion reactions, will also be swept away from the combustion front in a vapor state and condense downstream.

Kinetic effects that are commonly distinguished are pyrolysis effects and oxidation reactions. Realistically the nature of crude oil is so complex that individual modeling of each component is not feasible for simulation purposes. Hence, pseudo-components are commonly used. Several kinetic models are found in the literature[9,10]. Pyrolysis processes that are commonly distinguished are distillation, visbreaking (mild cracking) and (heavy) cracking[11]. Oxidation reactions are separated into low-temperature oxidation (LTO) and high-temperature oxidation (HTO)[12,13]. The latter is the complete combustion, at high temperatures, of heavy oil residue and coke. The former is the oxidation of liquid hydrocarbons at lower temperatures, resulting in the formation of alcohols, ketones, carboxylic acids and other partially oxidized hydrocarbons[14]. Both reaction types occur simultaneously at intermediary temperatures; the temperature determines which reaction is dominant.

Gravity override of injected gas occurs in in-situ combustion (Figure 2). Nevertheless most previous theoretical work considers the in-situ combustion process as a longitudinal, one dimensional problem. The propagation direction of the stream of injected gas and the various propagating waves are the same. The work presented here focuses on the thermal and chemical processes occurring in the direction perpendicular to the main gas flow direction. An experimental setup has been built, in which air flows through the horizontal part of a T-shaped quartz tube in which the vertical part is filled with an oil-sand mixture. At the interface between the vertical and horizontal parts of the tube, injected gas flows over the oil-saturated sand. This emulates the situation where gas in a reservoir overrides the reservoir liquids. It also resembles the situation encountered in a THAI setup, where a combustion front adjacent and parallel to a vertical gas stream propagates laterally. Clear understanding of this perpendicular behavior provides the knowledge necessary to accurately simulate the in-situ combustion process in 2D or 3D models.

First the experimental setup and procedures are described. Next the results of the experiments are presented. Then a discussion of the results and conclusions of the work follow.

Experiment and results

Experiment

An experiment has been devised with the purpose of observing the processes occurring during in-situ combustion in the direction perpendicular to the flow direction of the injected gas stream. A T-shaped quartz tube is used as a reactor. Its vertical part is filled with a mixture of sand and oil. Sand containing feldspars, of the same batch, is used for each experiment. When packed in the reactor the porosity (42.7%) is determined from the volume of the vessel, the densities of air and sandstone and the weight of the sand in the vessel. Three types of oil are used, a heavy, medium and light oil. Additionally, experiments are done with pure hexadecane as model oil. The densities and API gravities are given in

Table 1. Furthermore, an experiment with hexadecane, glass beads with a 650μm diameter, and nitrogen injection is done to gain extra insight in the coke formation process.

Experiments with injection of normal air and with injection of nitrogen are performed. Figure 3 shows a schematic representation of the set-up. The injected gas first passes through a back-pressure valve (1) which is set to two bars absolute, then through a regulating valve (2) that is used to control the flow rate. A buoyancy-based Matheson FM-1050 flow meter (3), calibrated with a Sierra Smart Trak 2 mass flow meter, measures the flow rate into the reactor (4). Next the gas flows into the reactor. At the exit of the reactor the pressure is determined by means of a manometer (5). The effluent gas is directed through a glass bottle (6), which is filled with cotton wool to capture oil droplets in the gas stream. This is necessary to avoid contamination and blockage of the flow lines and the columns of the gas chromatograph. Just before the gas enters the gas analyzer it flows through an extra gas liquid separating filter (7) that is connected to the analyzer. The gas analyzer is an Agilent 3000 MicroGC. It has been calibrated with a calibration gas mixture and pure air.

Three thermocouples (8) are positioned in the center of the vertical tube, into which the oil-sand mixture is loaded, to monitor the temperature at three different positions during the experiments. They are inserted through a rubber plug that closes off the bottom of the vertical part of the quartz tube. The upper thermocouple measures the temperature at the interface between the sand-oil mixture and the gas stream, where the horizontal and vertical parts of the tube meet. The other thermocouples measure respectively one centimeter and two centimeter below the interface. Temperature data are recorded each second. The top of the reactor consists of a concave protrusion through which the tube can be loaded with sand and oil. After filling, a quartz plug with a convex end that exactly fits this protrusion is clamped onto the reactor in order to close it off. The top of the intersection of the horizontal and vertical parts of the tube are wrapped in an electrical heating cord (9), which can be set to temperatures up to 900°C. An electrical power source with adjustable voltage is used to set the temperature. Finally, the heated part of the reactor is insulated using stone-wool fixed with heat resistant tape.

For each experiment the reactor is loaded with a mixture of sand and one of the crude oils or hexadecane. The mixture is made such that the liquid saturation is 50%. Once the reactor is loaded with the mixture, the top is closed with the plug and clamp, and the heating cord is wrapped around the intersection. The cord is wrapped in such a way that the upper two centimeters of the vertical part, as well as two centimeters of the horizontal part directly upstream of the intersection, are heated. Then the stone wool is applied around the heated area as insulation.

The initial flow is set to 390 ml/min for experiments with air, and to 800 ml/min for experiments with nitrogen, as these rates give the same reading from the Matheson buoyancy flow meter. The flow rate is not manually changed throughout the experiment. As the pressure in the reactor increases, the flow rate decreases to 20 ml/min for both gases. The pressure is kept constant throughout the experiment. The pressure attains, and stays at, a value of 1.80 bar for each successful experiment. If the pressure is lower the set-up is leaking, if it is higher there is liquid blocking, caused by condensing hydrocarbon components in the capillary tube that leads to the gas chromatograph. Therefore experiments for which the pressure deviates from 1.80 bar by more than 0.05 bar are aborted and considered failures.

Injected gas flows through the reactor and the pressure rises to 1.80 bar before the heat source is activated. For the experiments with nitrogen injection, the reactor is first purged until only trace amounts (under 0.2 mol%) of oxygen are left. The temperature of the heating cord is set to 900°C for all experiments. The actual experiment starts when the heat source is switched on. Temperature data are stored each second and gas samples are taken and analyzed each five minutes. The experiment is continued until the concentrations for each component are close to their original values.

The mass of coke that is deposited in each of the experiments is determined by weighing a sample of coke-covered sand and weighing again after removing the coke by heating the sample in an oven to 1000^{o}C under oxidizing conditions.

Results

All experiments show a sequence of reaction processes occurring in the sand perpendicular to the main flow direction. Clean sand is observed near the interface after air injection experiments. Such clean sand is not observed after nitrogen injection experiments. The presence of hydrocarbon gas in the effluent gas, produced as a result of cracking, indicates that while passing through the oxidation zone in the air injection experiments these gases are not oxidized. Sand on which coke has been deposited is observed for all experiments. In the experiment with glass beads, coke formation is also observed. The relative volumes of clean sand and coke that have been produced in each of the sand-experiments are schematically depicted in Figure 4.

Figure 5 to Figure 12 show graphs of the temperature and compositional data for the experiments. The maximum values for oxygen consumption, carbon mono- and dioxide production and hydrocarbon gas production for each experiment are found in Table 2.

Generally, carbon monoxide is formed first before carbon dioxide is observed. An exception is the light oil experiment, for which only carbon dioxide is formed. The maximum concentrations of carbon mono and dioxide are almost equal for heavy and medium oil, but for hexadecane the maximum carbon monoxide concentration is approximately twice the maximum carbon dioxide concentration. The hydrocarbon gases are produced simultaneously with the carbon monoxide and start to disappear when carbon dioxide is formed. More oxygen is consumed than required for the produced quantities of carbon mono- and dioxide. The observed processes resemble those observed in combustion tube experiments.

For nitrogen injection experiments the produced quantity of hydrocarbon gas is lower than for the corresponding air injection experiments, with the exception of the light oil experiment, for which exceptionally large quantities of hydrocarbon gas are produced during the nitrogen experiment but almost none during the air experiment. Trace amounts of carbon dioxide and oxygen are found for each of the nitrogen experiments.

The analysis of the effluent gas indicates the reactions begin at different times for different experiments. The formation of carbon monoxide coincides with the formation of hydrocarbon gases in the air experiments. The maximum amounts for the different hydrocarbon gases also coincide Table 3 shows the times at which the peak values are observed.

In the graphs of the temperature data, T1 represents the temperature at the interface, T2 the temperature one centimeter below it and T3 the temperature two centimeters below the interface. R1 to R3 are numerically determined temperature rates of temperature change. The temperature increase is caused by electrical heating and chemical reactions. For the air experiments, the highest temperature occurs closest to the interface between the sand and the overriding gas stream, with the exception of the heavy oil experiment for which the highest temperature after some time is encountered at the thermocouple one centimeter below the interface. This is because, after some time, when the sand level has dropped due to consolidation as oil is displaced and oxidized, this thermocouple is no longer covered by sand. For nitrogen experiments it usually is the thermocouple one centimeter below the interface that shows the highest temperature after some time. The maximum, minimum and average temperatures are found in Table 4.

For early times the maximum temperature rate is observed for the thermocouple closest to the surface. The rates steeply increase to around 100°C where they level off. The rates for the heavy oil experiments show steep dips at 100°C. Spikes in the rate to some degree are observed in all experiments. These occur at the times that compositional data indicate that reaction processes are occurring. It can be observed at a single thermocouple or at multiple thermocouples simultaneously. This behavior is more pronounced in the air experiments than in the nitrogen experiments. An exception is the nitrogen experiment with light oil (Figure 10), which displays a strongly spiking rate for the thermocouple at the interface throughout most of the warm-up period. The temperature at this thermocouple is lower than the temperature at the other thermocouples for the duration of the spiking rate behavior, but increases as the rate stabilizes. Higher rates are observed in the air experiments than in the nitrogen experiments.

The quantity of coke that is deposited for each experiment, in grams per kilogram of sand, is found in Table 5. For the experiment with air flow and hexadecane, after the experiment no zone with continuous coke deposition is observed, but a zone with patches of coke dispersed throughout the sand. Both below and above the zone with the coke patches, zones with only clean, dry sand are found. At the lower end of the vertical part of the reactor, a zone of liquid saturated sand is observed.

Discussion

First and foremost, the experiments have shown that oxidation reactions occur perpendicular to the main gas flow direction. Inspection of Figure 5 to Figure 8 shows that in all experiments where air is injected oxygen is consumed and carbon monoxide and carbon dioxide is formed. Moreover, for all air injection experiments a zone of clean-burned sand can be observed (Figure 4). This is not observed in the corresponding nitrogen injection experiments in which only coke-covered sand is observed. This further corroborates that a combustion reaction must have occurred. The lack of produced carbon mono- and dioxide in the nitrogen experiments shows that these experiments can serve to study only thermal processes, i.e., evaporation/distillation and cracking, without the interference of oxidation.

Figure 13 shows a schematic depiction of the situation in the vertical part of the tube after some time. It illustrates the various reaction and transport processes that play a role in this set-up. The interface with the overriding injected gas stream is located at the top of the zone with gas-bearing sand. On the left a schematic temperature profile is shown. The dashed line indicates how temperature increases with time, as conduction slowly distributes heat deeper into the lower end of the reactor. This continues until a steady state situation between generated and lost heat is reached, at which point the vertical temperature profile no longer changes.

Initially the whole vertical tube contains a mixture of sand with one of the crude oils or hexadecane. Figure 14 schematically shows which reactions occur in different temperature intervals. Reactions with oxygen are on the left, reactions without oxygen, but only resulting from heat, on the right. The temperatures that are shown in this figure are indicative values and vary for each crude oil. The processes are not mutually exclusive; they overlap and compete with each other. Temperature dictates which of the processes are dominant at any given time. As the heat source is turned on the temperature increases and evaporation of lighter components commences, effectively distilling the oil. As the temperature further increases, more of the liquid phase evaporates and the volume of the gas-bearing zone extends vertically. Consequentially, a heavy fraction of the liquid phase that does not evaporate at the current temperature is left. With further increase of the temperature, cracking and coking begin. Cracking forms lighter hydrocarbons, as observed in the effluent gas of the experiments. Rearrangement of molecules, dehydrogenation and polymerization all are part of the coking process. Ultimately all that is left in the reactor is coke and sand.

The presence of a vertical temperature gradient implies the presence of successive zones where different processes are dominant. Coke is formed in the upper zone, where the temperature is high enough to crack any present hydrocarbon components. For hexadecane, a zone where all liquid has evaporated but with temperatures too low for cracking is found below it, followed by a zone with a liquid phase. For the oils, there is coke-covered sand up to the depth where there is a liquid phase. In Figure 13 this would imply that the cracking zone's lower boundary coincides with the gas-liquid interface.

The gas-liquid interface slowly moves downwards as heat penetrates deeper into the vertical tube and more of the liquid phase evaporates.

For the oxidation reactions we distinguish high temperature oxidation (HTO) and low temperature oxidation (LTO). The upper part of the vertical tube will eventually be at temperatures in the range necessary for HTO, or combustion. The fact that three out of four figures with the compositional data for the air experiments (Figure 5 to Figure 8) show an initial carbon-monoxide peak followed by a carbon dioxide peak indicates that for those cases there initially is incomplete combustion, followed by complete combustion as temperature further increases. The exception is the light oil experiment (Figure 6), which displays an early carbon dioxide peak and no carbon monoxide peak, but does produce a 1.3cm long zone of burned-clean sand (Figure 4), which is probably connected to the relatively large quantities of hydrocarbon gas that distill from the light oil. Hexadecane shows a larger peak for carbon monoxide than for carbon dioxide, indicating a stronger degree of initial incomplete combustion followed by complete combustion.

Deeper down the vertical tube, temperatures drop below the value required for combustion. The presence of coke-covered sand, below the sand that has burned clean in the air experiments, indicates that coke is still formed at the lower temperatures encountered here (Figure 4). These temperatures are also within the range where low temperature oxidation occurs. Since low temperature oxidation reactions are homogeneous reactions between dissolved oxygen and liquid hydrocarbons, they can only occur in a relatively small region near the gas-liquid interface, of which the extent is determined by the diffusion coefficient for oxygen in the liquid phase. LTO reactions are exothermic reactions, so the heat they generate increases the temperature at the interface and assists in evaporating liquids, moving the interface further down.

In the vertical tube both free convection and diffusion occur. Since there is a vertical temperature gradient, there will be thermally driven free convection in the gas-bearing sand volume. Moreover there will be diffusion in a gas phase, which is relatively fast at the temperatures encountered here. These mechanisms transport (injected) gas between the bulk gas-stream and the gas-liquid interface. At this interface diffusion of gas in liquid, which is much slower, causes some of the injected gas to penetrate into the liquid zone. This facilitates the LTO-reactions in the liquid phase when the injected gas is air. At the interface evaporation occurs. For crude oil this is a distillation effect, which slows down the temperature increase. The simultaneous oxidation of the liquid hydrocarbons in air-injection experiments continually changes the composition of the liquid near the interface. This results in distillation behavior even for experiments with pure hexadecane. Hexadecane evaporates at the interface together with the alcohols, ketones and other partially oxidized hydrocarbons, which all have different boiling points. Gas moves upwards from the gas-liquid interface by convection and diffusion, through the zone that is at cracking temperature and eventually into the bulk (horizontal) gas stream.

As was mentioned before, after an experiment with air injection and hexadecane a succession, from top to bottom, of the following zones is observed: a zone with clean sand, a zone with patches of coke distributed throughout the sand, another zone with clean sand and finally a zone with liquid hexadecane. The generation of coke during the hexadecane experiments, implies that the production of coke from a heavy fraction of oil, is not the only coke-forming mechanism at work. A possible explanation for the coke generation from pure hexadecane can be found in the literature on refining[17]. Coke formation from hexadecane in the presence of silica-alumina components is documented there. The mechanism involves initial adsorption of hydrocarbon on the catalyst, followed by reactions of the adsorbed material. These reactions include condensation reactions, followed by direct dehydrogenation and the recombination of free radicals that are produced by cracking a hydrocarbon molecule, and direct hydrogen transfer. In refining alumina-silica catalyst offers the surface on which the initial adsorption takes place. This leads to believe that feldspar, a group of minerals often consisting of alumina-silica, possibly acts as a catalyst for this process, providing the surface at which coke deposition originates. However, the nitrogen-experiment in which glass beads replace the sand with feldspar also showed coke formation from hexadecane. This indicates that it is possible for coke to be formed directly from hexadecane in the gas phase, without any catalyst.

Gaseous hexadecane, and in the case of the air-injection experiments gaseous partially oxidized hydrocarbons, are supplied from the sand below the cracking zone. As gases produced at the gas-liquid interface are transported through the cracking zone they form a source of material that produces coke. The fact that feldspars are not evenly distributed throughout the sand possibly explains why coke is found in patches after an air injection experiment, as it could preferentially form around these minerals. With nitrogen injection, for sand as well as glass beads, the coke is distributed continuously throughout the porous medium, which further indicates that the coke formation process from gaseous components occurs in the absence of any catalyst. The relatively large carbon monoxide peak observed in the experiment with hexadecane and air-injection could indicate that the process of coke formation from gaseous components is slower than the process of coke formation from the heavy fraction, thus resulting in a limited availability of fuel at early times and thereby incomplete combustion.

The high temperature combustion reaction is a heterogeneous reaction between solid coke and oxygen[13]. The solid coke itself is porous[12]. The reaction mechanism involves transport of oxygen from the bulk gas-stream to the gas-solid interface, adsorption on the interface, reaction with fuel, desorption of reaction products and finally transport of reaction products back into the bulk gas-stream[13]. Figure 15 schematically depicts the situation of a gas reacting with a porous solid. In the boundary layer there is a laminar flow region through which an oxygen molecule diffuses either to the exterior surface of a coke particle or to the interior surface. The inner surface of the porous particle generally is several orders of magnitude larger than the outer surface. Therefore the reaction occurs mainly at the inner surface of the particle.

The process is a diffusion-reaction process[18]. The efficiency factor is obtained by dividing the diffusion flux through a spherical particle by the diffusion flux through a spherical particle of which the entire inner surface participates in the reaction. This results in a solution involving a dimensionless number, which was named after its inventor, the Thiele-modulus:

$$\phi = \sqrt{\frac{k^{''} A_g}{D}} R$$

Where:

k'' = reaction rate constant per unit surface area of coke [kg of coke / m^2 / s]

A_g = unit surface area [m^2 / kg of coke]

D = diffusion coefficient [m^2 / s]
R = radius of the particle [m]

This number relates diffusion to reaction rate. It follows for the efficiency factor η that:

$$\eta = \frac{3}{\phi^2}(\phi \coth \phi - 1)$$

When Φ is small the efficiency factor is close to one and when Φ is large the efficiency factor goes to zero. An efficiency factor close to zero indicates the reaction taking place mostly at the outer surface of the coke-particle, whereas an efficiency factor close to one indicates the entire inner surface of the coke particle is participating in the reaction. The former situation is referred to as reaction limited, the latter as diffusion limited[18]. For an increasing efficiency factor deeper penetration of the oxidation reaction occurs.

The same theory can be applied to determine the extent to which LTO-reactions penetrate into the liquid. This reaction takes place in the vicinity of the gas-liquid interface, which has a slab-like geometry. The Thiele-modulus for a slab is[18]

$$\phi = \sqrt{\frac{k}{D}} x_p$$

Here:
k = reaction rate constant [1 / s]
D = diffusion coefficient for gas in liquid [m^2 / s]
x_p = penetration depth [m]
The efficiency factor now becomes

$$\eta = \frac{\tanh \phi}{\phi}$$

Again, when Φ is small η goes to one and for large Φ, η goes to zero. An efficiency factor close to zero indicates that the reaction is concentrated at the surface; for an increasing efficiency factor there is an increasing penetration depth of the reaction. With deeper penetration there is a larger volume of fluid reacting. This would suggest that, assuming k to be of the same order of magnitude for different oils, a higher diffusion coefficient would mean a smaller Thiele modulus, which leads to an efficiency factor closer to one indicating a larger volume of liquid in which LTO occurs. Since the diffusion coefficient increases with viscosity, this means that heavier oil has a smaller Thiele-modulus and therefore a larger volume available for LTO. Based on this reasoning it would be expected for LTO to occur only in a relatively small zone near to the gas-liquid interface, due to the low diffusion rate of oxygen in hydrocarbon liquid. The extent of this zone decreases with decreasing diffusion coefficient. Since the diffusion rate is lower for oils with a higher viscosity, the production of oxidized hydrocarbons by the LTO reaction decreases for increasingly heavy oil.

Figure 4 shows that HTO occurs only up to a certain depth into the vertical part of the reactor. It is observed that the extent of the HTO zone increases with increasing density of the oil, also implying an increasing viscosity, with the exception of medium oil, which produces only a small burned-clean volume. Several factors determine whether, and to which degree, the reaction process will be possible, i.e., oxygen availability, fuel availability and temperature.

Figure 5 to Figure 8 show that there is no complete oxygen consumption at any time for any of the experiments, indicating that bulk oxygen availability is never the limiting factor. The mechanism of diffusion of the reactant from the bulk to the fuel surface requires that the localized oxygen concentration is sufficiently high for the reaction to occur. Whether this concentration is high enough, is in turn determined by the rate at which natural convection and bulk diffusion transport the gas throughout the upper, gas-bearing part of the porous medium. Table 2 shows the minimum concentrations of oxygen encountered in the experiments. The values for hexadecane and heavy oil are the lowest. This could indicate that for these experiments localized oxygen availability could indeed drop below the level required for HTO to occur. The values for light and medium oil never drop as low, indicating that for these experiments oxygen availability will most likely not be a limiting factor.

Table 4 shows that in the upper two centimeter of the vertical part of the reactor, the highest average temperature is found for heavy oil, followed by respectively light oil, medium oil and hexadecane. This holds for both air- and nitrogen-injection experiments. Figure 4 shows that this does not exactly match the trend of the extent of the HTO reaction, which is largest for heavy oil followed by, respectively, light oil, hexadecane, and finally medium oil, for which a relatively small volume of clean-burned sand is observed. There does appear to be a connection between the temperature and the volume of sand that is burned clean. It seems likely, however, that the higher temperatures are a result of more extensive HTO rather than that they are the cause for it. This explains the high temperatures for the heavy oil, which displays the most intense combustion, judging by the high oxygen consumption, burned-clean sand volume and carbon monoxide and carbon dioxide peaks. The second highest temperature encountered in the light oil experiment also produces the second largest volume of burned-clean sand, but displays less oxygen consumption than the hexadecane experiment. However the absence of a carbon monoxide peak and the early carbon dioxide peak indicate that HTO in light oil is fast. It is also observed that very little hydrocarbon gas is detected. However, for the nitrogen-injection experiment with light oil much hydrocarbon gas is detected. This indicates combustion of gas rather than coke, which explains the lesser degree of oxygen consumption. The third highest temperature, for the medium oil experiment, would indicate even less extensive HTO occurring here, which is corroborated by the fact that even less oxygen is consumed and only very little sand burned clean. However the lowest temperature, encountered in the hexadecane experiment, does not follow this trend, as it produced more than double the volume of burned-clean sand with respect to the medium oil experiment. It also displayed the highest degree of oxygen consumption. What distinguishes the results of the hexadecane experiment from the rest is the fact that there is a very significant carbon monoxide production; much more than the other experiments. Additionally, the reaction seems to take place over a longer period of time judging by the lateral stretch of the oxygen consumption (Figure 5), indicating a slower reaction process. This results in less heat generation by the reaction, explaining the lower temperature.

The third factor that could form a limitation for the HTO reaction is the fuel availability. Each air-injection experiment showed a zone of coke-covered sand directly below the burned-clean sand. In the case of hexadecane this zone has patches of coke distributed throughout the sand while in the other experiments the coke distribution is continuous. Table 5 shows the quantities of coke that have been deposited on the sand in each experiment. Data for the nitrogen-injection experiments show that pyrolysis generates similar amounts of coke for the heavy and light oil. The amount of coke production for hexadecane and medium oil is significantly lower, the latter having the lowest coke production. As was argued before, there are at least two mechanisms of coke formation, i.e., coke formation from cracking of the heavy fraction of the oil and coke formation from gaseous components moving upwards through the tube. Hexadecane will for obvious reasons only display the latter. The amount of coke formation being similar for hexadecane and medium oil could indicate that the nature of the heavy fraction of the medium oil makes it less suitable for the solid residue cracking mechanism, as a result of which the coke formation leans more heavily on the gaseous component cracking mechanism. However, more insight in the exact composition of the oil is required to make more conclusive remarks on this.

Data for the air injection experiments show a different situation. The least coke is formed in the light oil experiment. Slightly more coke is formed in the experiment with medium oil and finally most coke is, again, generated in the heavy oil experiment. There are no data available for hexadecane since the coke-covered sand is distributed patch-wise during the experiment and could not be extracted without mixing it with clean sand. For medium and heavy oil more coke is generated with air-injection than with nitrogen-injection experiments, but with light oil less coke is deposited in the air-injection experiment. LTO is known to increase the coke formation for certain crude oils[16]. This explains why more coke is found for the two heavier oils. It is reasonable to assume that LTO does not play a major role for the light oil. Light oil displays more evaporation relative to heavier oils, which means that there is a shorter time that the liquid phase is at LTO-temperatures. Less coke production in the air-injection experiment than with the corresponding nitrogen-injection experiment could possibly be related to combustion of some of the coke. The fact that the burned-clean sand volume for the light oil experiment is larger for light oil than for medium oil, even though the amount of coke is lower, can be explained by comparing Figure 6 with Figure 10. The latter shows that with nitrogen-injection much methane is produced, which is not the case for the air-injection experiment. Combined with the fact that for light oil only a carbon dioxide peak is observed, indicating complete combustion, this shows that the methane forms (in part) the fuel for the combustion observed in the light oil experiment. If the methane ignites, there is a quick onset of complete combustion of the coke in the upper part of the tube as well. As the methane runs out, the reaction stops again but generated heat facilitates combustion of some of the coke found on the sand below the zone with burned-clean sand, generates traces of carbon monoxide (Figure 6) and decreases the quantity of coke on the sand. This mechanism possibly creates a shortage of coke limiting the continuation of the reaction.

Summarizing, there are different limiting factors for the oxidation of the different liquids. For hexadecane there is a mechanism of slow coke formation from gaseous compounds and slower combustion, generating more carbon monoxide than carbon dioxide. The oxygen consumption is very large and local oxygen concentration is probably the limiting factor for this process. The combustion of light oil is related to ignition of methane gas. The supply of methane gas and the lower amount of coke-fuel are most likely to limit the continuation of the oxidation process for light oil. For heavy oil it is also most likely that the local oxygen concentration is the limiting factor, since oxygen consumption is large and coke levels are high. Medium oil having the most limited extent of oxidation is hardest to explain. It is possible, as the data suggest, that a combination of limited fuel deposition from the heavy fraction of the oil combined with the absence of sufficient quantities of light hydrocarbon gas to ignite the oil, play an important role in this.

Conclusion

1. An experiment has been designed that enables investigation of in-situ combustion processes occurring perpendicular to the main gas flow direction.
2. The experiment confirms that both pyrolysis and oxidation reactions occur perpendicular to the main gas flow direction.
3. A qualitative conceptual model explaining the various reaction processes and transport phenomena that occur in the transverse situation can be given.
4. In addition to the mechanism of coke formation from cracking of the heavy fraction of a crude, another coke formation mechanism involving cracking of gaseous components exists. This mechanism occurs without any catalyst. It plays a role in coke formation in the transverse direction.
5. Based on the Thiele-modulus it is theorized that the volume of liquid in which the LTO reactions take place is smaller when the oil is heavier. This suggests an increased importance of LTO-related factors with lighter oils.
6. The following tentative mechanisms are suggested for the different oils used for this study and hexadecane:
   a. In the case of hexadecane there is slow coke formation from cracking of hydrocarbon gas (hexadecane-gas with nitrogen-injection, hexadecane-gas and gaseous partially oxidized hydrocarbon components with air-injection), and slow combustion producing large quantities of carbon monoxide. Low oxygen concentration most probably limits the continuation of the reaction.
   b. For the light oil, coke deposition is low due to the smaller heavy fraction. Much methane is detected in the effluent gas of the nitrogen-injection experiment, but very little in the air-injection experiment. This indicates that evaporated light hydrocarbon forms the fuel for the combustion, leading to early ignition of the sand and fast, complete combustion. The available fuel, both in the form of hydrocarbon gas and coke, are most likely to determine the extent to which the HTO-reaction continues.
   c. The medium oil displays the least extensive combustion. A combination of limited coke formation and low hydrocarbon gas production from distillation and cracking is observed. It is asserted that combined these effects limit the reaction.
   d. Most coke is formed from the heavy oil. Large oxygen consumption is observed. As the distance from the main gas stream becomes larger the diffusion supply of oxygen becomes less and this is believed to limit the continuation of the reaction for the heavy oil.

Figures and tables

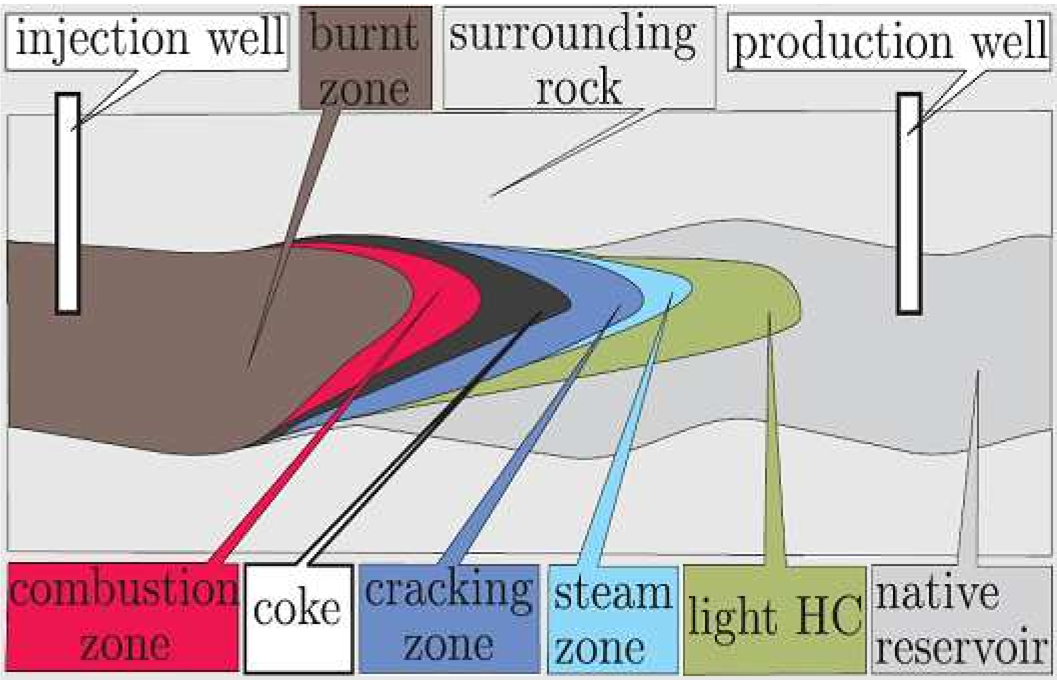


Figure 1: The wave-train concept[15]

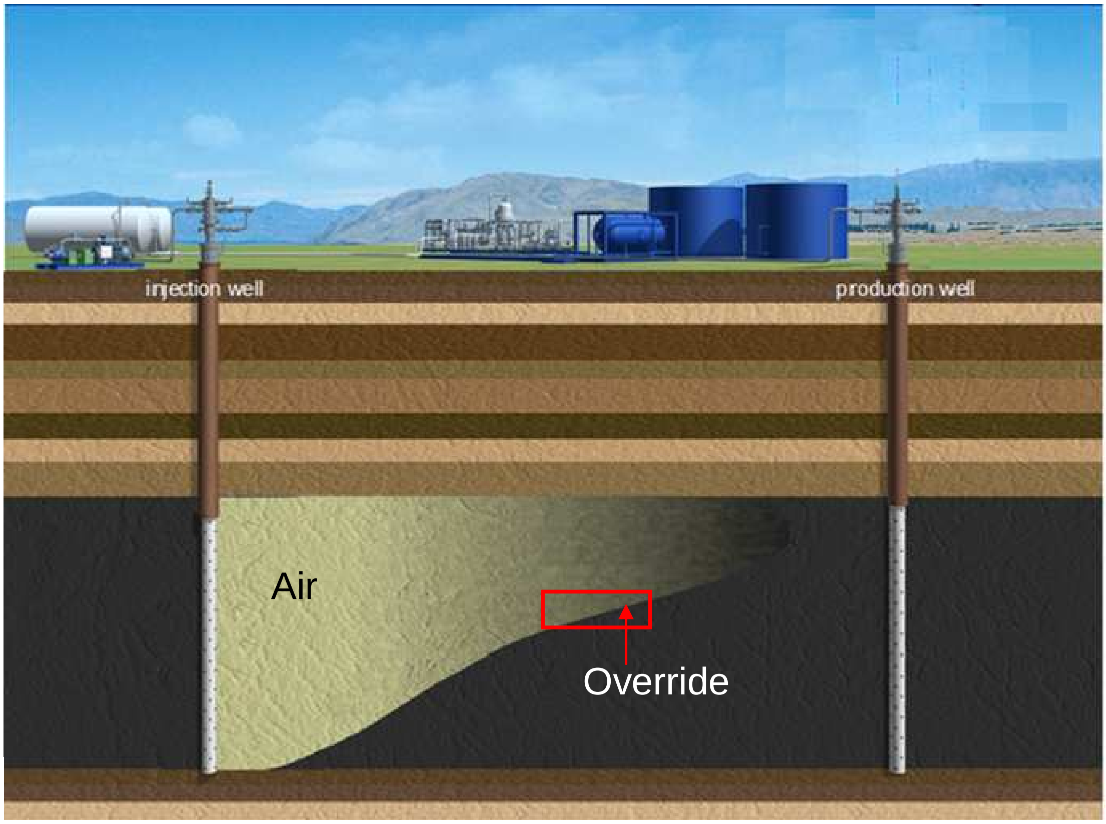


Figure 2: Gravity override illustrated

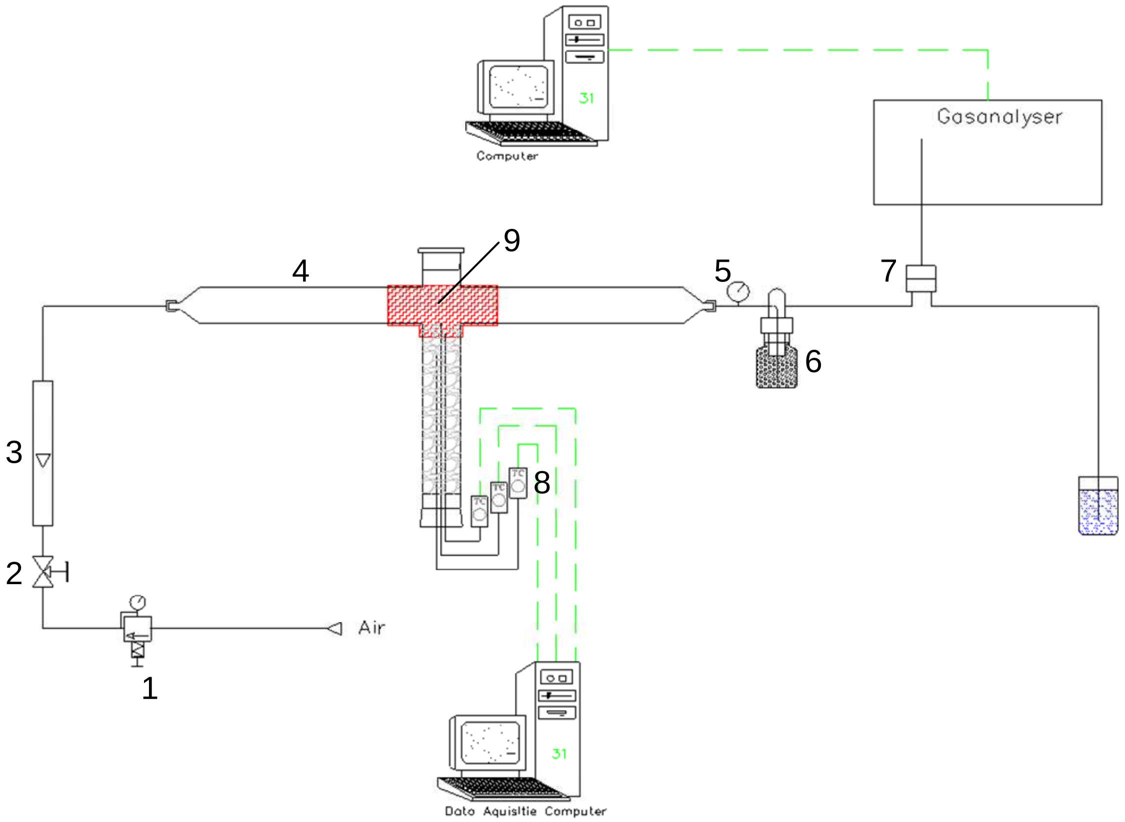


Figure 3: Experimental set-up

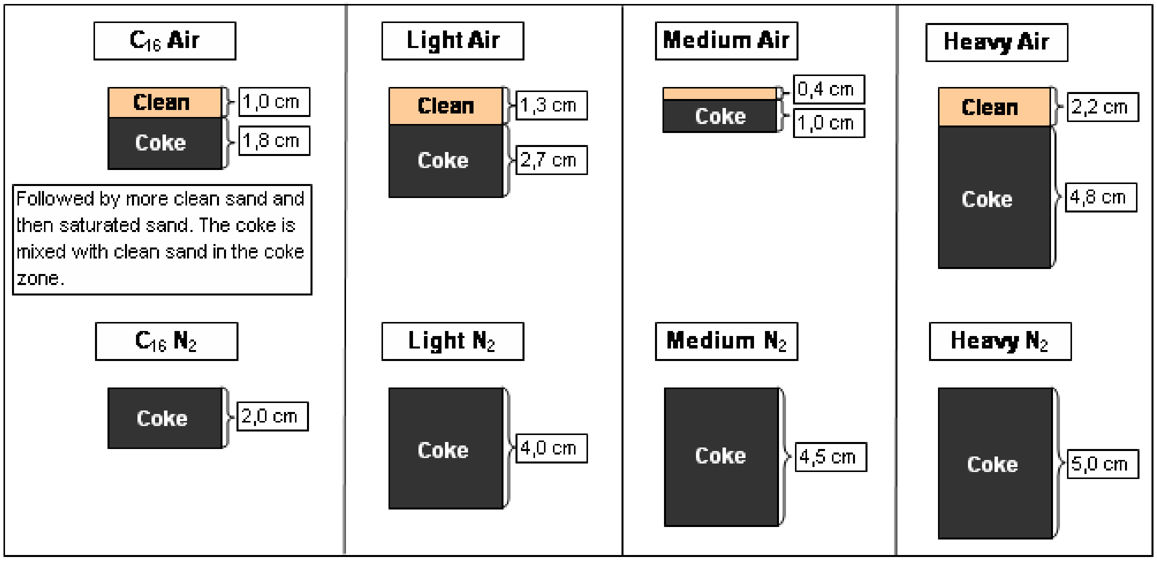


Figure 4: Coke and burned-clean sand zones at the end of the experiments. The total length of the vertical part of the tube is twelve centimeter.

Table 1: Densities and API gravities of the crude oils and hexadecane

	ρ [kg/m^3]	API
Heavy Oil	908	24.3°
Medium Oil	886	28.2°
Light Oil	867	31.7°
Hexadecane	773	51.6°

Table 2: Maximum values for oxygen consumption and production of carbon mono- and dioxide and HC gases in the respective experiments

C_{16} Air	**Mol%**	**Light Air**	**Mol%**	**Medium Air**	**Mol%**	**Heavy Air**	**Mol%**
O_2 min.	1.64	O_2 min.	5.21	O_2 min.	8.37	O_2 min.	2.10
CO max.	12.60	CO max.	Trace	CO max.	6.51	CO max.	10.53
CO_2 max.	6.21	CO_2 max.	9.46	CO_2 max.	6.10	CO_2 max.	10.20
Total HC-gas max.	13.77	Total HC-gas max.	Trace	Total HC-gas max.	3.25	Total HC-gas max.	7.38
C_{16} N_2	**Mol%**	**Light N_2**	**Mol%**	**Medium N_2**	**Mol%**	**Heavy N_2**	**Mol%**
O_2 min.	Trace	O_2 min.	Trace	O_2 min.	Trace	O_2 min.	Trace
CO max.	None	CO max.	Trace	CO max.	Trace	CO max.	Trace
CO_2 max.	Trace	CO_2 max.	Trace	CO_2 max.	Trace	CO_2 max.	Trace
Total HC-gas max.	1.73	Total HC-gas max.	29.98	Total HC-gas max.	1.21	Total HC-gas max.	6.40

Table 3: Times at which maximum values for carbon mono- and dioxide and HC gases are observed in the respective experiments

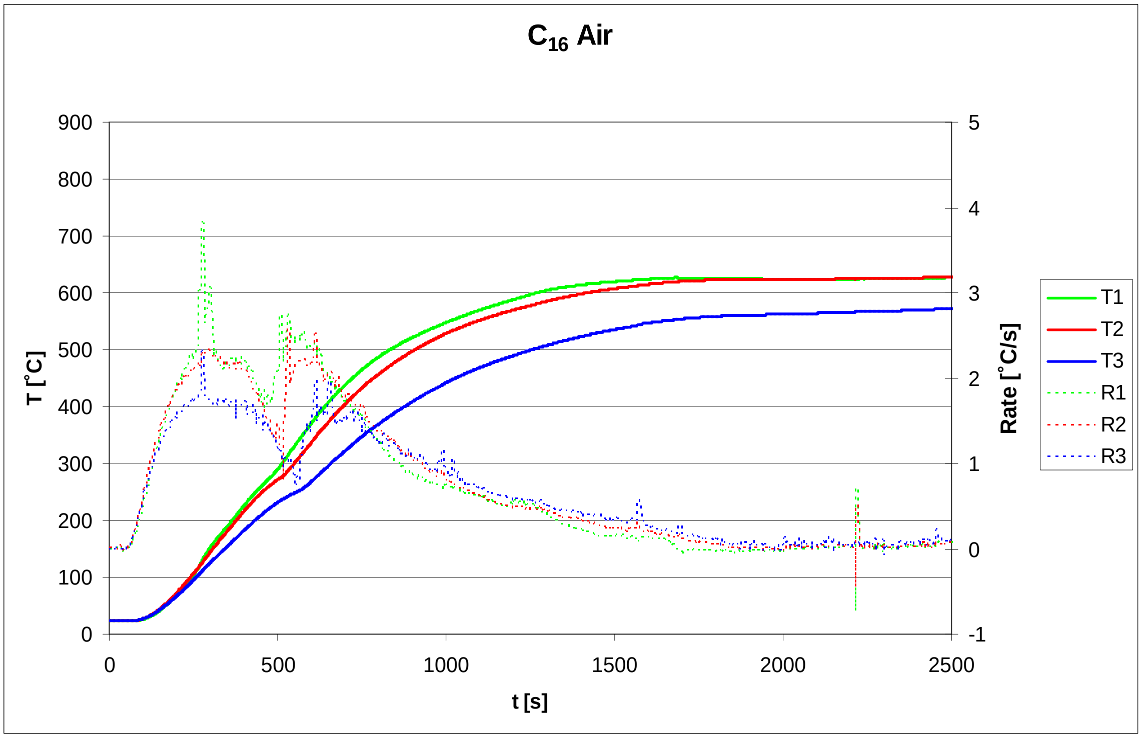
	Time observed [s]			**Time observed [s]**
Air	**Max. CO**	**Max. CO_2**	**N_2**	**Max. HC gas**
C_{16}	3000	5000	C_{16}	2500
Light		1000	Light	4000
Medium	2000	3000	Medium	1500
Heavy	1500	2500	Heavy	2000

Table 4: Maximum and minimum recorded temperatures and averaged value for temperatures over the three thermocouples for the experiments

	T_{max} [°C]	T_{min} [°C]	T_{av} [°C]
Heavy Air	839	810	820
Medium Air	699	549	640
Light air	793	600	707
C_{16} Air	628	573	609
Heavy N_2	753	715	735
Medium N_2	715	661	691
Light N_2	717	681	696
C_{16} N_2	669	612	618

Table 5: Quantity of coke that has deposited on the sand for the various experiments

Air	Coke Mass [g/kg]	N_2	Coke Mass [g/kg]
Light	5.82	Light	8.44
Medium	6.99	Medium	4.08
Heavy	12.47	Heavy	8.88
Hexadecane	Patches of coke	Hexadecane	4.98



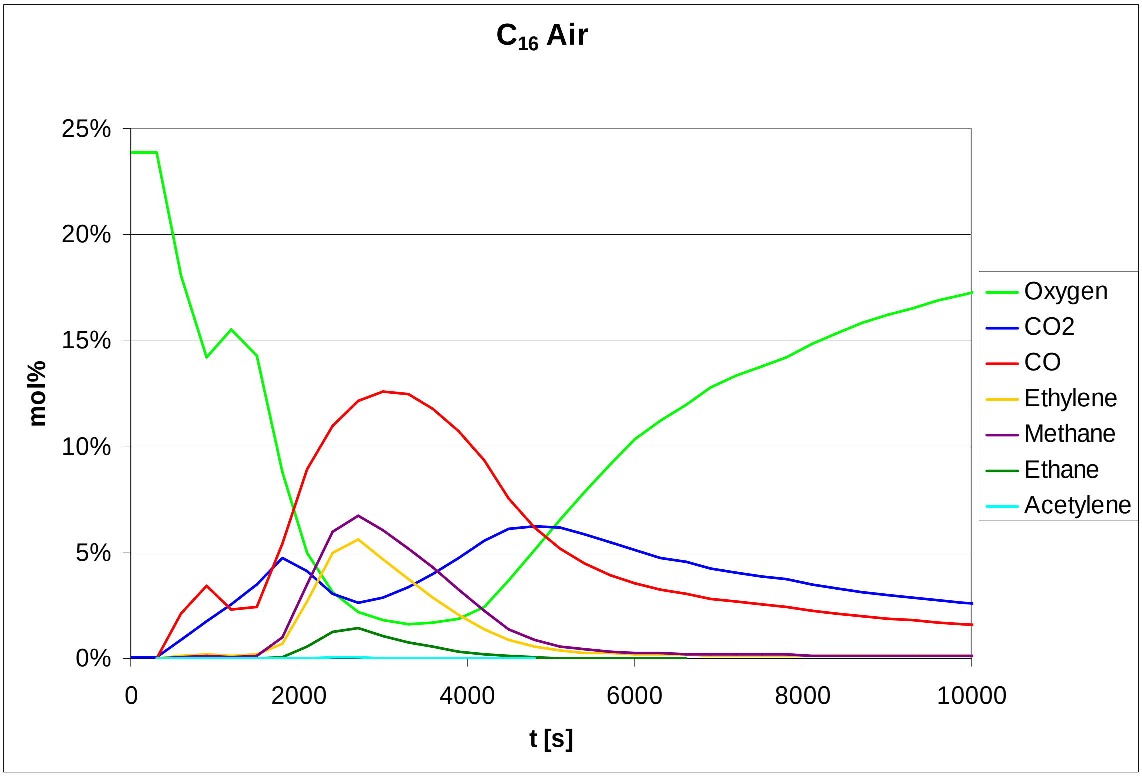
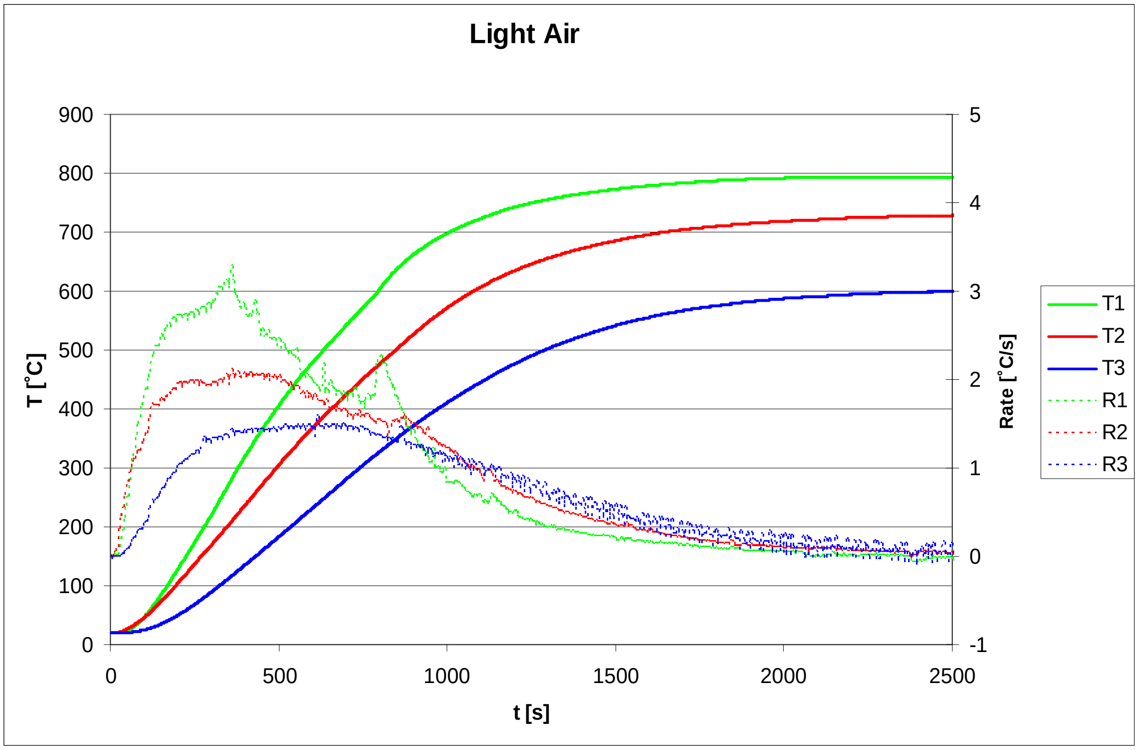


Figure 5: T1-T3 represent temperatures at thermocouple 1-3 (at the interface, one centimeter below it and two centimeter below it). R1-R3 represent numerical temperature rates. Spikes in the temperature rate date indicate oxidation. Much carbon monoxide is formed with respect to the other air-injection experiments.



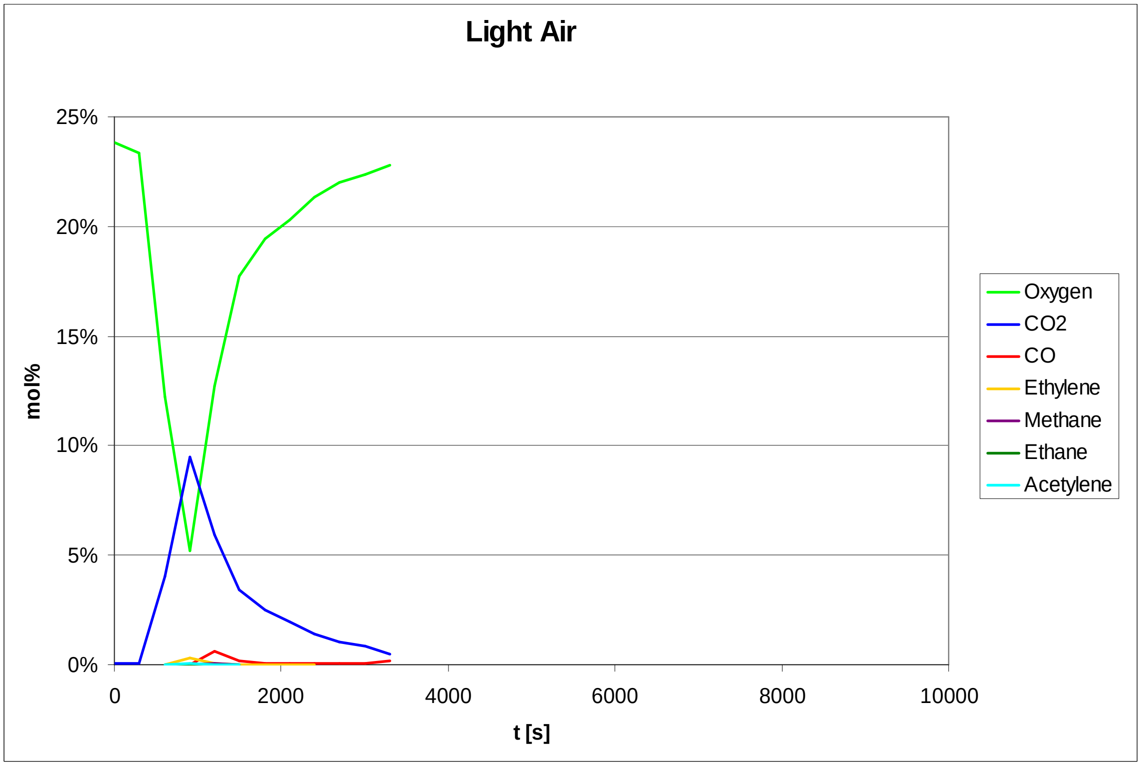
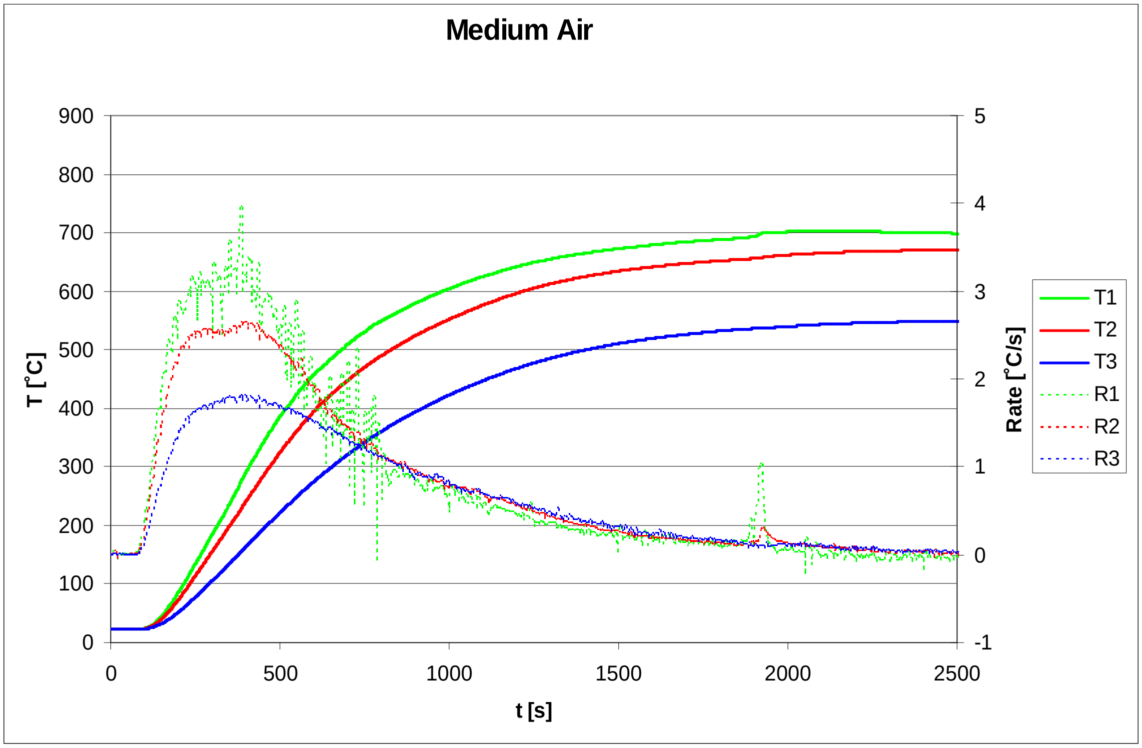


Figure 6: The carbon dioxide peak indicates there is complete combustion. The short duration and early onset of the combustion suggest that gas burns quickly, igniting the coke. The single peak observed in the rate-data of R1, around 800 seconds, confirms there is quick onset of a reaction that also ends quickly, further confirming this notion.



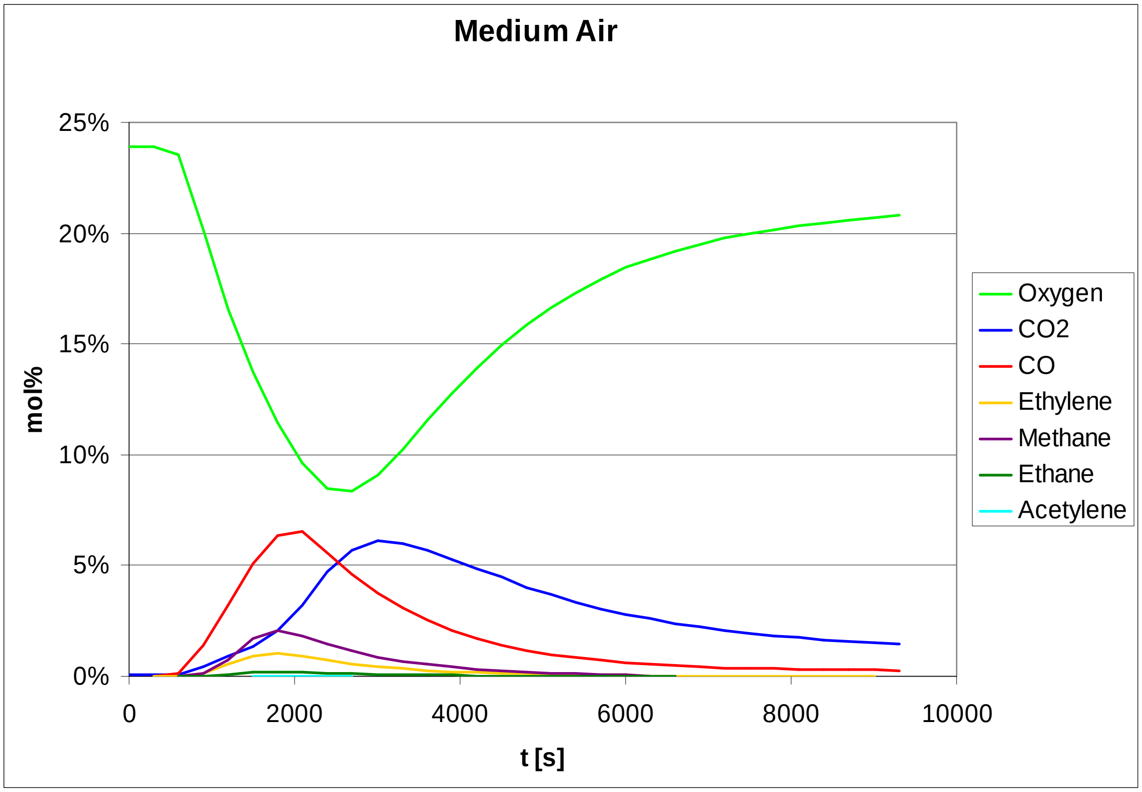
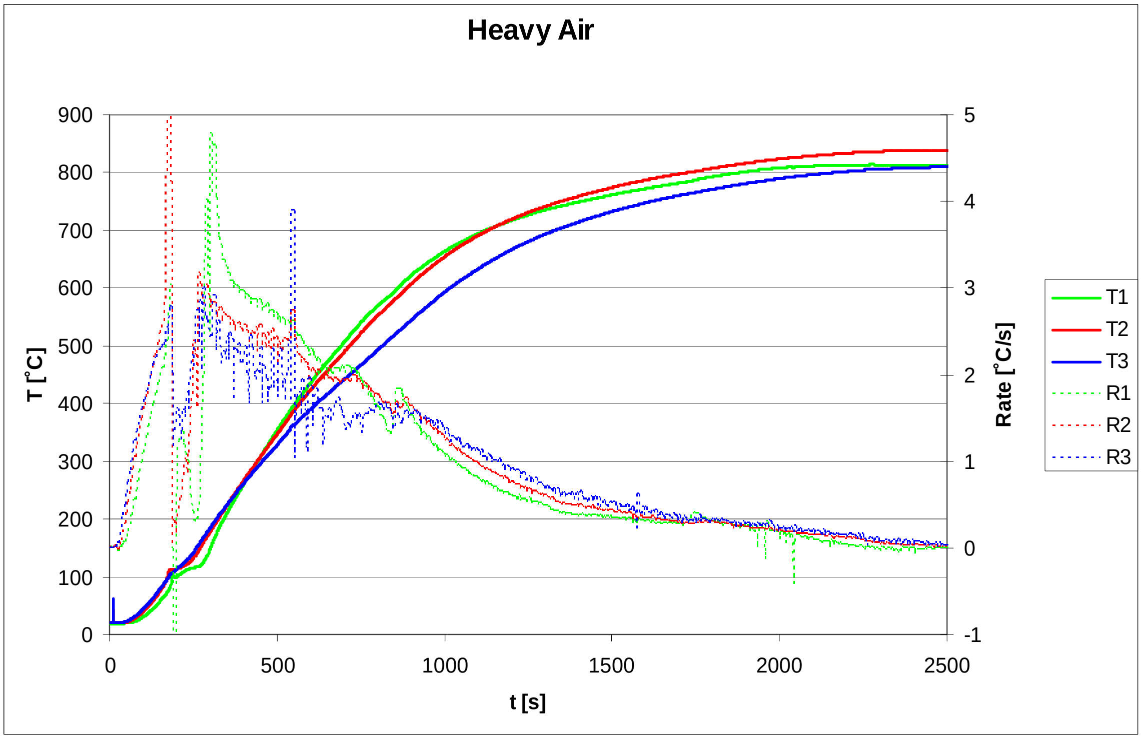


Figure 7: Incomplete combustion followed by complete combustion is indicated by the successive carbon monoxide and carbon dioxide peaks. Oxygen consumption is relatively low, as is hydrocarbon gas production. Proof of oxidation, in the form of spikes, is observed in the temperature rate-data. It is clear from the fact that only the upper thermocouple's data display spikes, that oxidation is localized very near the interface with the overriding gas-stream.



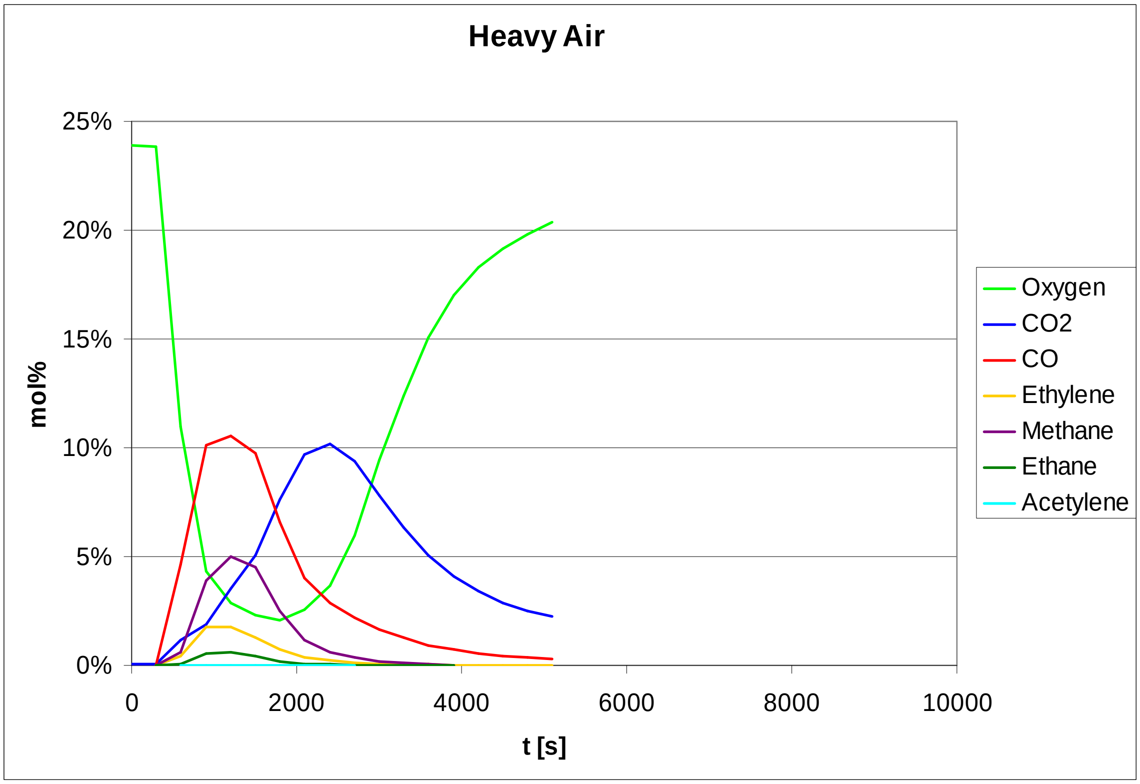


Figure 8: The dip around 100°C is related to evaporating water. The temperature T1 dropping below the temperature at the other thermocouples is caused by the upper thermocouple sticking out above the sand level after evaporation of crude has caused the sand to consolidate. Oxygen consumption is relatively large, as is production of carbon monoxide and carbon dioxide. Incomplete combustion is followed by complete combustion. Spikes in the rate-data for all three thermocouples indicate that combustion penetrates the sand.

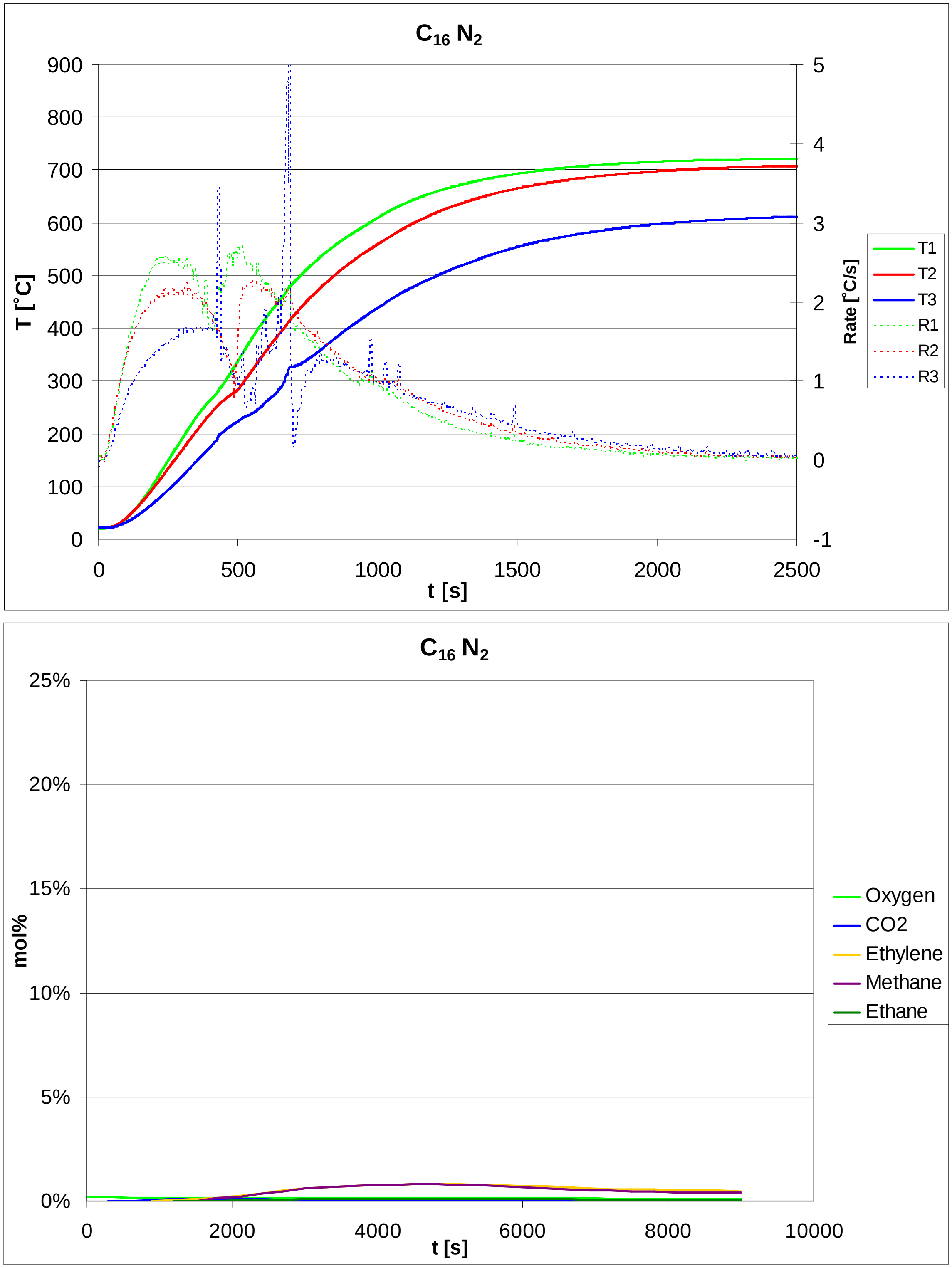
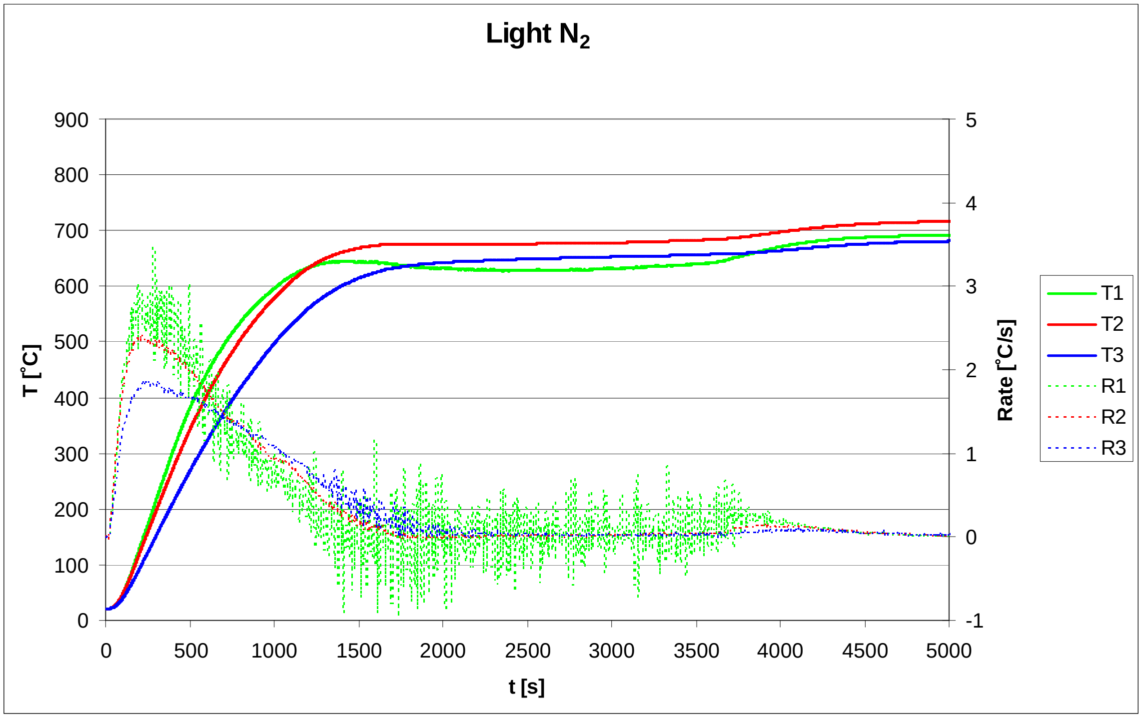


Figure 9: Little light hydrocarbon gas is detected. The spikes in the rate-data are connected to evaporation of pure hexadecane.



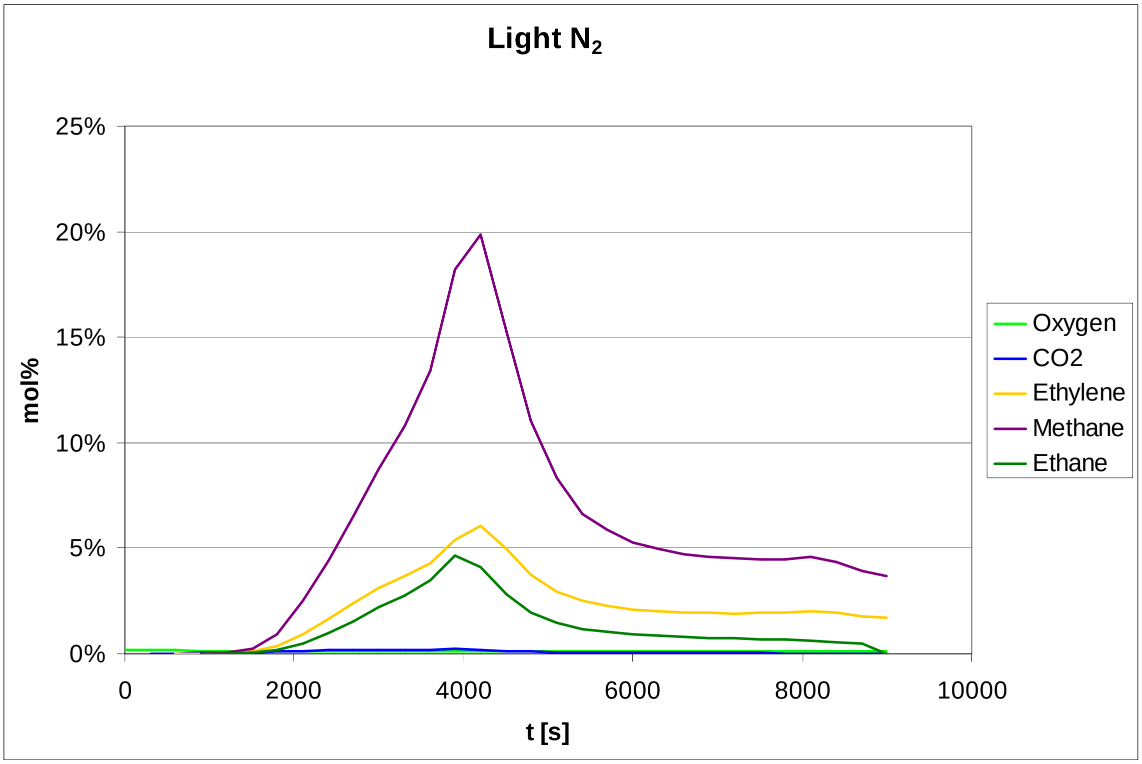
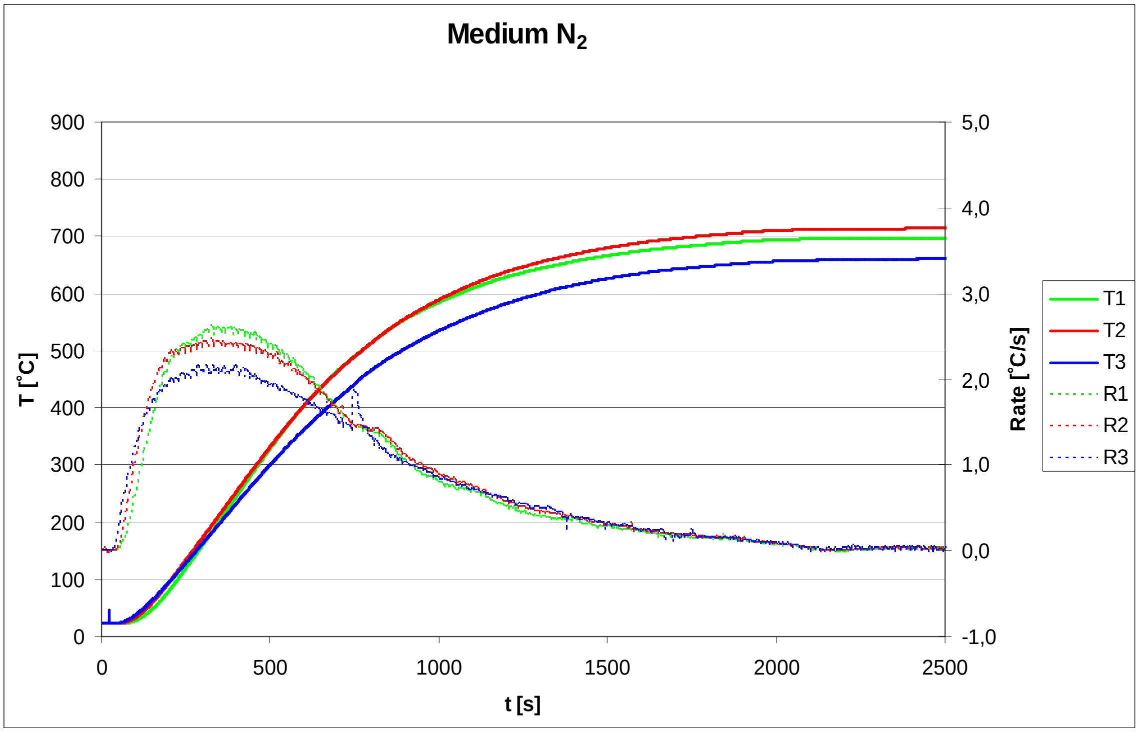


Figure 10: The erratic behavior of R1 and the late temperature increase at T1 are caused by evaporation of large quantities of methane and other hydrocarbon gases. Note that this is the only temperature graph for which the time-axis ends at 5000 seconds



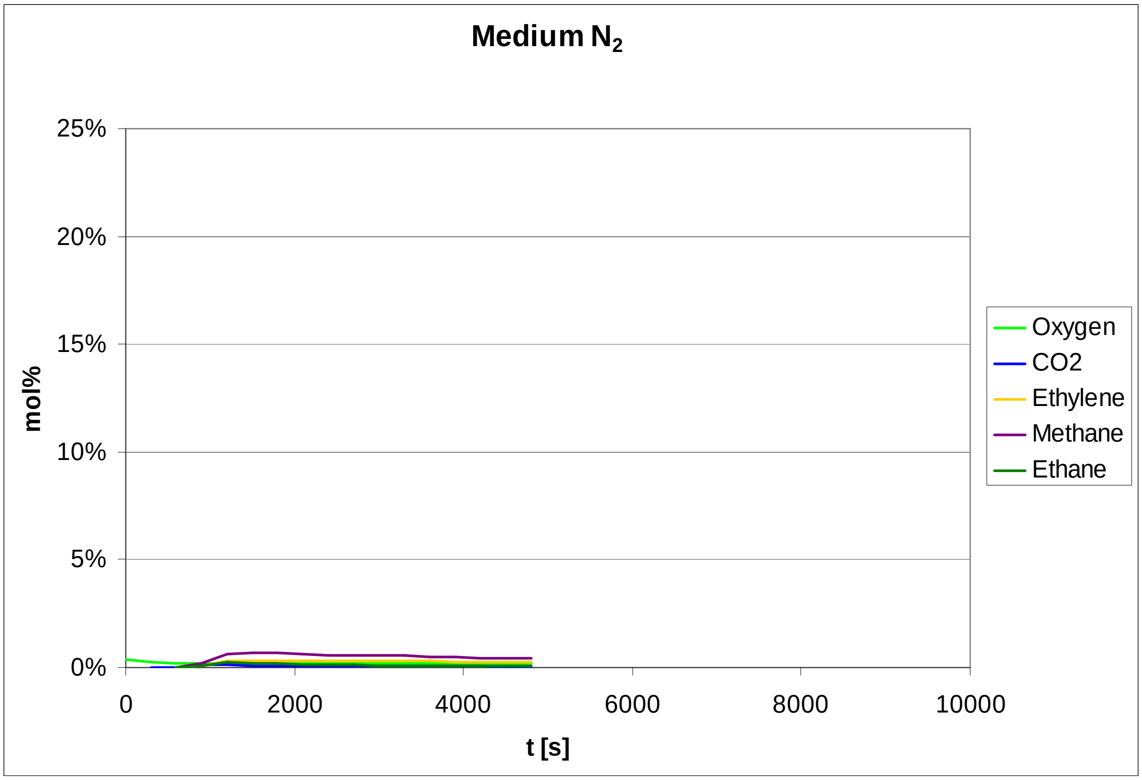


Figure 11: Very little gases are detected for this experiment.

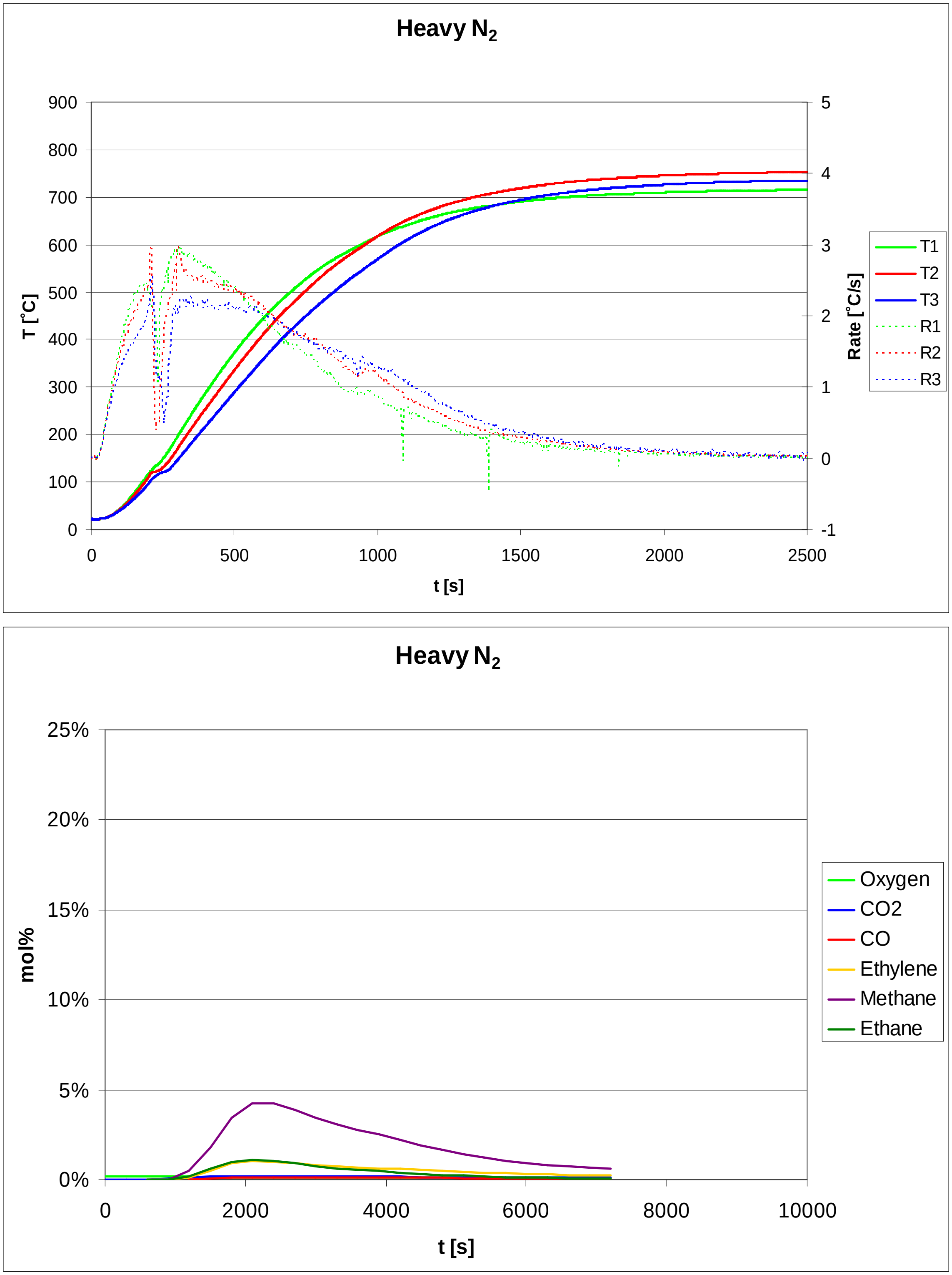


Figure 12: Some gas is produced from the heavy oil

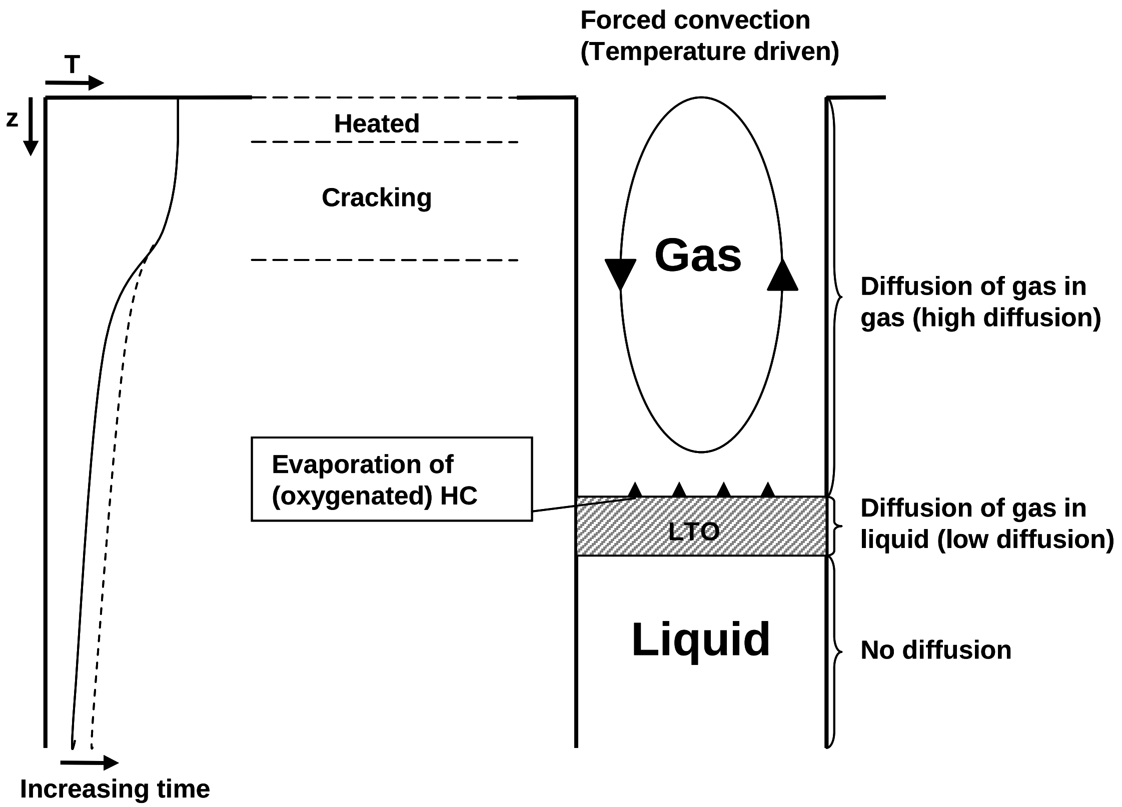


Figure 13: Situation in the vertical part of the sand-filled reactor after some time

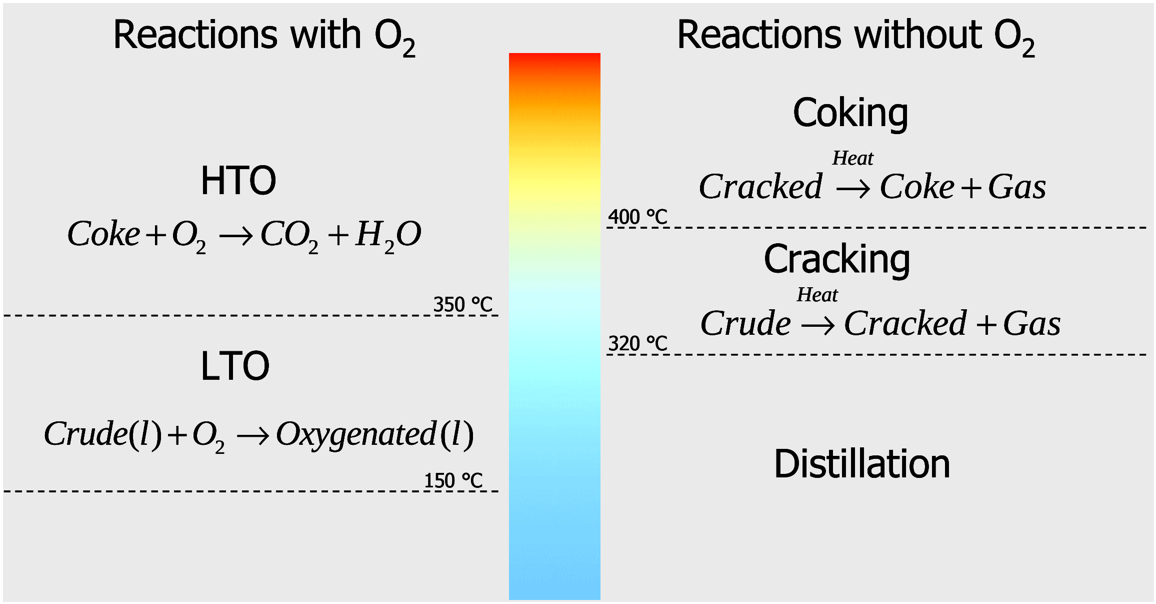


Figure 14: Reactions with and without oxygen

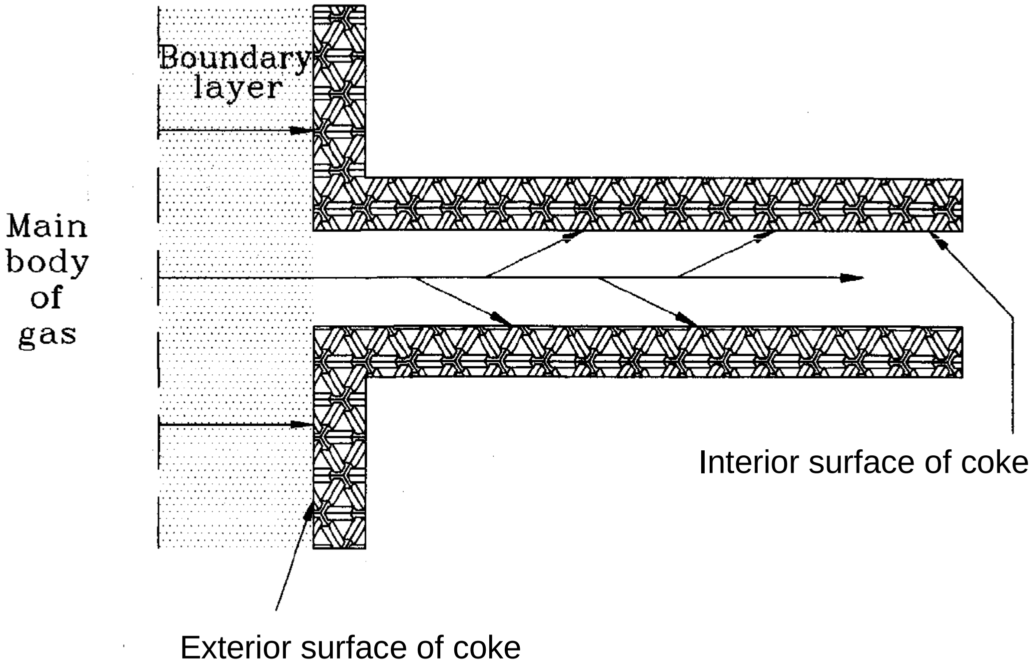


Figure 15: Schematic depiction of reaction mechanism of coke combustion[19]

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