



東京大学
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Master Thesis

A Study on the Thermal Cracking of Ethanol for Regenerative Cooling of Scramjet Engines

(スクラムジェットエンジンの再生冷却におけるエタ
ノールの熱分解に関する研究)

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Abstract

In this study, the thermal cracking reaction of ethanol for the regenerative cooling of scramjet engines was comprehensively investigated. Based on a thorough survey of the existing research on scramjet engines and thermal cracking as a regenerative cooling technique for those engines, the thermal cracking of ethanol was selected as a theme worthy of scientific interest, for which further research was still necessary.

An existing setup was improved in order to conduct flow-type experiments of the thermal cracking of ethanol, and suitable analysis methods were selected in order to identify and quantify the reaction products. In parallel, a simple simulation model based on the Cantera python package and the chemical kinetic mechanism developed by Mittal et al. [16] was developed for the thermal cracking of ethanol. The experiments were conducted for six different target conditions, at temperatures of 400, 450 and 500 °C and pressures of 5 and 7 MPaG, while the target mass flow rate remained unchanged, at 20 g/min.

The experimental results showed that hydrogen was the most abundant gas product, while carbon monoxide, methane, ethylene and ethane completed the gas mixture. They also indicated that the mass fraction of unreacted ethanol decreases both with temperature and pressure, and that the liquid products of the reaction are water and acetaldehyde. Finally, the experimental results showed good agreement with previous research on the thermal cracking of ethanol.

The numerical results, on the other hand, indicated a strong dependence of all product selectivities on reaction temperature, while only some were significantly affected by pressure (hydrogen, ethylene, ethane). In addition, the numerical results showed that the heat absorbed by the reaction is dependent on both temperature and pressure, with a maximum value of 500 kJ/kg at a temperature and pressure of 1050 K and 5 MPaG. Further, these results demonstrated that the real gas version of the model did not show any significant improvement with respect to the ideal gas one. Lastly, the numerical results exhibited a trend similar to the experimental measurements, but the model could not be properly validated due to a mismatch in reference temperatures between experiments and model.

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Chapter 1

Introduction

1.1 The scramjet engine

1.1.1 General background

Supersonic combustion ramjet (scramjet) engines are essentially ramjet engines in which the combustion happens in a supersonic flow. Their general working principle is illustrated by figure 1.1. Basically, the incoming supersonic flow is first compressed in the inlet, which slows it down, then combustion happens in the combustion chamber, and finally the flow is expanded in the nozzle, which re-accelerates it. For normal ramjet engines, although the flow may be supersonic at the inlet and outlet of the engine, combustion always happens in subsonic flow, whereas for scramjet engines, the flow remains supersonic throughout the engine, which implies that combustion also happens in supersonic flow. This key difference between ramjet and scramjet engines poses a significant technical challenge to the operation of scramjet engines. Indeed, not only does the aircraft need to fly at a high speed already for passive compression to function, as is already the case for regular ramjet engines, but flame ignition and stabilisation must be successful for the engine to produce thrust. Achieving such successful ignition and stabilisation in a supersonic flow is a difficult task, and one of the main challenges in the way of producing efficient scramjet engines.

Figure 1.2 presents a more detailed schematic of a scramjet engine. The main elements of the engine, such as the inlet, combustor and nozzle, can be seen. As the flow is supersonic, shocks are involved and the engine must be designed to correctly manage them and avoid any undesired effects. Thus, the inlet area is gradually reduced, and, more importantly, an isolator is added between the inlet and combustor in order to prevent shocks from happening in the combustor and

hindering combustion.

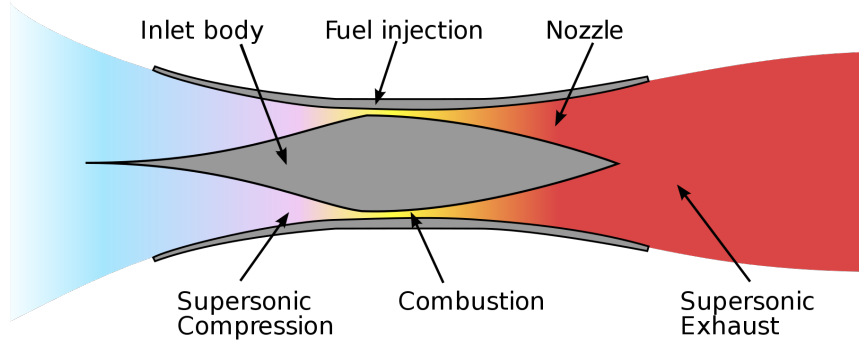


Figure 1.1: General working principle of the scramjet engine [32]

In the future, scramjet engines could be implemented either on hypersonic airplanes, or on atmospheric satellite or spacecraft launchers. The fact that they are air-breathing limits their usage to within the atmosphere, but provides the major advantage that no oxidiser must be carried on the aircraft, as the oxygen present in air is used as the oxidiser for combustion.

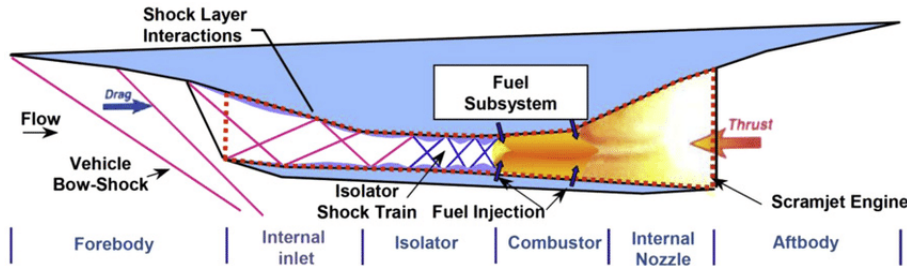


Figure 1.2: Detailed schematic of a scramjet engine [4]

1.1.2 Previous research

Supersonic combustion ramjet (scramjet) engines have been a subject of intense research during the past decades. Micka and Driscoll studied the combustion characteristics of a dual-mode ramjet/scramjet combustor with a cavity flame-holder [15]. In their study, they used hydrogen and a hydrogen-ethylene mixture as fuels, and found that the combustion stabilised at three locations for ramjet mode (cavity, jet-wake, and hybridly between the two) and only in one location for scramjet mode (cavity). This highlights the difficulty of achieving flame stabilisation in a scramjet engine combustor.

Barnes and Segal discussed and reviewed the knowledge about cavity-based flame-holding for chemically reacting supersonic flows [2]. They discussed the flow

field in such cavities and analysed the effects of fuel injection, mixing and combustion on it. In their work, they presented a comprehensive analysis of cavity flow and flame-holding in cavities by providing insights into different injection variants, as well as flame stability characteristics, such as blowout limits and unsteady behaviour.

Further, Ben-Yakar and Hanson also discussed cavity flame-holders as promising flame stabilisation devices for scramjet by looking at cavity flow field characteristics, and proposing ways to optimise them in order to achieve efficient and stable flame-holding [3]. They highlight the fact that cavity flame-holders have shown to be a promising device to achieve stable combustion in scramjet engines, and thus eventually lead to practical implementation of these engines.

At the Tsue-Nakaya laboratory, significant research about scramjet engines has also been carried out. In a first study, Nakaya et al. studied the ignition and supersonic combustion behaviours of ethanol in a scramjet model combustor [17]. They identified two combustion modes (intensive and transient), and found the reactivity of ethanol to be between those of ethylene and ethane. They also calculated and validated the combustion limits for liquid and gaseous injections.

In a second study, Nakaya et al. investigated the supersonic combustion behaviours of a methane/ethylene fuel mixture, and classified combustion into 6 different modes [18]. They realised that an increase in the ethylene concentration improved the supersonic combustion performance. Lastly, they also analysed the fundamental combustion frequencies and discussed their causes.

Finally, in a third study, Nakaya et al. further investigated more complex combustion instabilities [20], i.e. those for which the causes could not be explained by simple analysis methods, and by the means of more advanced analysis methods such as sparsity-promoting dynamic mode decomposition (SP-DMD), proposed explanations for the causes of these instabilities.

The results of the aforementioned research show that scramjet engines are a promising technology for future hypersonic airplanes, as well as atmospheric satellite or spacecraft launchers. However, this technology being relatively new, it is still not ready for use on actual aircraft or spacecraft launchers. In fact, extensive laboratory research and prototyping is still necessary before a full industrial implementation is possible.

1.2 Thermal cracking

1.2.1 General description

Thermal cracking is a chemical reaction in which a hydrocarbon fuel is broken down into smaller compounds solely by means of heat and pressure. It can be seen as the infinitely rich limit of a combustion reaction, where no oxidiser is present. It is generally an endothermic reaction, which is why it could be an interesting way to regeneratively cool a scramjet engine.

Indeed, the thermal cracking reaction would allow heat to be absorbed, thereby reducing or cancelling the need for external cooling of the engine parts, as well as easing fuel requirements. Using thermal cracking, cheaper, less-reactive and easier to handle fuels such as ethanol, heptane or decane, which also have a higher volumetric energy density, could be used instead of hydrogen or ethylene. In fact, the latter, better adapted fuels for scramjet operation would be products of the thermal cracking of the former.

Actually, the regenerative cooling of the scramjet engine would be carried out as a combination of sensible heat absorption (heat absorbed by increasing the fuel temperature) and heat absorbed by the cracking reaction, as the latter usually requires high temperatures to occur. This would further improve the heat absorption capacity of the process, as well supply hot fuel (cracking products), which is more reactive, to the combustor.

Finally, considering the current climatic issues, ethanol, due to its sustainable production, is expected to become a key fuel for future aircraft and spacecraft. Therefore, the thermal cracking of ethanol, more specifically, is thought to be a key way to develop future, sustainable scramjet engines.

1.2.2 Previous research

Thermal cracking is a subject that has been widely investigated. For example, Zhu et al. conducted experiments and numerical simulations of the thermal cracking of n-decane under supercritical conditions [36]. They analysed the flow and heat transfer behaviour of the cracking reaction, and found that lighter products are formed at medium and higher conversion. Their chemical kinetic model was coupled to a CFD model, which was most accurate when using and SST $k-\omega$ turbulence model. The model successfully predicted temperature distributions, but the chemical results did not agree so well, and, in the authors view, further experimental investigation is thus necessary.

Further, Zhong et al. investigated the thermal cracking reaction of kerosene, and looked at its applications to scramjet engines [35]. They studied the cracking of China No.3 aviation kerosene experimentally and analytically under supercritical conditions, and found that light hydrocarbon gases, such as methane, were the most abundant products. Their analytical model consisted of a one step lumped model which grouped the species into three categories: unreacted kerosene, gaseous products, and liquid products and carbon deposits.

Wu et al., on their side, looked at the cracking of n-heptane, and the effect of temperature and pressure on the reaction [34]. They found that alkanes were decomposed more easily than alkenes with the same number of carbons, but that alkanes were formed in higher amount with increasing pressure. They also remarked that ethylene was the product produced in the highest amount, but that it decreased the most with pressure. They also developed a chemical kinetic mechanism for the reaction, and remarked that their model performed better than an n-heptane mechanism from the Lawrence Livermore National Laboratory (LLNL) for the conditions studied. Lastly, they noted that while temperature had a strong influence on the reaction pathway and products, pressure, on the other hand, did not significantly affect the reaction.

Li et al. investigated the numerical modeling of the cracking reaction of hydrocarbon fuels under supercritical conditions [12]. They developed their own chemical kinetic model, and validated it on the basis of experiments. Their model was based on the primary and secondary decomposition mechanisms, and showed significant improvements when compared with their previous model.

Jin et al. investigated the thermal cracking and coking of endothermic hydrocarbon fuel [10]. They also looked at the influence of pressure, in addition to temperature, on the reaction. They remarked that the conversion increased at higher pressures, as well as the selectivities of hydrogen, methane and ethane, while those of ethylene and propylene decreased at higher pressures. They also noted that a higher pressure favoured coke deposition, with two types of coke being formed: filamentous and amorphous, depending on the conditions.

Thermal cracking was also investigated at the Tsue-Nakaya laboratory. Indeed, Nakaya et al. conducted thermal cracking experiments of n-dodecane and measured their products [19]. These products were then analysed and surrogate fuels best matching the products in composition were produced. Finally, these surrogate fuels were tested in a model scramjet combustor in order to understand their supersonic ignition and combustion behaviours.

In addition, Kinoshita [11] investigated the thermal cracking of heptane, iso-

octane and kerosene under supercritical conditions. The effects of temperature and volumetric flow rate on the reaction and products was looked at, and the abundance of each gaseous species was analysed in detail.

Nonetheless, while thermal cracking in general is a well documented subject, the thermal cracking of ethanol, specifically, is not so widely described in literature. Some studies, however, can be found.

For example, Park et al. proposed a theoretical description of the thermal decomposition of ethanol [22]. Most importantly, in their study, they specify the main decomposition paths of ethanol. They support their choice by an in-depth analysis of the reaction kinetics of ethanol, which looks at the bond and bond-breaking mechanics, as well as the kinetic rate constants of specific reactions.

Avedisian et al., on their side, conducted stationary pyrolysis experiments of ethanol under atmospheric pressure conditions [30]. In their study, they propose an original way to construct a reactor by having the reaction happen in a vapour film caused by the boiling of ethanol. Their study provides an analysis of the boiling mechanics of ethanol and the products resulting from its cracking. Hydrogen was found to be the most abundant product under the conditions studied, followed by carbon monoxide, methane and ethylene. In order to explain these results, they proposed a relatively detailed decomposition path for ethanol involving several branching reactions.

Further, Hashemi et al. studied the pyrolysis and oxidation of ethanol under high pressure [8]. They conducted pyrolysis and oxidation experiments, and determined the onset temperatures as well as measured the products (except hydrogen) for both reactions. They also developed a detailed chemical kinetic model and validated it against their own experiments as well as existing literature. The model predicted the onset temperatures, product compositions and ignition delays fairly well, while it showed less precision for the prediction of flame speeds.

In an old study, Barnard et al. also investigated the pyrolysis of ethanol [1]. They proposed an empirical relation yielding the rate constant for the decomposition of ethanol, and found that the main reaction products are acetaldehyde, hydrogen and some solid polymeric material.

Ijima et al. investigated the thermal cracking of ethanol under sub-critical and supercritical conditions [9]. They looked at the influence of pressure and temperature on the reaction, and measured the heat absorbed and identified the reaction products. Unfortunately, their study does not present quantitative results for the products, but it identifies hydrogen, methane and ethylene as products.

Finally, at the Tsue-Nakaya laboratory, Nishimoto conducted thermal cracking

experiments of ethanol under supercritical conditions [21]. He conducted a variety of experiments at different temperatures, volumetric flow rates and pressures. He analysed the influence of a catalyst and looked at the possibility of steam reforming as well. In his study, quantitative results are presented for the gaseous products, while only qualitative identification is proposed for liquid products.

The aforementioned research shows that, while thermal cracking in general is a well-studied subject, the thermal cracking of ethanol, which is a promising sustainable fuel, still lacks thorough investigation for certain conditions and applications.

1.3 Purpose of this study

In accordance with the context and background discussed in sections 1.1 and 1.2, the purpose of this study is to offer an in-depth understanding of the thermal cracking reaction of ethanol for the regenerative cooling of scramjet engines. Indeed, although the thermal cracking of ethanol has already been investigated to some extent, it still lacks some fundamental understanding, particularly when looking at its application as a way to regeneratively cool scramjet engines. For example, only three of the six studies presented in section 1.2.2 investigated flow-type cracking of ethanol [8, 9, 21], which is the only method relevant for the regenerative cooling of scramjet engines. Out of these three studies, one did not present any measurements for hydrogen [8], a key fuel for stable scramjet combustion, while another one did not present any quantitative measurement for any product [9]. Lastly, Nishimoto's study [21] presents a variety of factors influencing the cracking of ethanol, such as a catalyst or steam reforming, but when it comes to the cracking of pure ethanol, only two runs under two different target conditions were investigated.

Hence, the present study aims to provide this lacking knowledge of the thermal cracking of ethanol both through a set of comprehensive experiments, as well as a simple numerical simulation model. Further, it is hoped that this study will inscribe itself in a series of studies which may in the future make the regenerative cooling of scramjet engines through the thermal cracking of ethanol a real way to make industrially viable scramjet engines.

Chapter 2

Experimental work

2.1 Setup

The setup which was used for the investigation of thermal cracking is quite complex and consists of several subsystems. Figure 2.1 shows a global view of the system, where only the main elements are represented. The important subsystems will be described further in this chapter. The setup shown on figure 2.1 consists of the following parts: the fuel supply part, where the fuel is pressurised by nitrogen and its mass flow rate is measured, the pre-heating area, where the fuel is pre-heated to the desired reaction temperature, the reaction area, where the thermal cracking actually happens, and the collecting part, where the products are eventually collected. The important dimensions are the reactor length (distance between TC3 and TC4) and diameter (tube inner diameter): $l = 77$ cm, $d = 2$ mm, as well as the total preheating length (distance between the beginning of the flexible heater and TC3): $l_p = 291$ cm. The sample tank volume is $V_t = 2.25$ ℓ .

Six key parameters can be controlled in this system: the pressure, the flow rate, and the four temperatures T_1 , T_2 , T_3 and T_4 . The pressure in the system is controlled by the nitrogen regulator, while the flow rate is controlled by the metering valve situated between the reaction area and the collecting part. The regulator can be manually set to the desired system pressure p_s , and will ensure, by design, that the system pressure $p(t) = p_s$ at all times (some slight fluctuations may occur), as long as $p_t > p_s$, where p_t is the tank pressure. The metering valve is a needle valve which allows for fine tuning. It can be manually adjusted while looking at the value displayed by the flow meter, until the desired value is reached. The temperatures, on the other hand, are controlled by the heating system, which will be presented in detail in chapter 2.1.1.

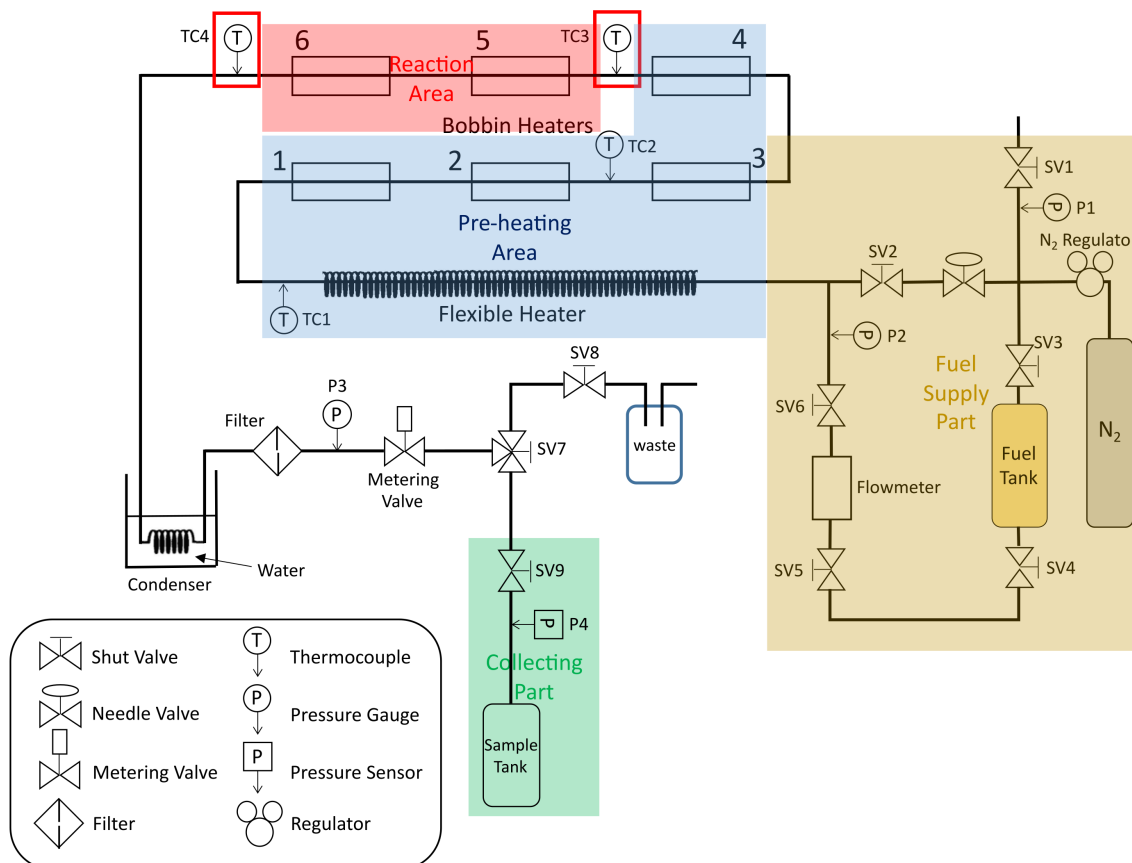


Figure 2.1: Experimental setup

2.1.1 Heating system

One of the important subsystems of the experimental setup is the heating system. It consists of four electrical circuits (flexible heater, A, B and C), which supply power to the flexible heater and the six bobbin heaters shown on figure 2.1. Figure 2.2 shows two of these circuits: the flexible heater circuit (figure 2.2a), and circuit A (figure 2.2b). Circuits B and C are not presented here because they are analogous to circuit A, with the only differences being that they control T_3 and T_4 , and supply bobbin heaters 3 and 4 and 5 and 6, respectively.

Figure 2.2a shows that, when the switch is closed, current flows from the AC power source to the flexible heater by passing through a solid-state relay (SSR). This relay acts as a dynamic switch which is controlled by the temperature controller (TCT). Indeed, the temperature controller reads the temperature measured by the thermocouple (TC1) and compares it to the target temperature which was manually set on the controller by the operator. If the actual temperature is lower than or equal to the target value, the controller outputs a control current, which allows the main current to flow through the relay, and power is supplied to the heater. However,

if the actual temperature exceeds the target value, the controller stops outputting this current, which prevents the main current from flowing through the relay, and power supply to the heater is stopped.

Thus, the temperatures T_1 , T_2 , T_3 and T_4 could be controlled in the following way. For each temperature, the target value was manually set on the corresponding controller. When any temperature exceeded its target value, the corresponding controller would switch off the power supply to the corresponding heater(s). Hence, that temperature would naturally decrease (due to heat losses) back below its target value, point at which the heater(s) would be switched back on. This would allow, given the right settings, to keep the temperatures within a small range around their target values.

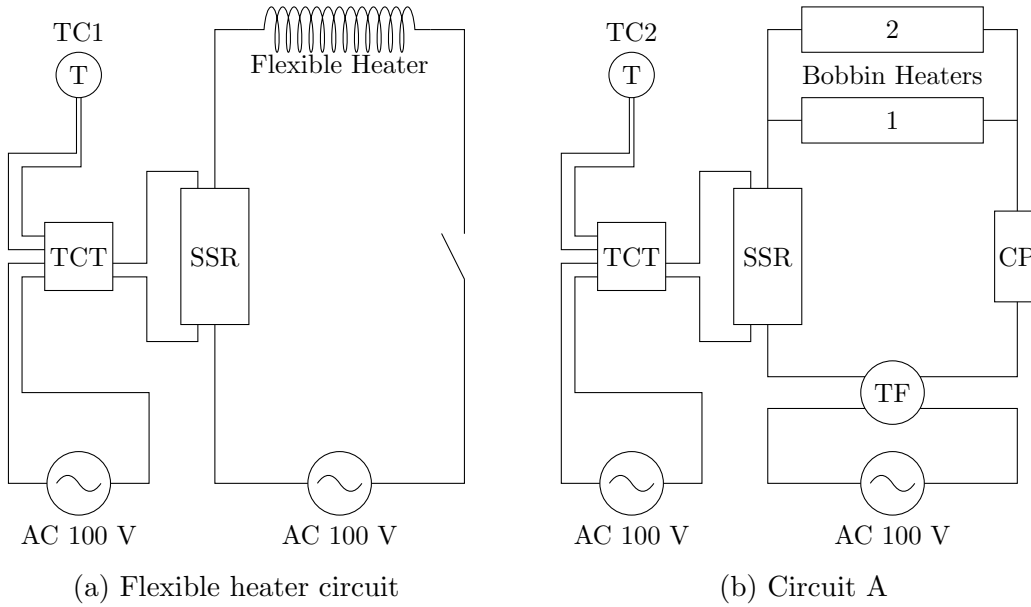


Figure 2.2: Heating system

Circuit A, shown on figure 2.2b, is similar to the flexible heater circuit. Indeed, the temperature control mechanism (and its corresponding sub-circuit) is identical to that of the flexible heater circuit. The main circuit, however, has a few important differences. Firstly, instead of one flexible heater, there are two bobbin heaters connected in parallel on the main circuit. Secondly, the main circuit is not directly supplied by a 100 V AC power source, but rather by a transformer (TF) whose output voltage can be adjusted. Lastly, a circuit protector (CP) is mounted in series on the main circuit in order to protect the components from an excessively high current (which can typically be caused by an erroneous setting of the transformer output voltage).

Having a transformer with an adjustable output voltage allows for the heating

power to be tuned according to the desired experimental conditions. The transformers which were used in this setup have a voltage range of 0-130 V. However, this entire range could not be used, as it was limited by the circuit protector rating. Indeed, the circuit protectors which were used have a maximum peak current rating of $\hat{I}_{\max} = 20$ A. Taking into account that the resistance of one bobbin heater is about $R_h = 9.2 \Omega$, the equivalent resistance of two heaters plugged in parallel becomes

$$\frac{1}{R_{2h}} = \frac{2}{R_h} \implies R_{2h} = \frac{R_h}{2} = 4.6 \Omega. \quad (2.1)$$

Neglecting the voltage drops in the relay and circuit protector, Ohm's law yields the maximum allowable RMS voltage as follows,

$$\hat{U}_{\max} = R_{2h} \hat{I}_{\max} \quad (2.2)$$

$$U_{\max} = \frac{\hat{U}_{\max}}{\sqrt{2}} = \frac{R_{2h} \hat{I}_{\max}}{\sqrt{2}} = 65 \text{ V}, \quad (2.3)$$

where $\hat{U}_{\max}$ is the maximum allowable peak voltage. In practice, as there are voltage losses in the relay, the circuit protector and the cables, a maximum voltage of $U_{\max} = 70$ V could be used without exceeding the maximum allowable peak current. Hence the actual voltage range for each transformer was of 0-70 V.

2.1.2 Data collection system

Another key subsystem of the experimental setup is the data collection system. It consists of a data logger to which all four thermocouples, the flowmeter and the pressure sensor were connected, and a PC to which the logger was in turn connected. This allowed the data from all six sensors to be collected throughout each experiment. Hence, for each experiment, the sampling time, the temperatures, the mass flow rate, and the gas pressure in the sample tank could be recorded. The thermocouples' output voltages were directly converted to temperature values expressed in Celsius by the logger, which is pre-calibrated to interpret voltages received from a variety of thermocouple types, including K-type thermocouples, which were the type used in these experiments. The flowmeter and pressure sensor output currents however, were not converted by the logger and were recorded directly, without change. These current values were converted a posteriori using calibration curves linking mass flow rate and pressure to current, respectively.

2.2 Procedure

The experimental procedure, which was followed for each experimental run, is described hereafter. Firstly, the system was heated with nitrogen flowing through it. Once the temperatures became close enough to their target values, the fuel was pressurised to the target pressure using nitrogen, and the fuel tank's valve was opened, letting fuel flow through the system. Then, once the reaction zone's inlet and outlet temperatures (T_3 and T_4) and the flow rate reached and stabilised around their target values, the products were collected in the sample tank, while the sampling time, temperatures, mass flow rate and pressure in the sample tank were recorded by the data logger. Finally, gases and liquids were separated and analysed in two different ways. For gases, a gas chromatograph with a thermal conductivity detector (GC-TCD) was used to determine composition and molar fraction, whereas for liquids, a combined gas chromatograph and mass spectrometer (GC-MS) was used to determine composition and mass fraction.

2.3 Analysis techniques

The reaction products being a mixture of liquid and gaseous compounds, as well as polarised and non-polarised compounds, their analysis is no simple matter. In this study, the products were analysed using different variants of gas chromatography (GC). Gas chromatography is an analysis technique which consists of injecting a sample of the mixture to be analysed into a gas chromatography column, which will separate the different compounds present in the mixture, and then detecting the amount of each compound as the compounds exit (elute) from the column at different times.

In more detail, the sample will first be injected into the injection port, where, if it is a liquid, it will be vaporised. Then, the sample will enter the GC column, in which carrier gas (usually helium, but can vary depending on the detector) is flowing. The column is the key element of the GC analysis line, as it is the element which will allow the different compounds present in the sample to be separated. There are many different types of columns which are all optimised to separate different types of compounds. For example, some columns will be well suited to separate atmospheric gases, while others will be well suited to separate light organic solvents and alcohols, or heavy alkanes and aromatic hydrocarbons. In general, the two main factors which will determine whether or not certain compounds can be separated by a given column are mass and polarity, i.e. most columns are optimised to separate compounds within certain mass and polarity ranges.

However, in general, the column alone is not sufficient to separate the different compounds present within a sample, and an adequate temperature program is necessary. On a gas chromatograph, the column is placed in an oven, whose temperature can be precisely controlled. This temperature will, in combination with the column characteristics, allow the different compounds to be separated. More specifically, the sample will first be injected into the column while it is held at a low (close to room) temperature. As the column is designed for the type of compounds present in the samples, these compounds will interact with the column surface, essentially slowing down their progression in the carrier gas stream. Then, the oven (and column) temperature will be gradually increased (usually linearly) until it reaches a specified final temperature (usually close to the maximum allowable column temperature). As the temperature increases, the compounds present in the sample will reduce their interaction with the column surface one after the other, usually starting with lighter compounds at lower temperatures and ending with heavier compounds at higher temperatures. When a certain compound reduces its interaction with the column surface, it will accelerate in the carrier gas flow and elute from the column. Hence, the compounds which entered the column together as one sample will elute from the column separately at different times. This controlled temperature increase, from a specified initial temperature to a specified final temperature at a specified rate, which causes compound separation to happen, is called a temperature program, and is a key parameter of any GC analysis.

Finally, once the different compounds have been separated in the column and elute at different times, they will each be detected by a detector, whose type and detection method can vary, which will measure the amount of each compound present in the sample. In general, regardless of the detector type, a gas chromatograph will output analysis results as a chromatogram, which is essentially a curve plotting the measured intensity (usually a voltage) against the retention time. On this curve, each detected compound will manifest itself as a peak, whose area is directly proportional to the amount (mass/mole) injected of that compound. This then allows the chromatograph to be calibrated by injecting known amounts of a certain target compound into it and correlating the resulting areas with these amounts.

In this study, gas chromatographs with three different types of detectors were used: a gas chromatograph with a thermal conductivity detector (GC-TCD), a combined gas chromatograph-mass spectrometer (GC-MS), where the mass spectrometer acts as the detector, and a gas chromatograph with a dielectric barrier discharge ionisation detector (GC-BID). Figure 2.3 gives an outline of which detector was used to identify and quantify each type of products. Sections 2.3.1-2.3.3 will

describe each detector in detail, including the reasons why a certain detector was used to analyse a certain type of products.

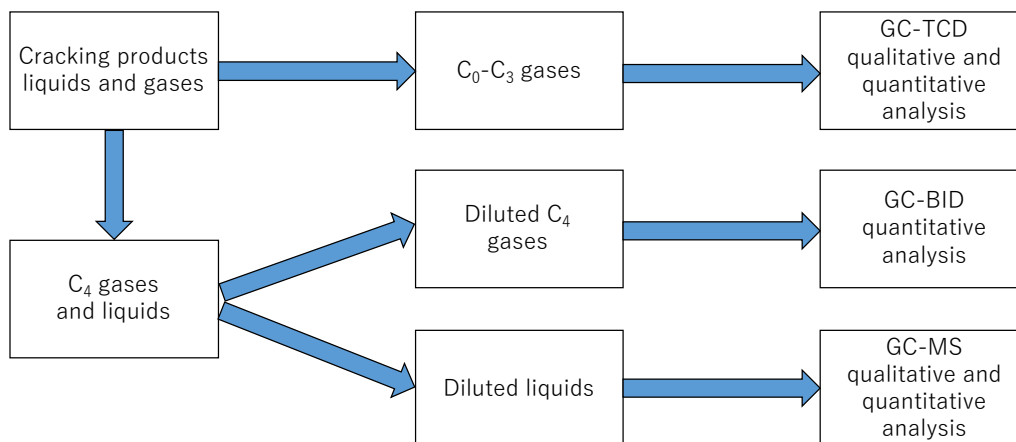


Figure 2.3: Analysis flowchart

2.3.1 GC-TCD

The GC-TCD is a gas chromatograph with a thermal conductivity detector; the detector's working principle is shown on figure 2.4. Basically, the detector consists of a Wheatstone bridge, where the two resistances R_1 and R_2 are fixed, while resistances R_3 and R_4 will vary. Indeed, resistor R_3 is placed in the gas flow which exits the GC column, while resistor R_4 is placed in a flow of carrier gas. As resistors R_3 and R_4 are essentially filaments, their resistance is a function of temperature as a consequence of the temperature dependence of electrical resistivity: $R(T) = \rho(T) \frac{l}{A}$, where ρ , l and A are the resistivity, filament length and area, respectively.

Therefore, when an analyte gas elutes from the column and flows around R_3 , the thermal conductivity of the environment surrounding the resistor will change and as a consequence, the resistor's temperature will also change, causing the resistance R_3 to change in turn. The resistance R_4 , as only pure carrier gas flows around it, serves as a reference to compensate for temperature variations of the detector caused by external factors, independent of the elution of analyte gases. As the current flowing through the detector is a controlled analysis parameter, the output voltage directly depends on the value of R_3 , and thus measures the amount of analyte gas which elutes from the column at a certain time during the analysis.

The main advantages of the TCD is that it withstands the analysis of pure samples, i.e. samples do not need to be diluted in a solvent before being injected into the GC, and that it can detect any compound different from the carrier gas. However, TCDs have a relatively low sensitivity (down to about 10 ppm [28]), which

can be a problem if trace components need to be detected. In that case, another detector, such as MS or BID may be more suitable.

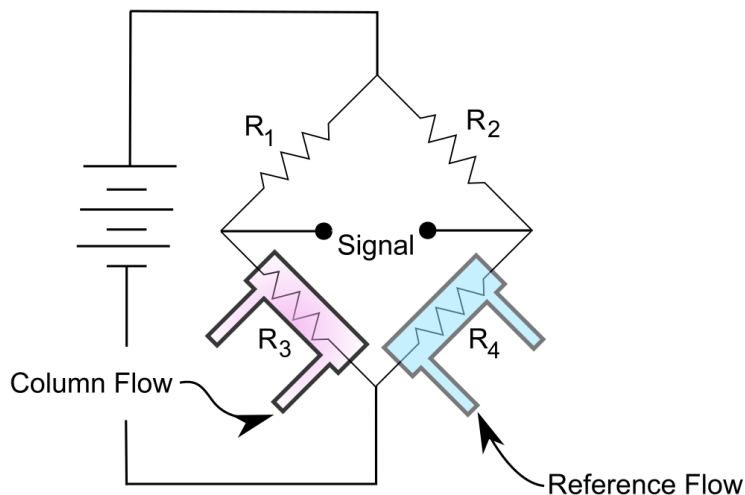


Figure 2.4: Thermal conductivity detector [33]

In this study, a Shimadzu GC-14B gas chromatograph (with a TCD) connected to a Shimadzu C-R8A Chromatopac data logger has been used for the qualitative and quantitative analysis of C_0 - C_3 hydrocarbons, as well as CO and CO_2 . The column which was installed in the device throughout the whole period during which it was operated is a Shinwa Shincarbon-ST 50/80 2.0 m $\times$ 3.0 mm (length $\times$ inner diameter), while argon was used as a carrier gas.

As a pre-emptive work, first a suitable temperature program which could successfully separate and detect all target gases was found, and then calibration was performed for all these gases. For clear identification and precise quantification to be possible, it is necessary to find program settings which detect the target compounds as sharp, isolated peaks. The program settings which were used for the calibration of the device as well as for the analysis of the reaction products are presented in table 2.1.

Once such good settings had been determined, calibration was carried out by analysing known amounts of each target gas and correlating the resulting areas with the injected amounts. For each target compound, at least three calibration points were measured, and a precise calibration curve was fitted through these points using a least squares linear regression method. Table 2.2 summarises the calibration values, presenting both the retention time and the conversion formula for each compound.

Table 2.1: GC-TCD program settings

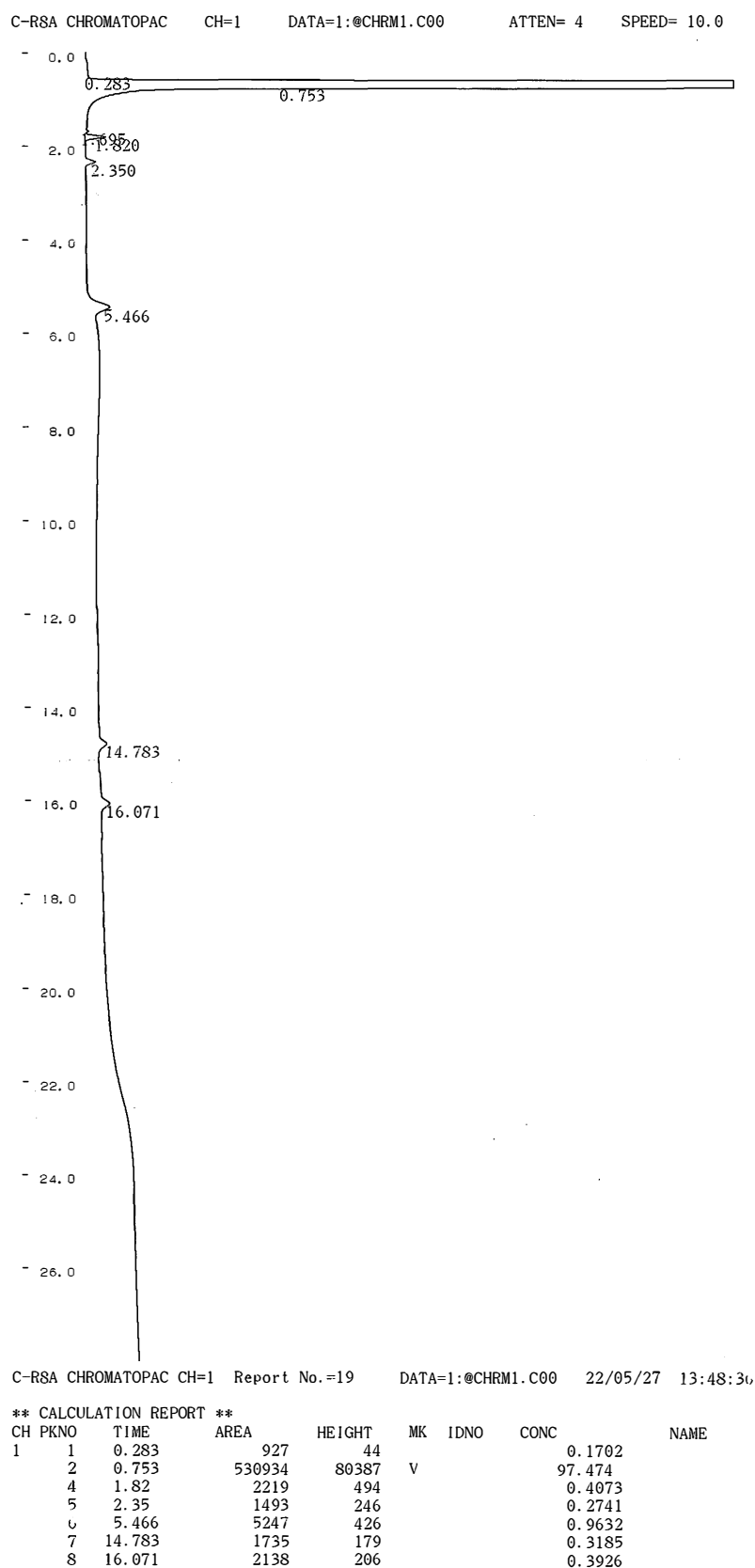
Parameter	Value	Unit
Initial temperature	40	°C
Initial time	5	min
Program rate	15	°C/min
Final temperature	300	°C
Final time	5	min
Injector temperature	300	°C
Detector temperature	300	°C
TCD temperature	300	°C
Det	4	-
Pol	2	-
Detector current	50	mA
Logger stop time	28	min

As an example, the analysis results of the products of run 3 are presented on figure 2.5. The peaks corresponding to each compound can clearly be seen, while the area of each peak can be read at the bottom of the figure (peaks no. 3 and 4 correspond to O₂ and N₂). For this analysis, a sample injection volume V_i of 0.5 ml was used. This caused the hydrogen peak to be saturated, and thus further analyses using an injection volume of 20 μ l were necessary in order to obtain accurate results for hydrogen.

Table 2.2: GC-TCD calibration

Substance	Conversion formula A : area, n : amount [mol]	Retention time [min]
H ₂	$n = 2.9 \cdot 10^{-11} \cdot A$	0.649
CO	$n = 2.6 \cdot 10^{-10} \cdot A$	2.289
CH ₄	$n = 8.0 \cdot 10^{-11} \cdot A$	5.391
CO ₂	$n = 2.2 \cdot 10^{-10} \cdot A$	9.776
C ₂ H ₄	$n = 9.6 \cdot 10^{-11} \cdot A$	14.609
C ₂ H ₆	$n = 7.5 \cdot 10^{-11} \cdot A$	15.871
C ₃ H ₆	$n = 1.1 \cdot 10^{-10} \cdot A$	21.961
C ₃ H ₈	$n = 8.2 \cdot 10^{-11} \cdot A$	22.519

In parallel to the aforementioned work, the existing Japanese version of the laboratory's user manual for the GC-TCD was translated into English and updated with additional information. It contains a detailed description on how to operate the gas chromatograph and is presented in appendix A.1.

Figure 2.5: GC-TCD analysis of the products of run 3 ($V_i = 0.5$ ml)

2.3.2 GC-MS

The GC-MS is a gas chromatograph where a mass spectrometer serves as the detector. The specificity of the mass spectrometer is that it is not only a detector which measures the amount of the compounds eluting from the column, but that it is also capable of identifying these compounds. Indeed, when a compound elutes from the column and enters the MS, it is firstly broken into ionised fragments, which then go through a mass analyser before being detected by an ion detector.

There are different types of mass analysers, but the most commonly used one with a GC is the quadrupole mass analyser. Its working principle is illustrated by figure 2.6. Basically, the ions are sent through the middle of the four rods, to which opposite voltages are applied. This will create a varying electric field, which will only allow ions of a specific mass to charge ratio (m/z) to pass through the quadrupole. As ions are generally only ionised once, $z = 1$ and the quadrupole allows the separation of ions based on their mass. Varying the voltages U and V while keeping the ratio U/V constant changes the mass for which ions which will be let through the quadrupole. Thus, the masses of the different ions produced by the eluting compound can be scanned and detected.

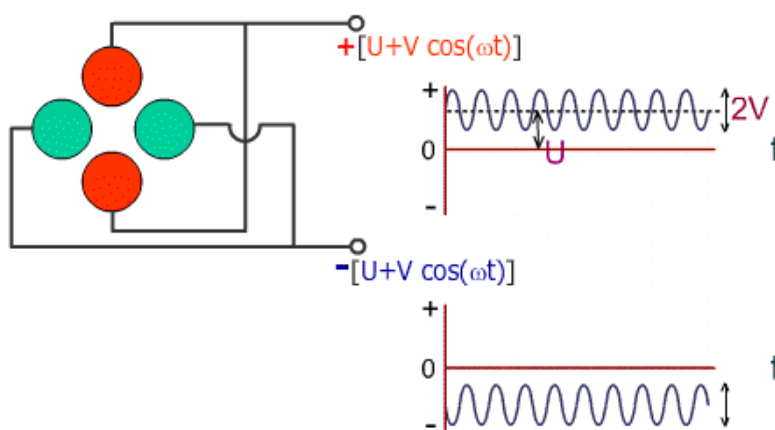


Figure 2.6: Quadrupole mass analyser [29]

Therefore, as shown by figure 2.7, the GC-MS does not produce a simple one-dimensional gas chromatogram, but rather a two-dimensional mass chromatogram and mass spectrum, which combine to form a total ion chromatogram. In other words, for each compound which elutes from the GC column at a certain time, there is a corresponding mass spectrum. This mass spectrum is what will allow the compound to be identified. Eventually, when superimposing the mass chromatograms, a total ion chromatogram, where each peak corresponds to a given compound and

its area is proportional to the amount of that compound in the sample and thus resembles a gas chromatogram, is obtained.

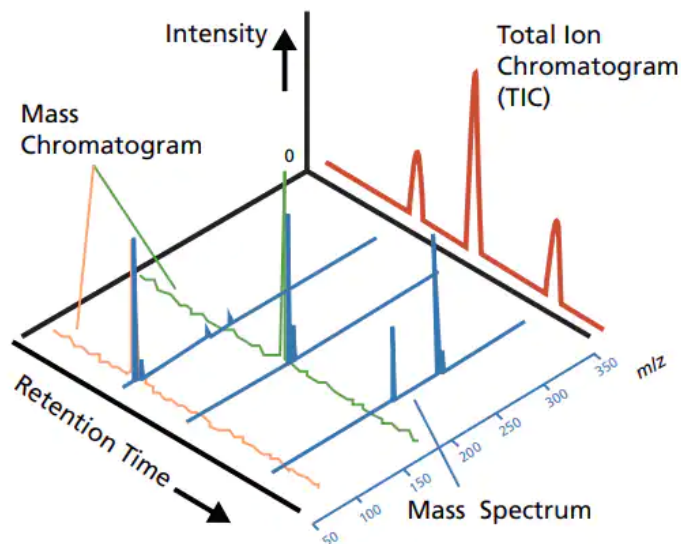


Figure 2.7: GC-MS Chromatogram [26]

The main advantage of the GC-MS is that it is able to identify unknown compounds by comparing the measured mass spectrum to a database of standard spectra for known compounds. This feature of providing not only a quantitative analysis, but also a qualitative analysis of the compounds present in the sample is unique to MS detectors. Other detectors, such as the TCD or the BID, do not provide such detailed qualitative analysis, and it is up to the operator to correctly identify to which compound a certain peak corresponds. The GC-MS' major drawback is, however, that it does not provide good precision for the quantitative analysis of compounds whose mass spectra are below $m/z = 45$ [25]. Hence, for the quantitative analysis of such compounds, other detectors are better suited. Moreover, the MS detector is sensitive and will deteriorate when used with GC columns which are packed with particles [24], therefore limiting the column choices to certain types (typically capillary columns).

In this study, a Shimadzu GCMS-QP2020 gas chromatograph-mass spectrometer system with a Shimadzu GC-2010 Plus gas chromatograph and a Shimadzu AOC-20i auto-injector has been used for the qualitative and quantitative analysis of ethanol, as well as for the qualitative analysis of water and acetaldehyde. The column which was used for the separation of these compounds is a GL Sciences TC-BOND Q 30 m $\times$ 0.25 mm with a film thickness of 8.00 μ m. Helium was used as a carrier gas, and acetone was used as a solvent for all samples. Acetone was chosen as a

solvent because of its high purity (99.5% purity for the grade used, see appendix B.1 for more details), good solubility, the fact that it does not pose any major safety hazard, and the fact that it does not contain ethanol as an impurity.

Similarly to the GC-TCD, firstly a good method was developed, and then calibration was performed by injecting known amounts of ethanol into the device and correlating them with their resulting areas. The key parameters of the method used are summarised in tables 2.3 and 2.4. For all analyses, an injection volume of 1 μl was used.

Table 2.3: GC settings

Parameter	Value	Unit
Initial temperature	40	$^{\circ}\text{C}$
Initial hold time	1	min
Program rate	5	$^{\circ}\text{C}/\text{min}$
Final temperature	250	$^{\circ}\text{C}$
Final hold time	5	min
Vaporisation chamber temperature	250	$^{\circ}\text{C}$
Injection mode	Split	
Flow control mode	Velocity	
Total flow rate	31.8	ml/min
Column flow rate	1.23	ml/min
Linear velocity	40	cm/s
Purge flow rate	6	ml/min
Split ratio	20	-

As acetone was used as a solvent, its concentration in all samples was very high. In general, detection of high concentration samples by the MS should be avoided because it damages the detector, and produces a huge, saturated peak which prevents any compound with a similar retention time from being measured, and decreases accuracy of the analysis as a whole. Therefore, as is shown on table 2.4, the detector was turned off around the retention time of acetone, i.e. between 17.1 and 20.5 min.

The GC-MS calibration process is slightly different than that of gas chromatographs with other detectors. Indeed, when using an MS, it is not the whole peak area corresponding to the compound of interest which is correlated to the concentration value, but rather the peak area corresponding to a specific ion which is correlated to the concentration value. In other words, a certain mass chromatogram, rather than the total ion chromatogram, is selected for each compound and used for calibration. In the case of ethanol, ion $m/z = 46$ u/e was selected, as it was the one which yielded the most accurate results. In general, heavier ions, particularly

with $m/z > 45$ u/e yield better results, as they tend to be less easily saturated and tend to offer better reproducibility. However this is not necessarily true for all compounds, and the selection of the ion used for calibration should be made on a case by case basis.

Once a good ion had been selected based on the results of the four standard samples which were analysed with the GC-MS, calibration was performed directly by the computer software. The software automatically correlated the concentration values with the measured areas, and a calibration curve was created. Similarly to the calibration of the GC-TCD, a straight line was fitted through the points based on a least squares linear regression. This curve was then saved to the method file and directly used by the software to calculate the concentration of ethanol in the unknown samples.

Table 2.4: MS settings

Parameter	Value	Unit
Ion source temperature	200	°C
Interface temperature	200	°C
Detector start time 1	0	min
Detector stop time 1	17.1	min
Detector start time 2	20.5	min
Detector stop time 2	48	min
Detection mode	Scan	
Scan start	10	u/e
Scan stop	300	u/e

As an example, the analysis results of run 3 are presented on figure 2.8. Only the first part (0-17.1 min) of the chromatogram is presented here because the second part (20.5-48 min) does not present any relevant results, the only detected compound being a small amount of benzene, which was found to be a solvent impurity. On figure 2.8, the reaction products: water, acetaldehyde and ethanol, as well as methanol, which is a solvent impurity, and nitrogen, which is a result of slight unavoidable air leaks and dead volumes, can clearly be seen.

In parallel to the aforementioned work, the existing Japanese version of the laboratory's user manual for the GC-MS was translated into English and updated with additional information. It contains a detailed description on how to operate the GC-MS and is presented in appendix A.2.

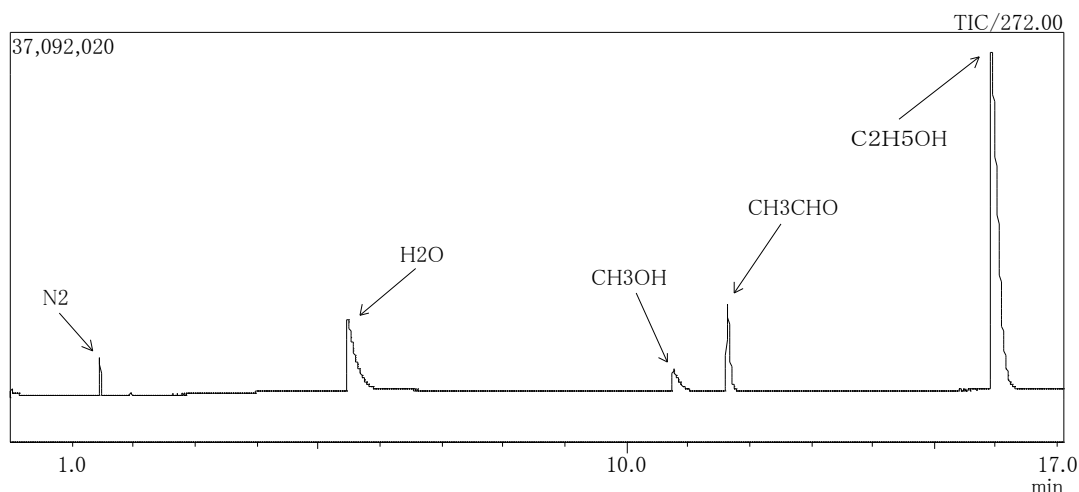


Figure 2.8: GC-MS analysis of the products of run 3

2.3.3 GC-BID

The GC-BID is a gas chromatograph with a dielectric barrier discharge ionisation detector, which is fundamentally a discharge ionisation detector (DID) with an added dielectric barrier which improves durability by protecting the detector. In this detector, the eluting compound will be ionised by a plasma discharge, and then be detected as a voltage. Its detailed working principle is illustrated by figure 2.9. Firstly, the discharge gas (high purity helium) is excited by an electric discharge, which brings it into an excited state. Then, as the helium returns to its ground state, it releases a quantum of energy (under the form of plasma) which ionises the analyte that just eluted from the column. The ion is finally collected by the collection electrode, and thus converted into a voltage.

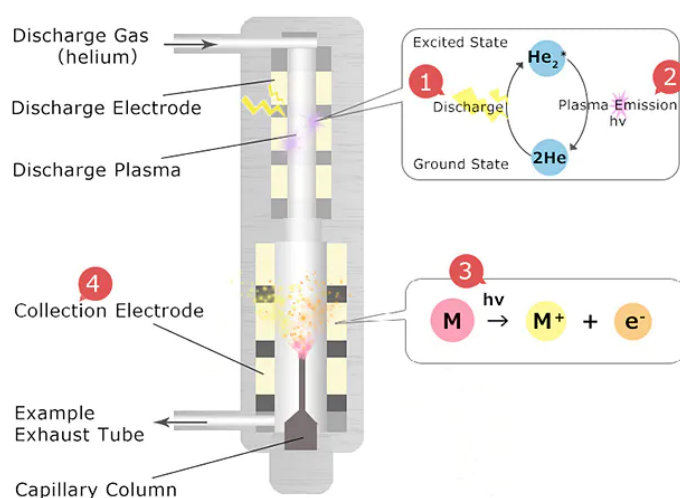


Figure 2.9: Dielectric barrier discharge ionisation detector [27]

The BID is a very universal detector, which is one of its major assets. Indeed, since the emission energy of helium is very high: $E_{\text{em,He}} = 17.7$ eV [31], any compound, except neon ($E_{i,\text{Ne}} = 21.6$ eV [13]) and helium itself ($E_{i,\text{He}} = 24.6$ eV [13]), can be ionised, because $E_{\text{em,He}} > E_i$, where E_i is the ionisation energy of the compound. Another important advantage of the BID is its high sensitivity. It can detect analytes down to a concentration of about 0.05 ppm [28], which is about 200 times lower than the minimum concentration which can be detected by a TCD. Thus, even trace components can be detected by using a BID. Nevertheless, due to its very high sensitivity, the detector saturates for injected compounds of higher concentrations (around about 10%). Hence, in order to obtain accurate results, samples can never be injected directly into it, but always need to be diluted with some solvent. This complicates the sample preparation procedure, and can be an additional source of errors, especially when gaseous samples need to be diluted.

In this study, a Shimadzu GC-2010 Plus gas chromatograph (the same one as for the GC-MS) with a Shimadzu BID-2010 Plus barrier discharge ionisation detector has been used for the qualitative and quantitative analysis of C_4 hydrocarbons, as well as for the qualitative verification of the results obtained by the GC-TCD. As the GC-BID offers good precision for the quantitative analysis of light compounds, it may have been preferable to perform the quantitative analysis of the liquid products with it. However, this was not possible, as the only suitable column for the separation of the liquid products obtained (GL Sciences TC-BOND Q) was already fitted with MS nuts. One option for future research would be to buy an additional TC-BOND Q column, which shall be used for the GC-BID, and would thus solve that problem. The column which was used for the separation of the aforementioned gaseous compounds is a Shinwa Micropacked ST 2 m $\times$ 1 mm. High purity helium was used both as a carrier gas and discharge gas.

As no C_4 gases have been detected in any of the analyses, only the products of runs 1, 2, 3 and 5 have been analysed with the GC-BID, while it was assumed, based on the total molar fraction of detected gases obtained as a result of the GC-TCD analysis, that no C_4 gases were produced in runs 4, 6 and 7. Basically, the total molar fraction of detected gases of run 4 was compared to that of run 3, while those of runs 6 and 7 were compared to that of run 5. As this showed that the total fractions of runs 4, 6 and 7 were greater than those of runs 3 and 5, respectively, it was assumed that no C_4 gases were formed for these runs. This therefore made the GC-BID analysis redundant, as it now only served to qualitatively verify the GC-TCD results, which had already been done for runs 1, 2, 3 and 5, and was thus dropped in order to simplify the analysis procedure and reduce the time necessary

for it.

For the analysis of the products of runs 1 and 2, nitrogen was used as a solvent gas because of its low cost and chemical stability, however, for runs 3 and 5, that solvent was changed to helium because the latter allows the carbon monoxide peak to be visualised on the resulting chromatogram. Indeed, when using nitrogen as a solvent, a large saturated peak is produced on the chromatogram, and, while this does not harm the detector, this large peak will overlap with and thus hide the peaks of other compounds with a similar retention time to that of nitrogen. When using helium as a solvent however, this is not an issue as helium is not detected at all by the BID, allowing thus all compounds to be visualised within the limitations of the column and method.

Similarly to the GC-TCD and GC-MS, firstly a good method was developed, and then calibration was performed by injecting known amounts of n-butane into the device and correlating them with their resulting areas. Calibration was performed for n-butane before executing the experiments because n-butane was available at the laboratory and there was a possibility of obtaining it as a reaction product (especially in the case of the cracking of a fuel blend of ethanol and n-heptane or iso-octane, which were initially planned to also be part of this study). If other C₄ gases had been found in the reaction products, they would have had to be firstly identified with the GC-MS, before calibration samples could have been purchased, and then the GC-BID would have been calibrated for these extra compounds. However, no C₄ gases were detected in the reaction products, so this procedure turned out not to be needed. The key parameters of the method used are summarised in table 2.5. For all analyses, an injection volume of 1 µl was used.

Calibration was performed by analysing eight standard samples of butane at three different concentration levels. Nitrogen was used as a solvent for all of them, as the retention times of nitrogen and butane are very different. Similarly to the GC-MS, calibration was carried out directly by the computer software. The software automatically correlated the concentration values with the measured areas, and a calibration curve was created. As for the GC-TCD and GC-MS, a straight line was fitted through the points based on a least squares linear regression. This curve was then saved to the method file and could directly be used by the software to calculate the concentration of n-butane in the unknown samples if butane was detected.

Table 2.5: GC-BID settings

Parameter	Value	Unit
Initial temperature	35	°C
Initial hold time	3	min
Program rate	20	°C/min
Final temperature	300	°C
Final hold time	17	min
Vaporisation chamber temperature	200	°C
Injection mode	Split	
Flow control mode	Velocity	
Total flow rate	38	ml/min
Column flow rate	7	ml/min
Linear velocity	28.3	cm/s
Purge flow rate	3	ml/min
Split ratio	4	-
Detector temperature	300	°C
Discharge gas flow rate	50	ml/min

As an example, the analysis results of run 3 are presented on figure 2.10. Only a selected part (0-15 min) of the chromatogram is shown on the figure, because no compound has been detected in the latter part of the analysis (15-33.25 min). The peaks corresponding to hydrogen, carbon monoxide, methane, ethylene and ethane, which are also detected by the GC-TCD, can clearly be seen. In addition, the peaks of oxygen and nitrogen show that some air is involuntarily added into the gas mixture. The cause of this could be dead volumes and air leaks happening during the sample preparation process, as well as the dead volumes which are unavoidably present in the machine. The sample preparation process could possibly be improved by reducing such leaks and dead volumes, but some amount of air addition is unavoidable. The small peak occurring around a retention time of 8 min probably corresponds to CO₂, which is probably present in the air that leaks into sample.

In parallel to the aforementioned work, the existing Japanese version of the laboratory's user manual for the GC-BID was translated into English and updated with additional information. It contains a detailed description on how to operate the GC-BID and is presented in appendix A.3.

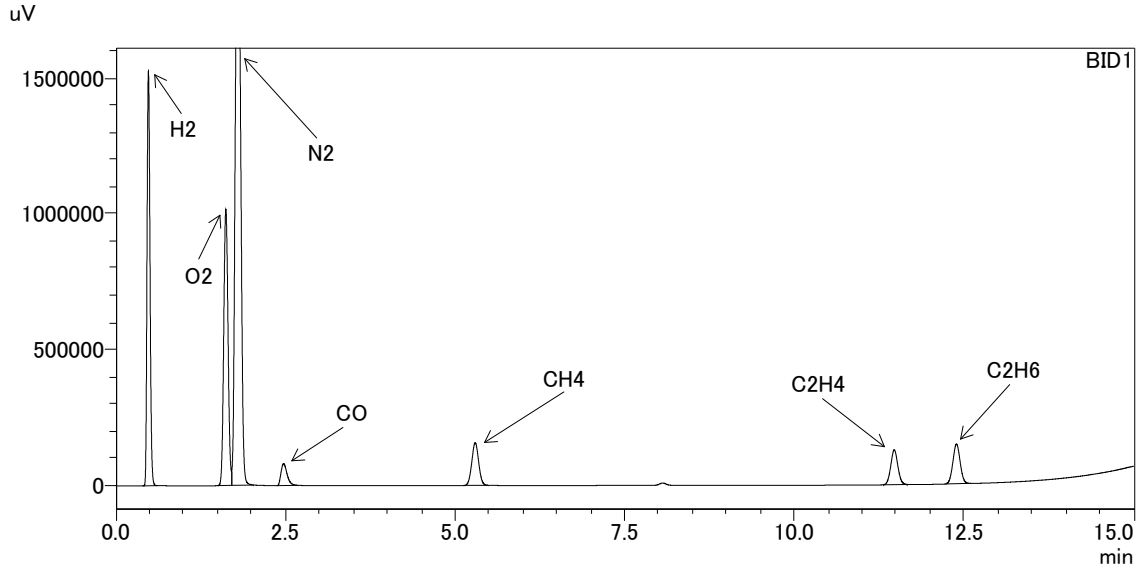


Figure 2.10: GC-BID analysis of the products of run 3 (solvent: He)

2.4 Experimental conditions

The results presented in chapter 4.1 have all been obtained from flow-type thermal cracking experiments. The reason for this being that flow-type thermal cracking (as opposed to stationary thermal cracking) is the only relevant method for engine regenerative cooling.

Seven different experimental runs have been carried out. For all of them, pure ethanol (99.5 %, see appendix B.2 for more details) was used as a primary fuel. Table 2.6 presents the target conditions for each run, where p , $\dot{m}$, T_3 and T_4 are the pressure, mass flow rate and reaction zone inlet and outlet temperatures, respectively.

Table 2.6: Target experimental conditions

Run	p [MPaG]	$\dot{m}$ [g/min]	T_3 [°C]	T_4 [°C]
1	7	20	400	400
2	7	20	450	450
3	7	20	500	500
4	7	20	500	500
5	5	20	400	400
6	5	20	450	450
7	5	20	500	500

The critical pressure and temperature of ethanol are $p_c = 6.3$ MPa and $T_c = 514$ K = 241 °C, respectively [13]. Hence, runs 1 through 4 have been performed

under supercritical conditions ($p > p_c$, $T_3, T_4 > T_c$), while runs 5 through 7 have been performed under sub-critical conditions ($p < p_c$). Experiments conducted under supercritical conditions, as is shown by the results presented in chapter 4.1, exhibit much more stable mass flow rates and temperatures than those conducted under sub-critical conditions. This is due to the fact that working under supercritical conditions prevents any sudden phase change, and thus improves the overall stability of the experiments. In addition, it can be seen from table 2.6 that runs 3 and 4 present the same target conditions. Indeed, run 4 serves as a verification run in order to confirm the repeatability and accuracy of the experimental procedure.

Chapter 3

Numerical simulation model

3.1 Cantera package

In addition to the aforementioned experimental research, a numerical simulation model has also been developed. This model was developed using the python-based Cantera package [7], which is commonly used for many kinds of chemical reaction models. Cantera offers many tools, as well as examples, which are useful to create numerical simulations of chemical reactions. Its extensive documentation is also helpful to understand and take advantage of all its specialised functions.

The simulation model developed in this study is based on Cantera's plug flow reactor example. Basically, this example was taken and adapted to match the experimental case studied. That way, the model can be used to confirm the experimental procedure and the experiments can be used to validate the model. The plug flow reactor example proposes two ways of simulating the plug flow reaction: a Lagrangian particle simulation, where a Lagrangian particle which travels through the reactor is considered, and a chain of reactors, where the main reactor is divided into a chain of small reactors which are solved iteratively. For the model developed in this study, the chain of reactors method was chosen because it is also the method which is used in the Cantera surface plug flow reactor example, an example which simulates a plug flow reactor problem where the chemistry is surface chemistry and is thus suited for the simulation of reactions which include a catalyst. Hence, by using the same simulation method as for the surface plug flow reactor example, the developed model can easily be adapted to include the effect of a catalyst into the simulation, which could be an interesting future improvement.

3.2 Chemical kinetic mechanism

An important part of any chemical reaction simulation model is the chemical kinetic mechanism. Of course, Cantera includes simple mechanisms which are sufficient to simulate simple reactions, but in order to obtain an accurate simulation of more complex reactions, such as the thermal cracking of ethanol, more advanced, specialised mechanisms are necessary. Such mechanisms are usually developed by research groups which specialise in the detailed and precise modelling of the kinetics of specific reactions.

In this model, the mechanism developed by Mittal et Al. at the Combustion Chemistry Centre, National University of Ireland Galway [16] was used. This mechanism is composed of 710 elementary reactions, and involves 113 species. It was chosen through consultation with other laboratory members who were also developing simulation models for other combustion problems. This mechanism, like most ones, has been developed to model the combustion of ethanol, and it can be applied to the thermal cracking of ethanol by considering thermal cracking as a limit case of combustion where the fuel-to-oxidizer equivalence ratio tends to infinity (rich condition). Of course, a mechanism which specifically models the cracking of ethanol may achieve higher precision, but such kind of mechanisms are less common in literature, as they are less general than combustion mechanisms.

Moreover, other mechanisms developed by different research groups, such as the ones developed by Marinov at the Lawrence Livermore National Laboratory (LLNL) [14] or Saxena et Al. at the Center for Energy Research, University of California, San Diego [23], may yield more accurate results, and an interesting prospect would be to compare the results of various mechanisms and select the one which yields the best results for the numerical modelling of the thermal cracking of ethanol. However, such work exceeds the scope of this study and is left as a possible direction for future investigations.

Finally, it is important to note that all three mechanisms mentioned above use a thermodynamic model based on the ideal gas equation of state and mixture averaged transport properties. Thus, if any of these mechanisms is to be used as part of a real gas model, it must be updated in order to use a Redlich-Kwong equation of state and high pressure transport properties, which are the best way to simulate real gases in Cantera.

3.3 Heat transfer model

Many parts of the Cantera plug flow reactor example had to be adapted in order to model the experiments presented in this study. One important feature which was added to the initial example is a heat transfer model. Indeed, the plug flow reactor example is a simple zero-dimensional model which only simulates a reactor having no interaction with the exterior environment, except for its inlet and outlet. However, the reactor used for cracking (see section 2.1) is heated on its whole length in order to supply the heat needed for the cracking of ethanol, as it is an endothermic reaction. Therefore, in order to develop a simulation model representative of the experiments, a heat transfer model had to be added to it.

As a first, simple approach, a heat transfer model based on a Nusselt number correlation, with a constant convection coefficient throughout the reactor was used. More specifically, the Nusselt number correlation was used to evaluate the convection coefficient at the reactor entrance, and then, this coefficient was used for the whole reactor. The convection coefficient was calculated as follows. First, the Reynolds and Prandtl numbers are evaluated at the reactor entrance,

$$\text{Re} = \frac{\rho u d}{\mu} \quad \text{Pr} = \frac{\mu c_p}{k}, \quad (3.1)$$

where ρ , u , μ , c_p and k are the density, velocity, dynamic viscosity, constant pressure heat capacity and thermal conductivity of the fuel at the reactor entrance, respectively, and d is the reactor tube's inner diameter. Then, the Nusselt number is calculated based on the values of Re and Pr obtained from equation (3.1) and the heat transfer boundary conditions. If $\text{Re} < 2300$, then

$$\text{Nu} = \begin{cases} 3.66 & \text{if } T_t = \text{cst} \\ 4.36 & \text{if } q_t'' = \text{cst} \end{cases} \quad (3.2)$$

where T_t and q_t'' are the tube temperature and surface heat flux, respectively. If $\text{Re} > 10000$ and $0.7 \leq \text{Pr} \leq 160$, then

$$\text{Nu} = 0.023 \text{Re}^{4/5} \text{Pr}^n \quad \text{where} \quad n = \begin{cases} 0.4 & \text{if } q_t'' > 0 \\ 0.3 & \text{if } q_t'' < 0 \end{cases} \quad (3.3)$$

and $q_t'' > 0$ means that heat is added to the fluid, while $q_t'' < 0$ means that heat is

removed from the fluid. If $3000 < \text{Re} \leq 5 \cdot 10^6$ and $0.5 \leq \text{Pr} \leq 3000$, then

$$\text{Nu} = \frac{f}{8} \frac{(\text{Re} - 1000) \text{Pr}}{1 + 12.7 (f/8)^{1/2} (\text{Pr}^{2/3} - 1)} \quad (3.4)$$

where $f = (0.790 \log \text{Re} - 1.64)^{-2}$ is the friction factor. Finally, the convection coefficient is obtained from the definition of the Nusselt number,

$$\text{Nu} = \frac{hd}{k} \implies h = \frac{k}{d} \text{Nu}. \quad (3.5)$$

The major limitation of this model is that the convection coefficient cannot be evaluated when the flow is in the transition regime, i.e. for $2300 \leq \text{Re} \leq 3000$, as well as for very low and very high Prandtl numbers.

For the case modelled in this study, the tube temperature is assumed constant, as this best fits the experimental case, where the reactor is heated such that the inlet temperature T_3 is equal to the outlet temperature T_4 . In addition, as the cracking reaction is endothermic, the tube is being heated and q_t'' is set to be positive. The heat transfer model presented here can however be adapted to simulate cases where the heat flux is held constant, or where the reactor is cooled. This gives the model a certain flexibility, as it is not only restricted to the specific case modelled in this study. For more complex boundary conditions, however, this model cannot be used, and a more advanced heat transfer model must be developed.

3.4 Model summary

The global simulation model, which was developed on the basis of the Cantera plug flow reactor example, and includes, among other additions and modifications, a heat transfer model, is illustrated by figures 3.1 and 3.2.

Figure 3.1 shows how the reactor is modelled as a whole. Its dimensions correspond to those of the actual reactor and are $l = 77$ cm and $d = 2$ mm. The fuel enters the reactor at a temperature $T_0 = T_r$ and composition $\vec{x}_0$, where T_r is the target reaction temperature and $\vec{x}_0$ is a vector whose entries are the relative mole fractions of the species composing the fuel. The pressure p is assumed uniform throughout the reactor and its value is set to the target reaction pressure, while the tube temperature is assumed constant and its value is set to the target reaction temperature, i.e. $T_t = T_r$. As a consequence of the plug flow assumption, the velocity profile u is uniform and satisfies $u = \dot{m}/(\rho A)$, where $\dot{m}$, ρ and $A = \pi d^2/4$ are the mass flow rate through the reactor, density of the mixture and cross sectional area,

respectively. The velocity is allowed to vary in the axial direction, as the density of the mixture may vary along the reactor.

In order to be simulated iteratively, the reactor model shown in figure 3.1 was divided into small sections of length $dz = l/n_s$, where n_s is the number of simulation steps, i.e. the number of sections the reactor was divided into. Each section was then modelled as illustrated by figure 3.2.

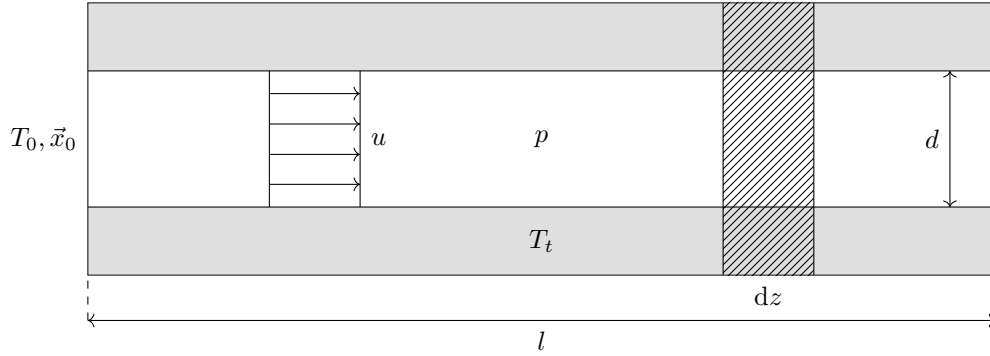


Figure 3.1: Reactor model

The reacting part of the section was modelled as a reactor of volume $dV = A dz$, while the reacting parts of the preceding and following sections were modelled as reservoirs connected to the reactor by a mass flow controller (MFC) and a pressure controller (PC), respectively. The mass flow controller ensured that the inlet mass flow rate was set to $\dot{m}$ at all times. The pressure controller is linked to the upstream mass flow controller and defines the outlet mass flow rate as $\dot{m}_{\text{out}} = \dot{m} + K_v(p_1 - p_2)$, where the second term accounts for the transient pressure difference between the reactor and the downstream reservoir, and K_v is the proportionality constant between the pressure drop and the mass flow rate. The constant K_v is a parameter of the pressure controller and it had to be manually set to the appropriate value; in this case, $K_v = 10^{-5}$ was used.

The tube was also modelled as a reservoir, but one containing metal at a constant temperature, not a mixture of species (see appendix C.3 for the source code defining the steel applied to the tube reservoir). It was connected to the reactor through a wall, which controlled heat transfer between the tube and the reservoir. The wall controlled heat transfer by being specified both the convection coefficient h , as well as the surface area $dS = \pi d dz$.

In summary, in order to simulate the flow-type thermal cracking reaction through the reactor presented in figure 3.1, each part was successively simulated as shown by figure 3.2, starting from the most upstream section and ending with the most downstream one.

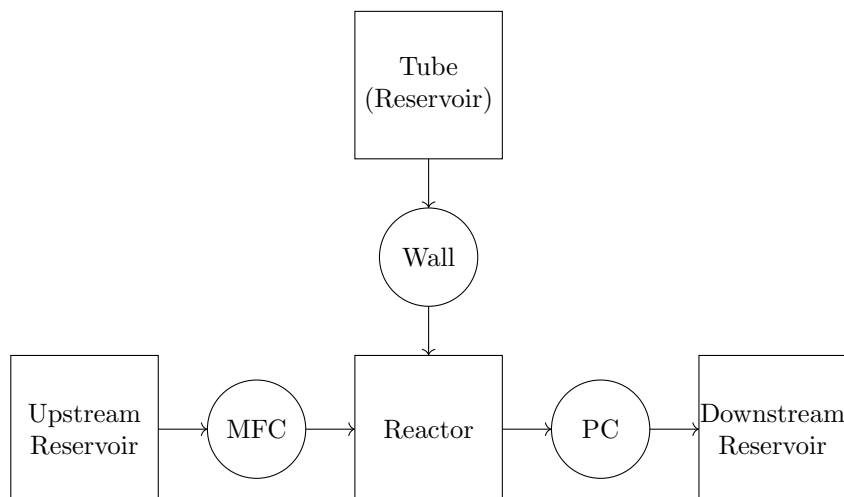


Figure 3.2: Model of one reactor section

3.5 Model versions

Two versions of the simulation model summarised in section 3.4 were actually developed: one in which ethanol and the other species involved were modelled as ideal gases, and one in which they were modelled as real gases based on the Redlich-Kwong equation of state.

The development of the ideal gas version did not require any specific changes or modifications related to the thermodynamic model, as both the kinetic mechanism and the Cantera plug flow reactor example had already been programmed such that all species were modelled as ideal gases. Hence, after adapting the Cantera example to the case studied (by adding elements such as the heat transfer model mentioned in section 3.3), the ideal gas version was complete and ready for use. The source code for this version is presented in appendix C.1.

The development of the real gas version, on the other hand, required some major changes to the mechanism file, as well as a few changes to the main code. In the mechanism file, general thermodynamic and transport models must be defined, and these were easily changed from ideal gas and mixture averaged to Redlich-Kwong and high pressure. However, as each species taking part in the reaction mechanism is defined separately, and for each species an equation of state must be specified, each species' equation of state had to be changed from ideal gas to Redlich-Kwong. When setting any species equation of state to Redlich-Kwong, the constants a and b are required. For some compounds, these constants are directly calculated by Cantera based on the critical temperatures and pressures of these compounds, and need not be specified. For the other compounds, which make up the majority of

the species defined in the mechanism, however, a and b must be specified. Thus, for all compounds for which it was possible, a and b were calculated from the critical temperatures and pressures found in the NIST database [13] with the following formulas,

$$a = \frac{1}{9(\sqrt[3]{2} - 1)} \frac{R^2 T_c^{2.5}}{p_c} \quad b = \frac{\sqrt[3]{2} - 1}{3} \frac{R T_c}{p_c}, \quad (3.6)$$

where R is the ideal gas constant, and T_c and p_c are the critical temperature and pressure of the compound. For the species for which T_c and p_c were not available (mostly transition compounds), the constants were set to $a = b = 0$, which reduces the Redlich-Kwong equation to the ideal gas one. Through the changes discussed here, the ideal gas version of the model could be adapted to the real gas version. The source code for this version is presented in appendix C.2.

The real gas version is expected to yield more accurate results than the ideal gas one, especially for simulations for which ethanol is under supercritical conditions. Indeed, under supercritical conditions, the accuracy of the ideal gas law should be reduced significantly and show different results from the Redlich-Kwong equation of state. Nonetheless, the ideal gas model should also be significantly less demanding in computational resources, and should therefore need much less time to perform a simulation. This is an important advantage as it allows to test different parameters and configurations in a short amount of time, which can be key to developing a good model or finding optimal parameters for the real gas model.

Chapter 4

Results and Discussion

4.1 Experimental work

This section presents the experimental results obtained and discusses their validity. First, for each run, the actual flow conditions, i.e. the mass flow rate, temperatures, gas pressure in the sample tank and Fourier transform of the mass flow rate, are presented in detail (section 4.1.1). Then, in section 4.1.2, important global reaction results, such as conversion, gas yield, selectivity and mass fraction are shown and compared between runs. Finally, in section 4.1.3, the results are discussed in detail. Among other things, a chemical reaction pathway is proposed to explain them, and their validity is assessed by comparing them to existing literature.

4.1.1 Actual flow conditions

Figure 4.1 shows the time history of the mass flow rate for run 1. In all experiments, the mass flow rate was controlled as well as possible with the metering valve in order to obtain a constant mass flow rate at its target value. However, as can be seen on figure 4.1, a certain amount of oscillations was always unavoidable. Indeed, although the mass flow rate is centered on its target value ($\dot{m} = 20$ g/min), it is relatively unstable, with peaks reaching maximum values of about 60 g/min and minimum values of about 12 g/min. These instabilities were probably caused by the fact that the cracking reaction involves multiple species in different phases, which form at different rates. This causes strong and sudden variations in density, which in turn affect the mass flow rate. The average mass flow rate is $\bar{\dot{m}} = 20.71$ g/min with a standard deviation of $\sigma_{\dot{m}} = 5.13$ g/min. This highlights the fact that the mass flow rate is well centered around its target value, but has some oscillations.

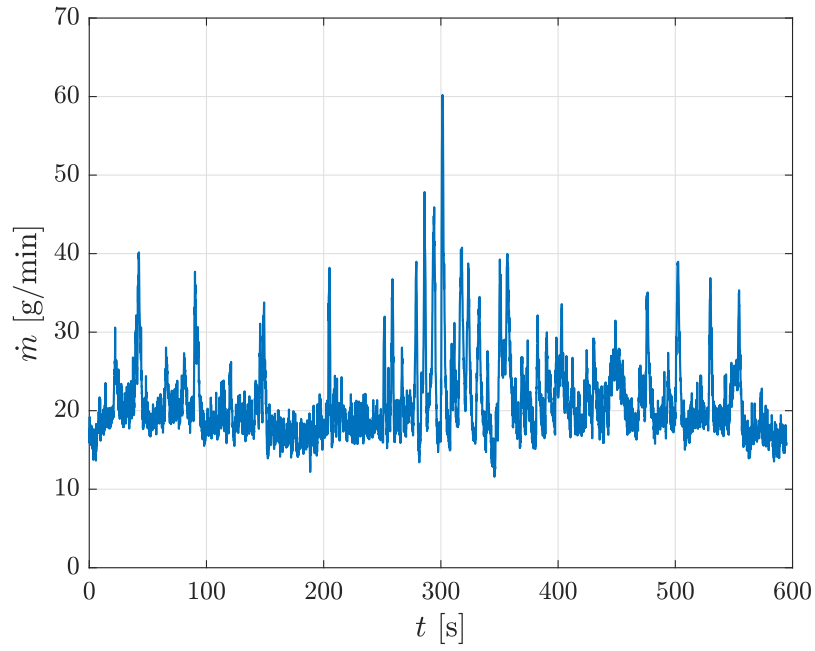


Figure 4.1: Mass flow rate as a function of time (run 1)

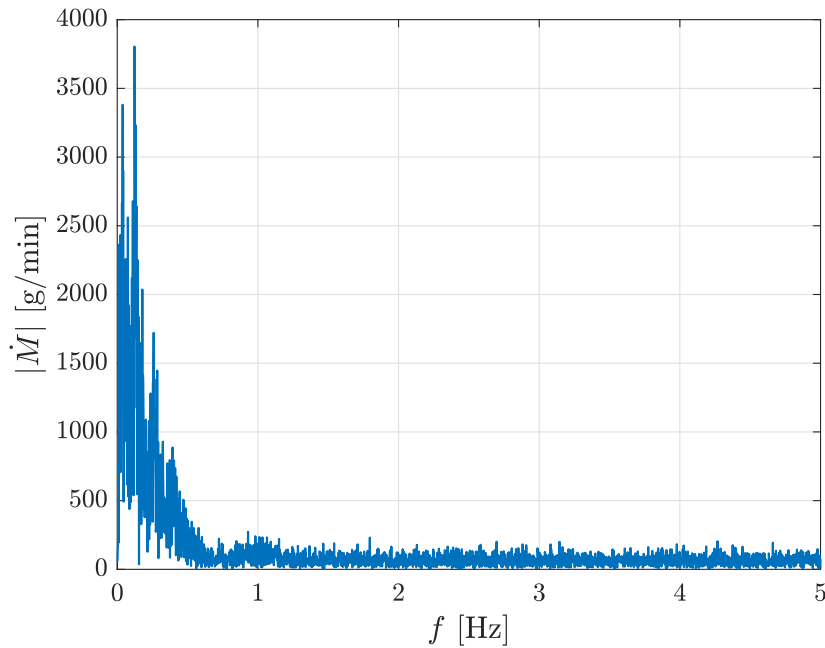


Figure 4.2: Frequency spectrum of the mass flow rate (run 1)

Figure 4.2 shows the frequency spectrum of the mass flow rate for run 1, which gives a more detailed understanding of the oscillations of the mass flow rate. It can be seen there are two dominant frequencies at 0.04 and 0.12 Hz, which may correspond to the peaks appearing between 0 and 250 s and 400 and 600 s, and

250 and 400 s, respectively. However, as a relatively wide band of low frequencies (0-0.6 Hz) appear with relatively high amplitudes, it shows that the oscillations are a mixture of many different frequencies, making it hard to identify a clear dominant one. Note that, for all frequency spectra presented in this study, the maximum frequency is 5 Hz, and not the sampling frequency (10 Hz). This is because the highest frequency resolution one can obtain for a certain sampling frequency is the Nyquist frequency, which is defined as $f_N = f_s/2$.

Figure 4.3 presents the temperatures measured by the four thermocouples placed at different points in the system for run 1. However, the most important ones are T_3 and T_4 , which are the reactor inlet and outlet temperatures respectively. These were aimed to match the target reaction temperature as well as possible. As can be seen on figure 4.3, T_3 and T_4 oscillate somewhat around their target value. This is due to the thermal inertia of the system because, even though the heaters were switched off when they exceeded the target temperature, the temperature would still increase for a bit until a maximum value was reached and the system cooled down again. This was improved in further runs by better tuning the heater voltage, which led to more stable temperatures with less overshoot. The high frequency oscillations which can be seen for all temperatures are probably a direct consequence of the mass flow rate oscillations, as the mass flow rate influences the heat carried away by the flow and thus the flow temperature. The average temperatures are $\bar{T}_3 = 402.5$ °C and $\bar{T}_4 = 407.3$ °C with standard deviations $\sigma_{T_3} = 14.9$ °C and $\sigma_{T_4} = 10.7$ °C.

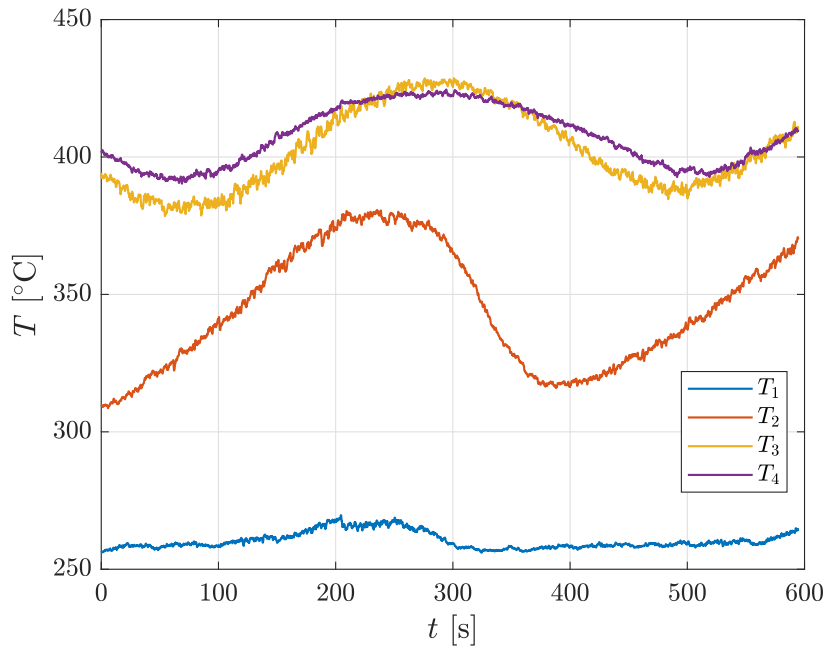


Figure 4.3: Temperatures as a function of time (run 1)

Figure 4.4 shows the gas pressure in the sample tank throughout the experiment for run 1. The gas pressure increased quite linearly throughout the experiment. This shows that gases were continuously produced during the experiment. It can be noted, however, that there is a sudden increase in the curve's slope between $t = 250$ and $t = 350$ s. This can be explained by the fact that during this time, the temperatures T_3 and T_4 were at their highest, which, as the conversion for thermal cracking reactions increases with temperature, increased the conversion and thus the gas yield. Therefore, more gas was produced during this period, which translates into a steeper slope on figure 4.4.

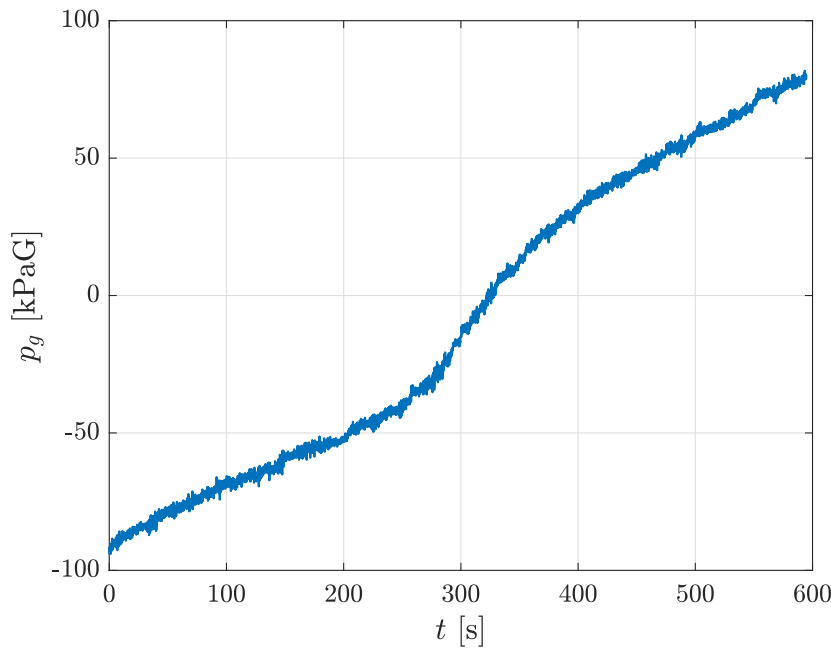


Figure 4.4: Gas pressure in the sample tank as a function of time (run 1)

Figure 4.5 shows the time history of the mass flow rate for run 2. With peaks reaching maximum values of about 54 g/min and minimum values of about 0 g/min, the mass flow rate seems generally more stable than in run 1. However, the average mass flow rate is $\bar{m} = 21.09$ g/min with a standard deviation $\sigma_{\dot{m}} = 6.58$ g/min. This shows that, although the minimum and maximum values are less extreme than for run 1, the mass flow rate is less well centered and stable around its target value than in run 1. The general causes for the occurrence of the oscillations are thought to be the same as for run 1, but, because the conversion and gas yield increase with temperature, the oscillation phenomenon becomes stronger than in run 1.

Figure 4.6 shows the frequency spectrum of the mass flow rate for run 2. Again, a relatively wide band of frequencies (0-0.6 Hz) is present with a large amplitude.

A few dominant frequencies can be identified at around 0.04 Hz. They could correspond to the main oscillations visible on figure 4.5, but again, due to the variety of frequencies involved, such a statement is hard to confirm.

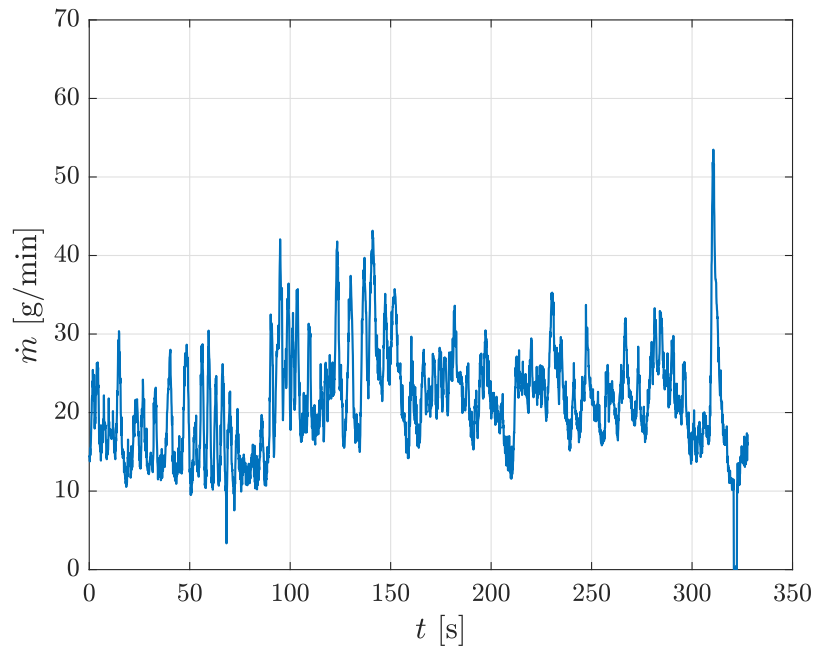


Figure 4.5: Mass flow rate as a function of time (run 2)

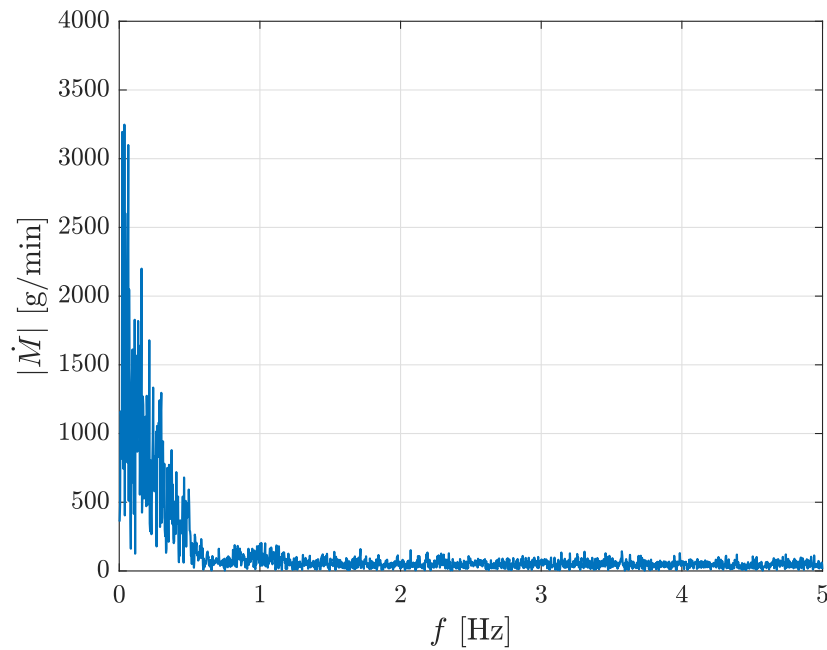


Figure 4.6: Frequency spectrum of the mass flow rate (run 2)

Figure 4.7 shows the temperatures for run 2. Here, T_3 and T_4 are much more

stable than in run 1. Indeed, the average temperatures are $\bar{T}_3 = 450.2\text{ }^\circ\text{C}$ and $\bar{T}_4 = 455.9\text{ }^\circ\text{C}$ with standard deviations $\sigma_{T_3} = 6.5\text{ }^\circ\text{C}$ and $\sigma_{T_4} = 7.5\text{ }^\circ\text{C}$, which is significantly better than run 1. This improvement is mostly due to a finer tuning of the heating system, which reduced temperature overshoots and oscillations.

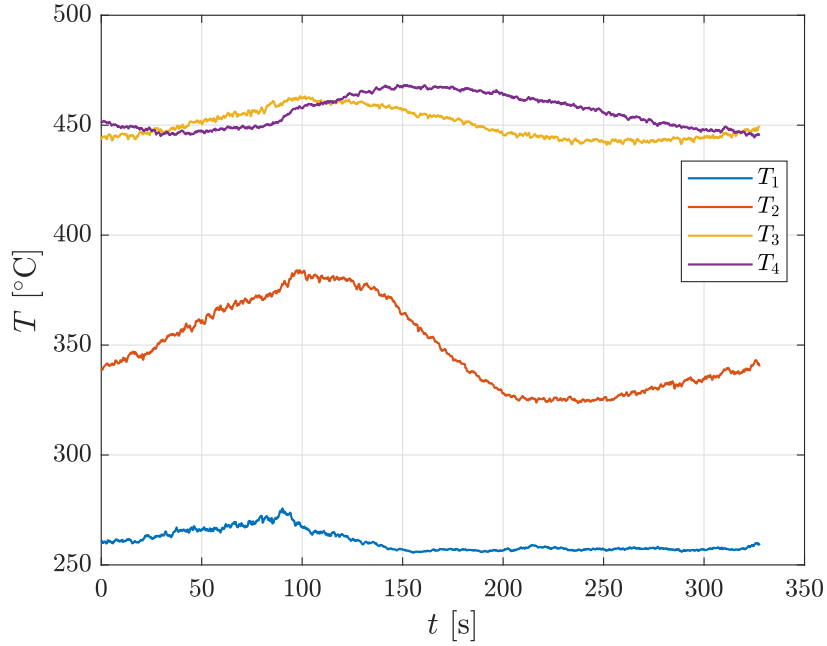


Figure 4.7: Temperatures as a function of time (run 2)

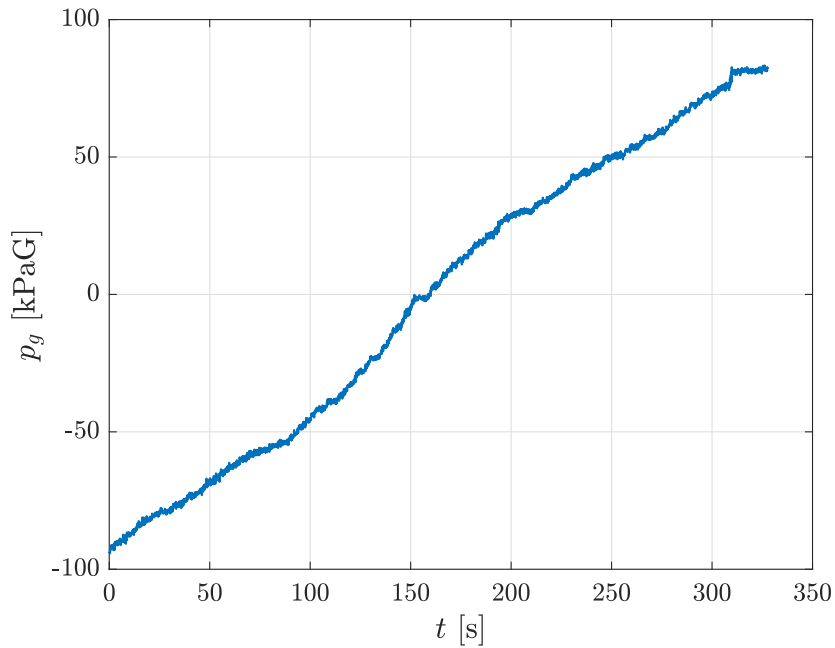


Figure 4.8: Gas pressure in the sample tank as a function of time (run 2)

Figure 4.8 shows the pressure in the sample tank for run 2. Similarly to run 1, the pressure increases quite linearly with time. In this case, as the temperatures were more stable, less slope variations are seen on figure 4.8 and the pressure's increase rate varies little throughout the experiment.

Figure 4.9 shows the mass flow rate for run 3. Although the maximum and minimum peak values are about 45 and 2 g/min respectively, it can be visually seen that the mass flow rate is less stable for run 3 than for both runs 1 and 2. Indeed, the average mass flow rate is $\bar{m} = 18.15$ g/min with a standard deviation of $\sigma_{\dot{m}} = 8.94$ g/min, which is less centred and stable than runs 1 and 2. Again, the cause behind the occurrence of the oscillation phenomenon is the same as for runs 1 and 2, and the cause of its amplification is the same as for run 2 (higher temperature meaning higher conversion and gas yield).

Figure 4.10 shows the frequency spectrum of the mass flow rate for run 3. On this spectrum, it is much easier to identify dominant frequencies, as there are clear peaks for certain frequencies instead of a band of low frequencies all having large amplitudes. A dominant frequency can be identified at 0.31 Hz, while secondary frequencies can be identified at 0.13 and 0.35 Hz. This dominant frequency corresponds to the frequency of the oscillations which can be observed on figure 4.9. Similarly to runs 1 and 2, no frequency higher than about 1 Hz is involved in the oscillation phenomenon.

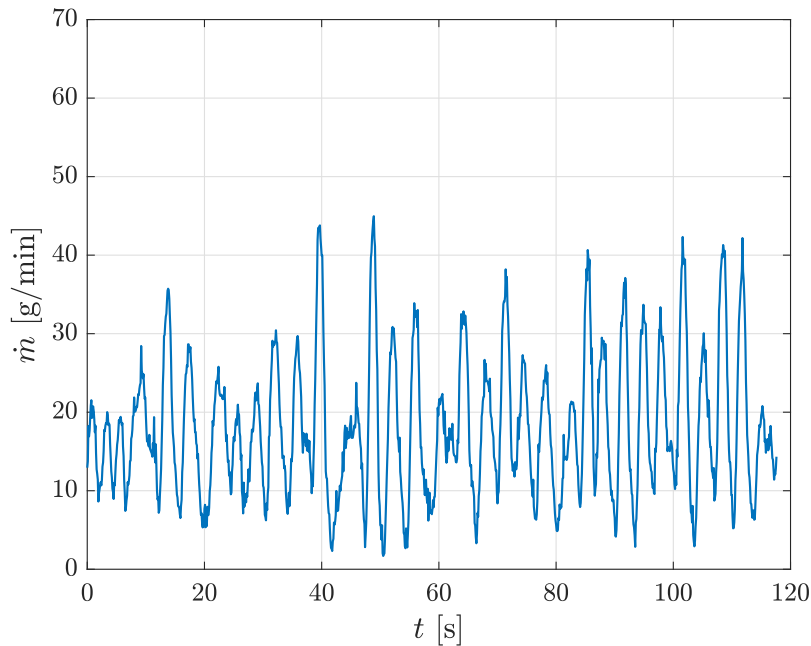


Figure 4.9: Mass flow rate as a function of time (run 3)

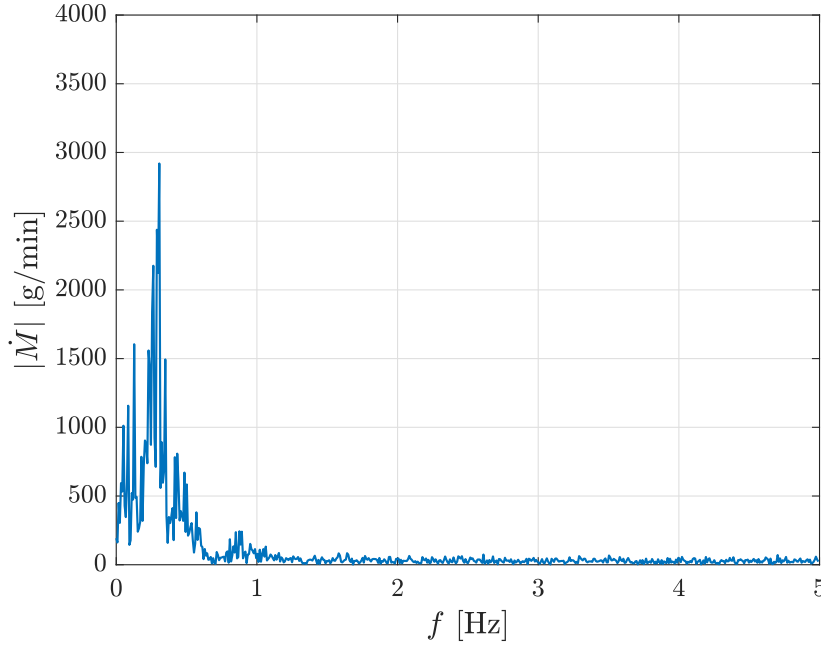


Figure 4.10: Frequency spectrum of the mass flow rate (run 3)

Figure 4.11 shows the temperatures for run 3. In this run, an excellent temperature stability was achieved, especially for T_3 and T_4 . Indeed, the average temperatures are $\bar{T}_3 = 504.2\text{ }^\circ\text{C}$ and $\bar{T}_4 = 506.6\text{ }^\circ\text{C}$ with standard deviations $\sigma_{T_3} = 2.5\text{ }^\circ\text{C}$ and $\sigma_{T_4} = 4.3\text{ }^\circ\text{C}$, which shows that, although the average values of both temperatures are slightly above their target values, the temperatures varied very little throughout the experiment. The offsets of the average values is comparable to those of run 2, but these very small standard deviations show a significant improvement in the stability of the temperatures in time when compared to runs 1 and 2. The reasons behind this excellent stability may be both a better tuning of the heating system and the short duration of the experiment, which gave less time for instabilities and oscillating behaviours to settle in. The necessary duration of each experiment became shorter as the temperature increased, because, as the gas yield increased with temperature, less time was needed to fill the sample tank with gas (to a pressure of about 80-100 kPa).

Figure 4.12 shows the evolution of the pressure in the sample tank throughout run 3. As a consequence of the excellent stability of temperatures T_3 and T_4 , the pressure increase is almost perfectly linear, with, except for slight transient variations, a constant slope throughout the experiment.

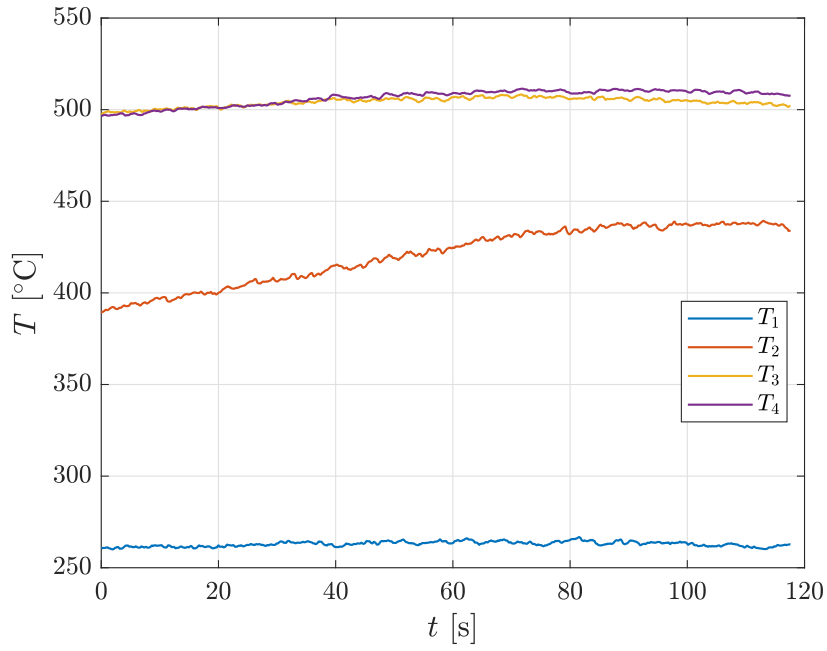


Figure 4.11: Temperatures as a function of time (run 3)

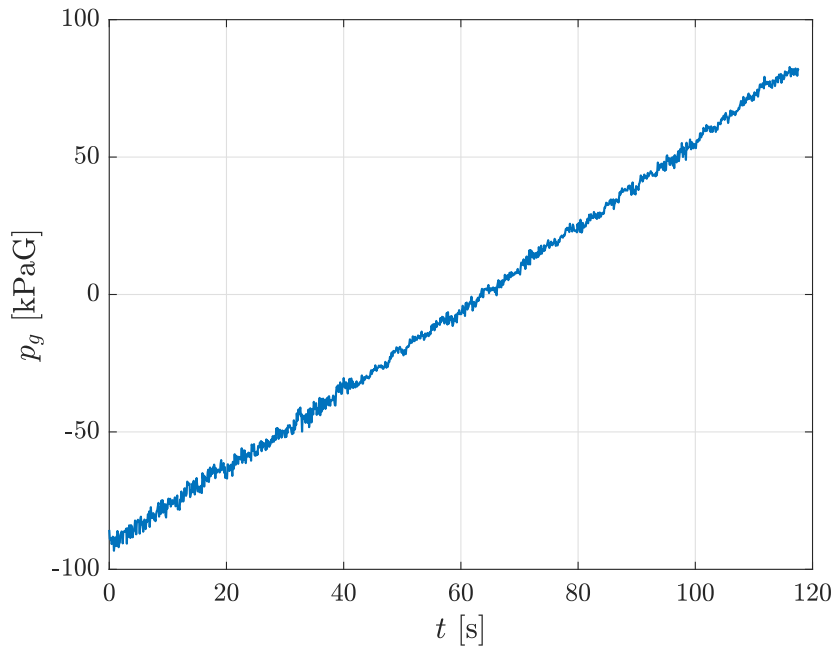


Figure 4.12: Gas pressure in the sample tank as a function of time (run 3)

Run 4 serves as a verification run for the reliability and repeatability of the experimental procedure as a whole. Therefore, the target conditions were the same as for run 3 (see table 2.6). Nonetheless, as there are some physical limitations as to how precisely the target conditions can be reached, the conditions for run 4, as

will be detailed below, were slightly different than those for run 3, which influenced some of the general results presented in section 4.1.2.

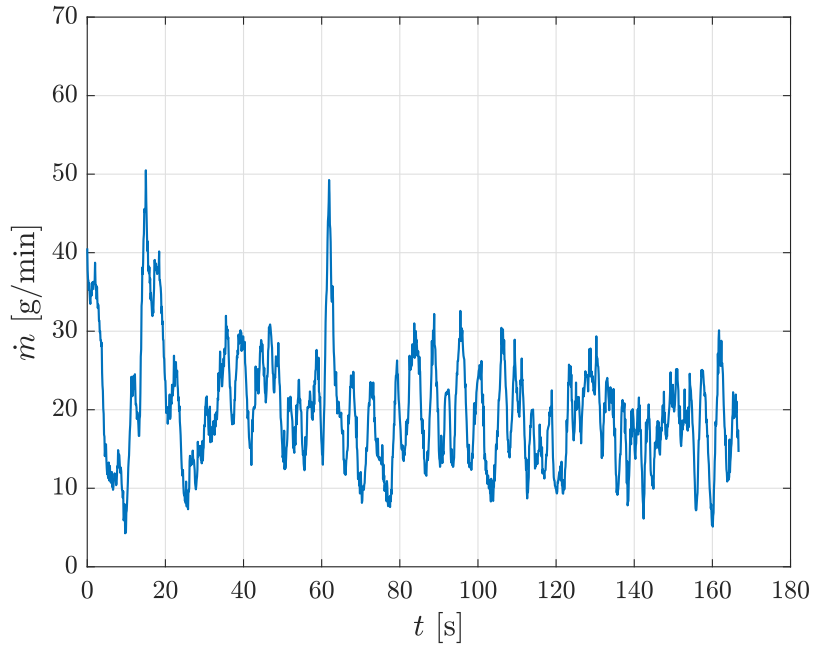


Figure 4.13: Mass flow rate as a function of time (run 4)

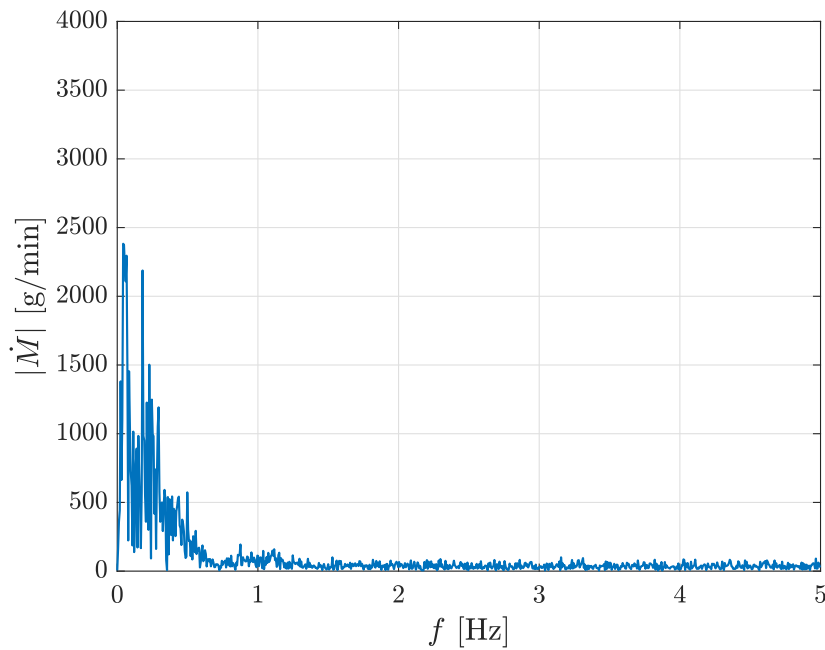


Figure 4.14: Frequency spectrum of the mass flow rate (run 4)

Figure 4.13 shows the mass flow rate for run 4. Similarly to run 3, the mass flow rate exhibits an oscillation pattern, however, the amplitude of the oscillations

is much smaller than in run 3, with maximum peak values of about 33 g/min and minimum peak values of about 5 g/min (except for a few peaks reaching 40-50 g/min). When looking at time independent values, the average mass flow rate is $\bar{m} = 19.75$ g/min with a standard deviation $\sigma_{\bar{m}} = 7.20$ g/min, which exhibits better accuracy and stability than run 3.

Figure 4.14 shows the frequency spectrum of the mass flow rate for run 4. Two dominant frequencies can easily be identified at 0.05 and 0.18 Hz, while other frequencies in the 0-0.7 Hz band are also involved in the oscillation phenomenon, although with much smaller amplitudes. These two dominant frequencies probably correspond to the oscillations that can be seen on figure 4.13. Their amplitudes are also smaller than the amplitudes of the dominant frequencies of run 3, confirming what can be seen when comparing figures 4.9 and 4.13, i.e. that the amplitude of the oscillations is smaller in run 4 than in run 3.

Figure 4.15 shows the temperatures for run 4. Similarly to run 3, all temperatures, especially T_3 and T_4 , are very stable when comparing with runs 1 and 2. However, the average temperatures are $\bar{T}_3 = 494.6$ °C and $\bar{T}_4 = 499.9$ °C with standard deviations $\sigma_{T_3} = 3.9$ °C and $\sigma_{T_4} = 5.2$ °C, which shows that, although the stability characterised by the standard deviations is similar to that of run 3, the average temperatures are lower by about 10 and 7 °C respectively. This difference may seem minor, but as conversion and gas yield vary strongly with temperature around these values, the consequences on the general results will be significant.

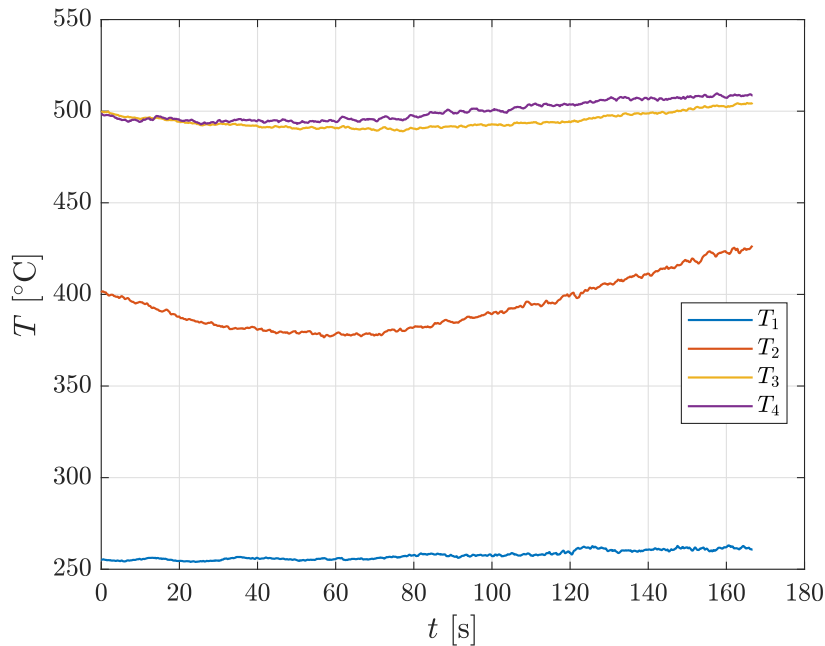


Figure 4.15: Temperatures as a function of time (run 4)

Figure 4.16 shows the pressure evolution in the sample tank throughout run 4. Similarly to run 3, as the temperatures are very stable, the pressure increases almost linearly in function of time. Here, however, the relationship is not as perfectly linear as in run 3. Indeed, the curve's slope is slightly steeper between about 0 and 30 s, before decreasing and becoming a bit flatter between 30 s and the end of the experiment. The reason behind this change in slope is unclear, and may be linked to the higher average mass flow rate which is present between 0 and 30 s: $\bar{m} = 22.09$ g/min for $t \in [0, 30]$ s.

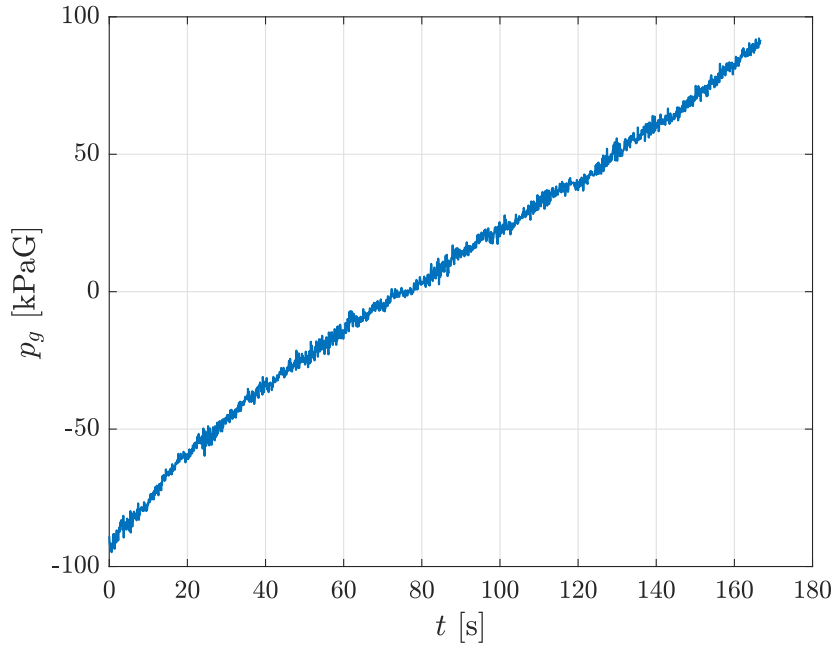


Figure 4.16: Gas pressure in the sample tank as a function of time (run 4)

Runs 5 through 7 have been conducted under sub-critical conditions, whereas runs 1 through 4 have been conducted under supercritical conditions. Hence, the mass flow rates of runs 5-7 have much stronger oscillation phenomena than those of runs 1-4, which leads to generally increased instability, as an unstable mass flow rate affects temperatures and pressure. This is due to the fact that while supercritical conditions prevent any sudden phase change of ethanol during the pre-heating procedure, under sub-critical conditions the phase changes suddenly from liquid to gas, which implies sudden density variations and thus sudden mass flow rate variations. These variations in turn affect the phase change phenomenon, which creates a feedback effect, eventually triggering oscillations. Therefore, when comparisons are made between runs 1-4 and runs 5-7, they must be made with care, taking into account that the conditions for runs 5-7 were very unstable.

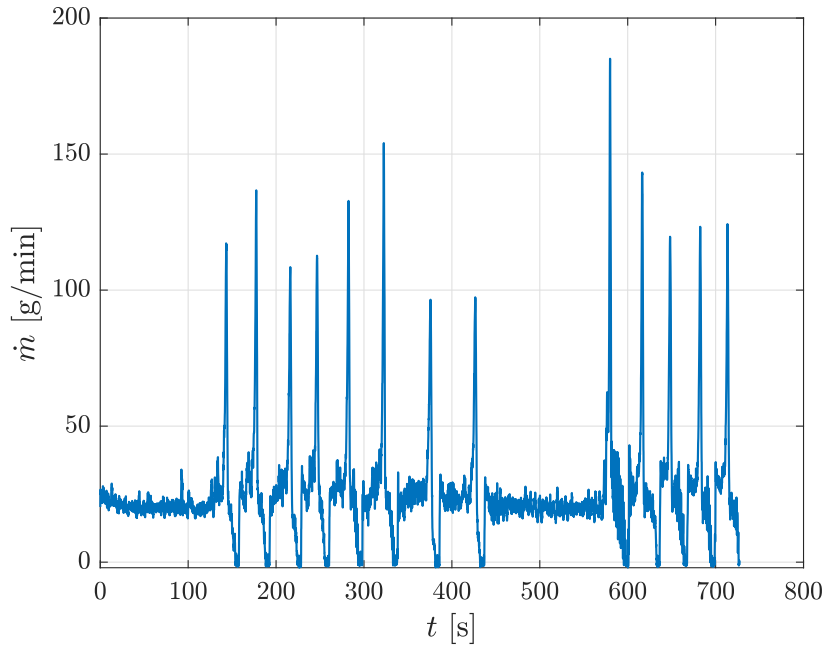


Figure 4.17: Mass flow rate as a function of time (run 5)

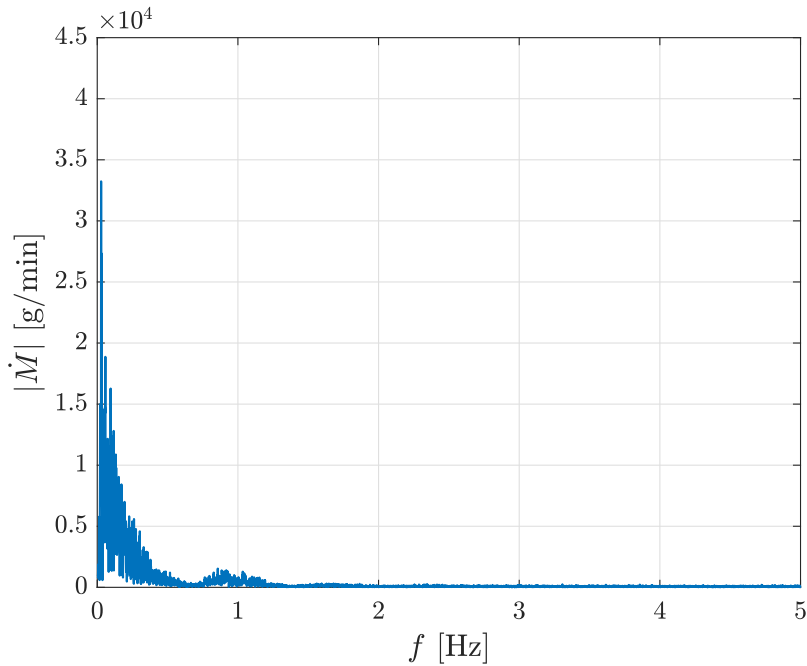


Figure 4.18: Frequency spectrum of the mass flow rate (run 5)

Figure 4.17 shows the time history of the mass flow rate for run 5. Large instabilities can be clearly seen with maximum and minimum peak values reaching about 180 and 0 g/min respectively. These instabilities are a consequence of the fact that run 5 was conducted under sub-critical conditions, as mentioned above. The average

mass flow rate is $\bar{m} = 25.01$ g/min with a standard deviation of $\sigma_{\dot{m}} = 19.65$ g/min, which further emphasizes not only that the average mass flow rate is offset from the target mass flow rate value, but also, more importantly how unstable the mass flow rate is, as the value of the standard deviation is similar to that of the average.

Figure 4.18 shows the frequency spectrum of the mass flow rate for run 5. A dominant frequency can clearly be identified at 0.03 Hz, while two bands of low frequencies (0-0.5 Hz and 0.7-1.2 Hz) are also involved in the oscillation phenomenon, although with much smaller amplitudes. This dominant frequency seems to correspond to the large peaks which can be seen on figure 4.17 for times between 130 and 440 s and between 570 and 725 s, as they are separated by about $1/0.03 = 33.3$ s.

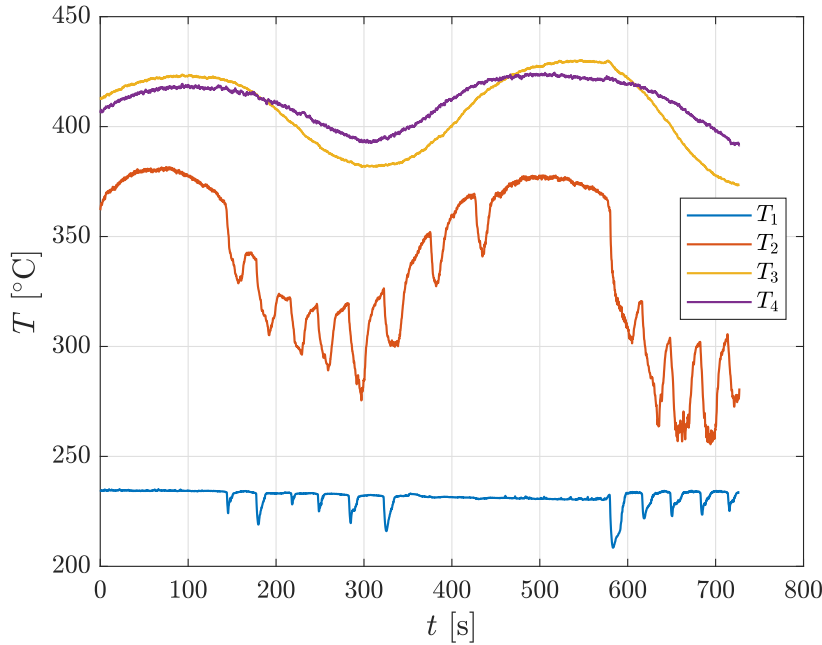


Figure 4.19: Temperatures as a function of time (run 5)

Figure 4.19 shows the temperatures for run 5. The temperatures are much less stable than for any of the runs under supercritical conditions, especially when compared to runs 2-4. Indeed, the average temperatures are $\bar{T}_3 = 407.8$ °C and $\bar{T}_4 = 411.6$ °C with standard deviations $\sigma_{T_3} = 17.2$ °C and $\sigma_{T_4} = 9.5$ °C, which shows significant offset and instability. Moreover, while T_3 and T_4 show a normal, sinusoidal oscillating behaviour, T_1 and T_2 on the other hand, exhibit not only sinusoidal oscillations but also sudden dips. These dips seem to approximately correspond to the large peaks in mass flow rate which can be seen on figure 4.17, thus showing a coupling between mass flow rate and temperature oscillations. The reason why T_1 and T_2 are more directly affected by the sudden changes in mass flow rate than

T_3 and T_4 may be because the former temperatures are closer to the phase change temperature of ethanol at 5 MPaG, which means that the thermocouples TC1 and TC2 are closer to the phase change region in the pre-heating tube. Therefore, when the mass flow rate changes, TC1 and TC2 may go from being surrounded by mostly gaseous ethanol to being surrounded by mostly liquid ethanol, which implies brutal changes in heat conductivity, and thus in temperature.

Figure 4.20 shows the pressure in the sample tank throughout the experiment. As a consequence of the unstable mass flow rate and temperatures, the slope of the pressure curve varies quite a lot. The general trend still tends towards a linear increase in function of time, but several sections have different slopes.

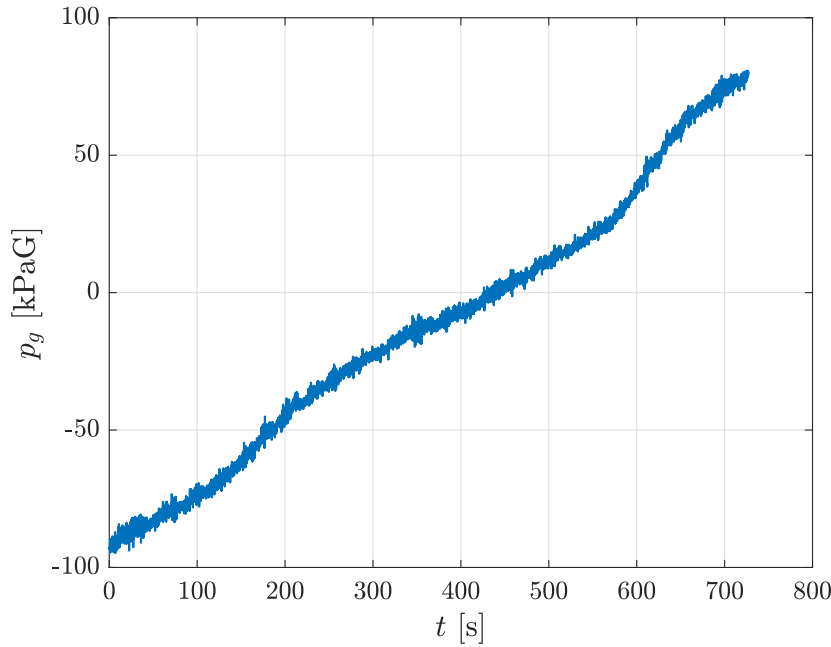


Figure 4.20: Gas pressure in the sample tank as a function of time (run 5)

Figure 4.21 shows the mass flow rate for run 6. Similarly to run 5, the mass flow rate shows very strong oscillations with maximum and minimum peak values of about 150 and 0 g/min, respectively. The average mass flow rate is $\bar{m} = 27.98$ g/min with a standard deviation of $\sigma_{\dot{m}} = 24.24$ g/min, which also highlights this highly unstable behaviour. When compared with run 5, the maximum peak values may not be as high, but the offset and general instability characterised by the average and standard deviation are worse than for run 5. Moreover, as for run 5, the standard deviation is almost equal to the average, which further highlights the scale of the instabilities. The reasons behind this unstable behaviour are thought to be the same as for run 5.

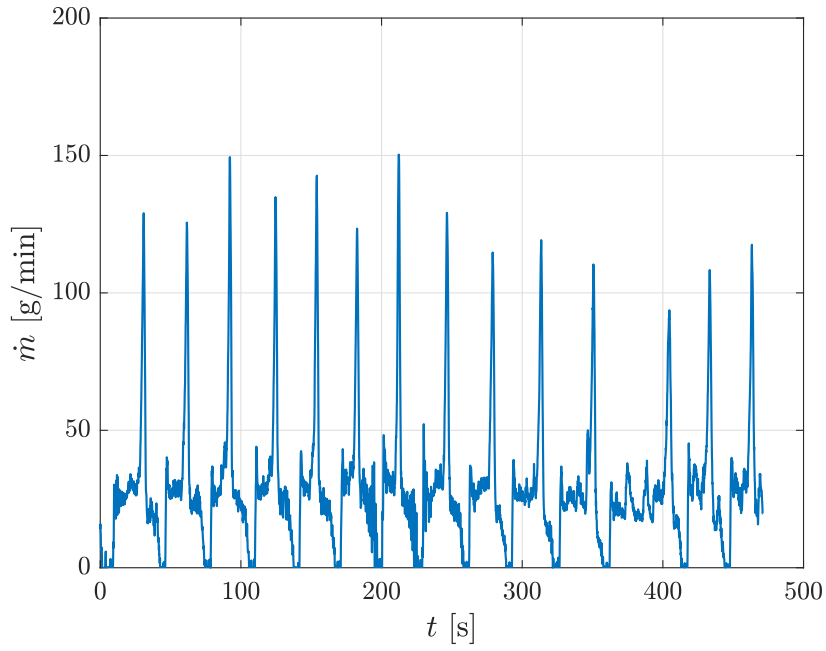


Figure 4.21: Mass flow rate as a function of time (run 6)

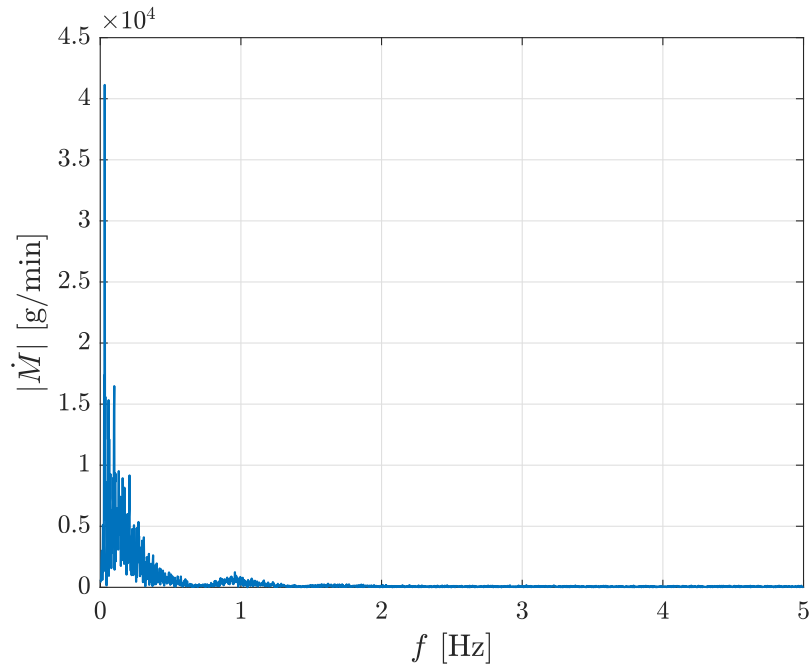


Figure 4.22: Frequency spectrum of the mass flow rate (run 6)

Figure 4.22 shows the frequency spectrum of the mass flow rate. A dominant frequency can clearly be identified at 0.03 Hz, while two bands of low frequencies (0-0.6 and 0.8-1.2 Hz) are also involved in the oscillating behaviour, although with much smaller amplitudes. This dominant frequency corresponds to the large peaks

which can be seen on figure 4.21, as the peaks are spaced by about $1/0.03 = 33.3$ s.

Figure 4.23 shows the temperatures for run 6. Although T_1 and T_2 show similar sudden dips as in run 5 and are thus relatively unstable (especially T_2), T_3 and T_4 are much more stable than in run 5. Indeed, the average temperatures are $\bar{T}_3 = 454.3$ °C and $\bar{T}_4 = 454.0$ °C with standard deviations $\sigma_{T_3} = 11.4$ °C and $\sigma_{T_4} = 6.3$ °C, which shows much better accuracy and stability than in run 5. This improvement in the stability and accuracy of T_3 and T_4 is thought to be due to a better tuning of the heating system, as well as a longer waiting time before starting the experiment, which thus allowed the conditions to better stabilise. The dips in temperature which occur for T_1 and T_2 also seem to be correlated with the peaks in mass flow rate seen on figure 4.21.

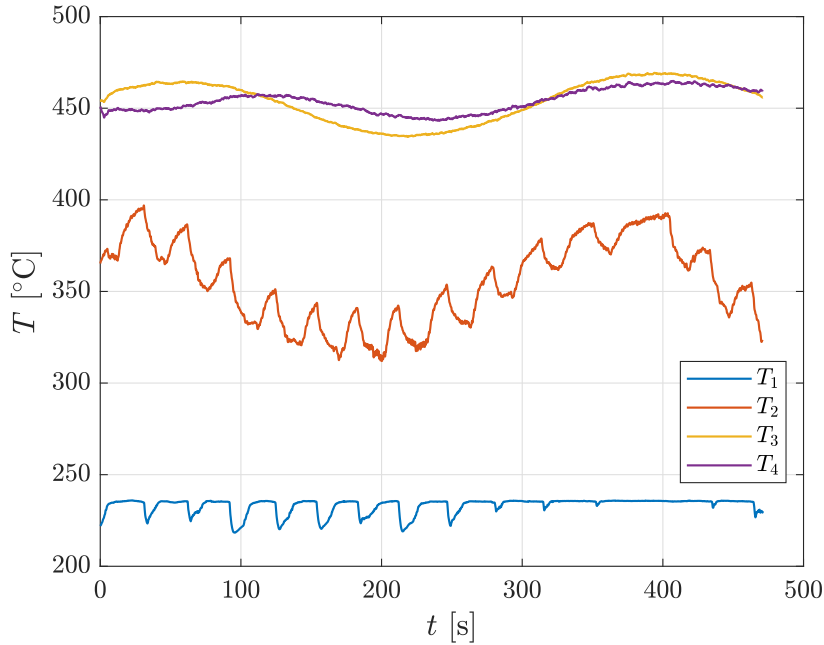


Figure 4.23: Temperatures as a function of time (run 6)

Figure 4.24 shows the pressure in the sample tank throughout the experiment. As a consequence of the more stable temperatures, the pressure increase is generally linear, although the slope is not completely constant and drops a bit between about 210 and 320 s, which roughly corresponds to the period when T_4 is minimal. Note that in this run, due to an operational mistake, the pressure increased above 100 kPaG, which is undesirable as the pressure sensor used has a specified range of -100 - 100 kPaG (which corresponds to an output current of 4 - 20 mA). However, although the pressure sensor's range is specified as -100 - 100 kPaG, it actually measures the pressure accurately until its saturation output current (21 mA), which corresponds

to a pressure of about 112.5 kPaG. Thus this manipulation error should have had no incidence on the measured pressure, as the maximum pressure reached is about 109.6 kPaG.

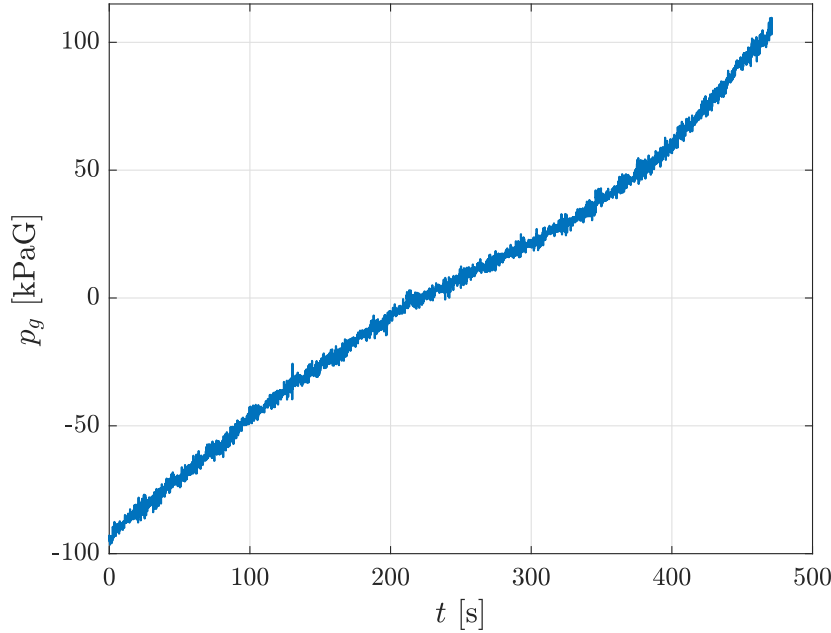


Figure 4.24: Gas pressure in the sample tank as a function of time (run 6)

Figure 4.25 shows the mass flow rate for run 7. With maximum peak values of about 50 g/min (except for the two peaks reaching about 120 g/min) and minimum peak values of about 0 g/min, the mass flow rate for run 7 is much more stable than for runs 5 and 6. Indeed, the average mass flow rate is $\bar{m} = 20.94$ g/min with a standard deviation of $\sigma_{\bar{m}} = 15.42$ g/min, which although still much less stable than any of the runs 1-4, is significantly better than runs 5 and 6. The reason behind this improvement is probably that at the higher temperature conditions of run 7, the flow is naturally more stable than at the lower temperature conditions of runs 5 and 6. More specifically, the phase change may happen in a more stable fashion, e.g. steady film boiling versus transition between nucleate and film boiling for runs 5 and 6. Note that the sudden instability which resulted in the two peaks reaching about 120 g/min at around 180 s was caused by a manual pressure correction. In fact, during the experiment, the pressure generated by the regulator had dropped slightly, and, in order to correct that, the pressure was manually increased a bit, which in turn caused the mass flow rate to suddenly increase and oscillate.

Figure 4.26 shows the frequency spectrum of the mass flow rate. Two dominant frequencies can clearly be identified at 0.03 and 0.29 Hz, while two bands of low frequencies (0-0.65 Hz and 0.7-1.3 Hz) are also involved in the oscillation phenomenon,

although with much smaller amplitudes. The higher of these two dominant frequencies seems to correspond roughly to the oscillation pattern which can be seen on figure 4.25, while the lower one may be linked to the two sudden peaks which happened around $t = 180$ s, although that remains hard to confirm.

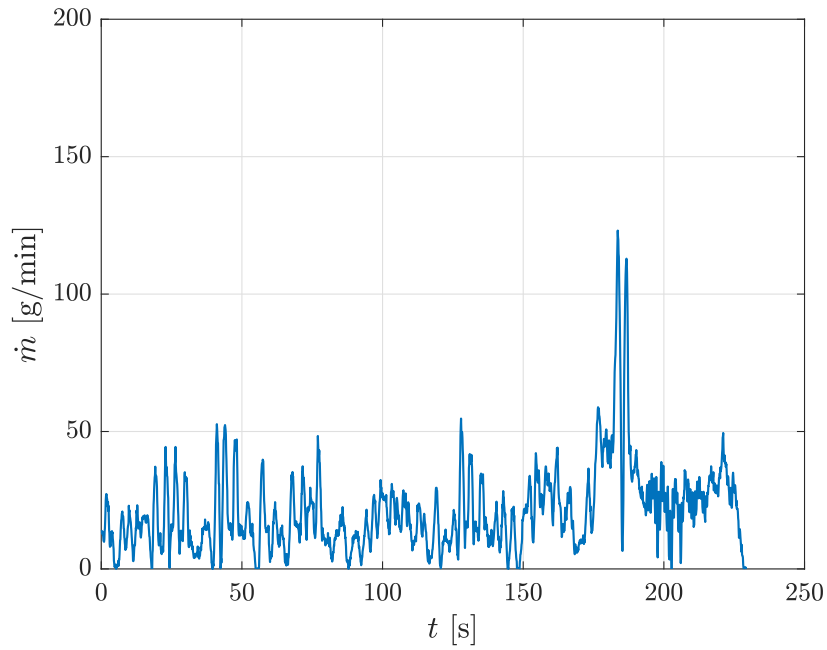


Figure 4.25: Mass flow rate as a function of time (run 7)

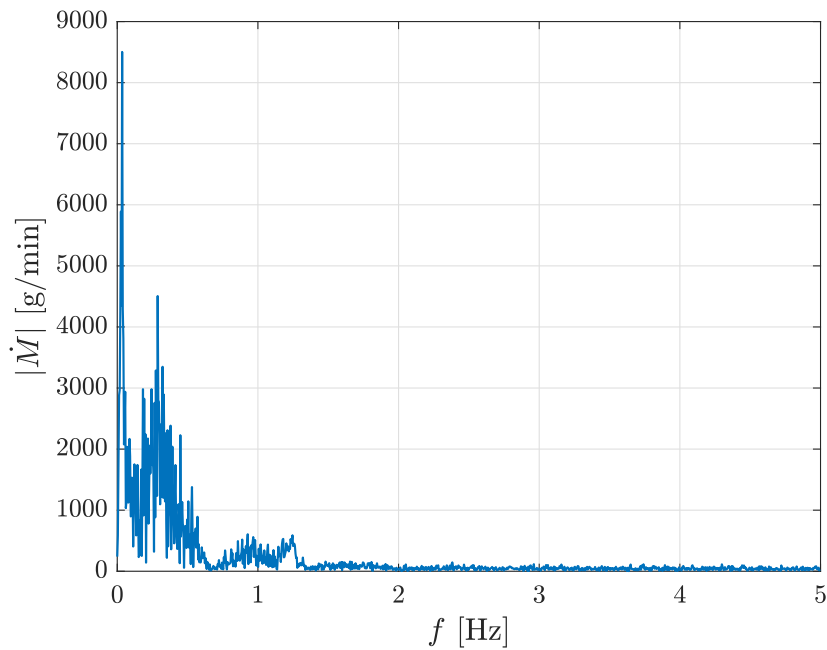


Figure 4.26: Frequency spectrum of the mass flow rate (run 7)

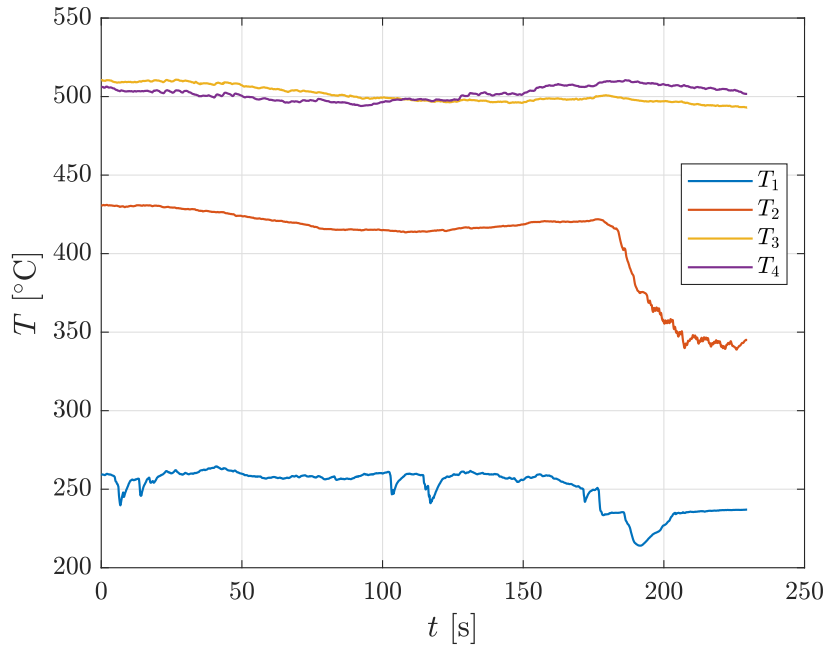


Figure 4.27: Temperatures as a function of time (run 7)

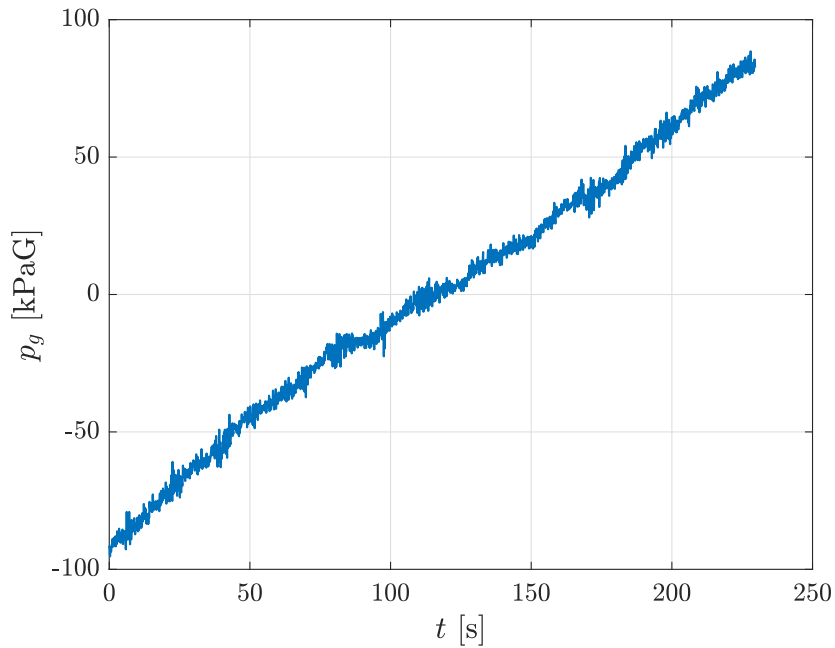


Figure 4.28: Gas pressure in the sample tank as a function of time (run 7)

Figure 4.27 shows the temperatures for run 7. Overall, the temperatures are very stable, especially T_3 and T_4 . Indeed, the average temperatures are $\bar{T}_3 = 501.0$ $^{\circ}\text{C}$ and $\bar{T}_4 = 502.1$ $^{\circ}\text{C}$ with standard deviations $\sigma_{T_3} = 5.2$ $^{\circ}\text{C}$ and $\sigma_{T_4} = 4.3$ $^{\circ}\text{C}$, which highlights the excellent stability and accuracy of T_3 and T_4 . This makes run 7,

together with run 4, one of the runs having the most stable temperature conditions. The reason behind such excellent stability is believed to be the fairly stable flow rate shown on figure 4.25, as well as a good tuning of the heating system. Nonetheless, due to the sudden increase in mass flow rate around $t = 180$ s, T_1 and T_2 show sudden drops at around the same time.

Figure 4.28 shows the pressure in the sample tank throughout run 7. As a consequence of the very stable temperatures, the pressure curve is almost perfectly linear and the curve's slope remains quasi-constant throughout the whole experiment.

4.1.2 Thermal cracking behaviour

Global results gathered from all seven runs are presented in this section. These results characterise the thermal cracking reaction as a whole and allow runs to be analysed and compared between each other. The results presented here offer a key insight into the thermal cracking of ethanol.

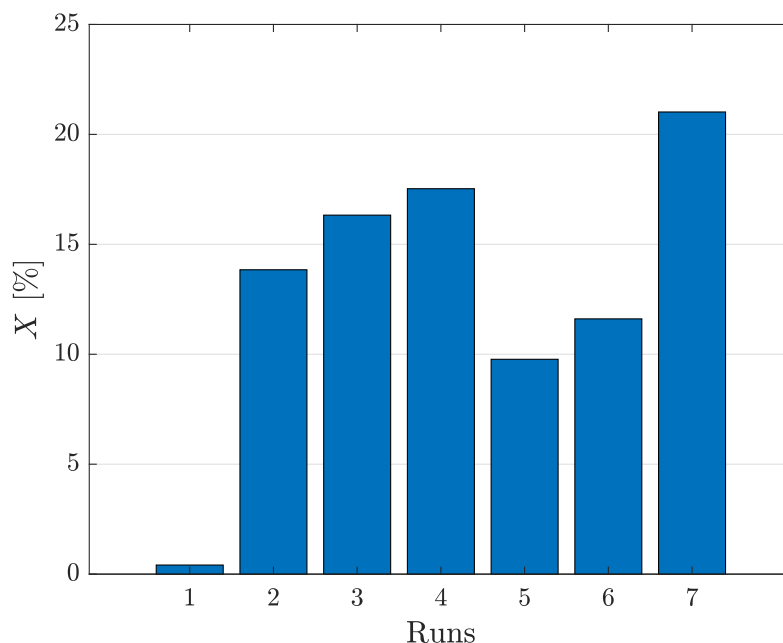


Figure 4.29: Conversion

Figure 4.29 presents the conversion for each run. The conversion is defined as

$$X = \frac{n_p}{n_f} = 1 - \frac{n_{\text{C}_2\text{H}_5\text{OH}}}{n_f}, \quad (4.1)$$

where n_p , n_f and $n_{\text{C}_2\text{H}_5\text{OH}}$ are the moles of products, fed fuel and remaining ethanol after the reaction, respectively. It represents how much of the fuel has reacted to

form products. As can be seen on figure 4.29, the conversion increases with reaction temperature, which is expected. Regarding the effect of pressure on conversion, it is hard to determine a clear trend based on the results from figure 4.29. Indeed, runs 5 and 7 exhibit higher conversions than their higher pressure counterparts (runs 1 and 3 and 4), while run 6 exhibits a lower conversion than run 2. Thus, further investigation may be necessary to determine the clear influence of pressure on conversion. The few percent difference in conversion between runs 3 and 4 is thought to be due to measurement errors mostly.

Figure 4.30 shows the gas yield for each run. The gas yield is defined as

$$Y_g = \frac{n_g}{n_f}, \quad (4.2)$$

where n_g and n_f are the total moles of gas produced and the moles of fed fuel, respectively. The gas yield represents how much of the fuel has reacted to form gases. As can be seen on figure 4.30, gas yield increases with both temperature and pressure (runs 5, 6, 7 having lower gas yields than runs 1, 2, 3/4). The significant difference between runs 3 and 4 is thought to be due to the fact that although both runs had the same target conditions, run 4 had a higher mass flow rate and lower temperatures T_3 and T_4 , which both decrease the gas yield. Indeed, as figure 4.30 shows it, gas yield increases with temperature, and a higher mass flow rate reduces the residence time in the reactor which in turn inhibits the reaction.

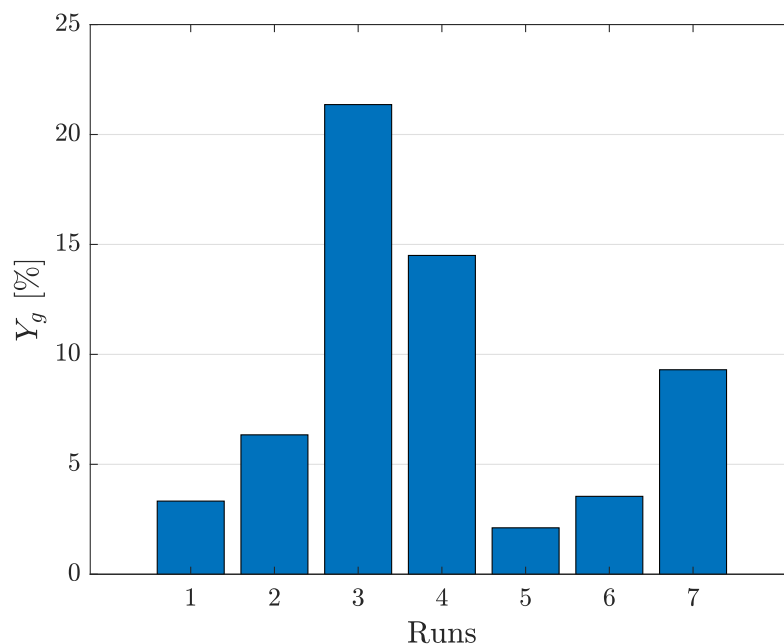


Figure 4.30: Gas yield

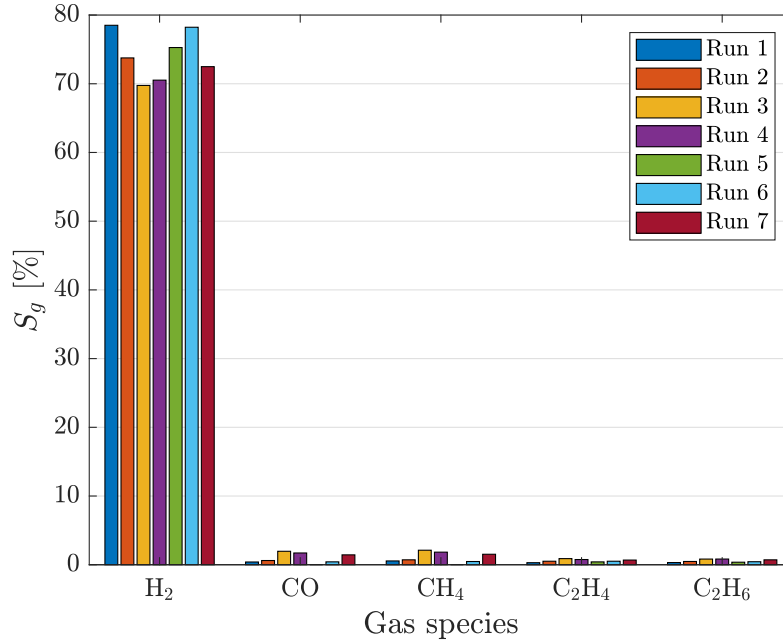


Figure 4.31: Gas selectivity for each gaseous product

Figure 4.31 shows the gas selectivity of all the gas species that were detected as products of the thermal cracking of ethanol. The gas selectivity for each gas species is defined as

$$S_{g,i} = \frac{n_i}{n_g}, \quad (4.3)$$

where n_i are the of moles of gas i and n_g are the total moles of gas produced. When looking at figure 4.31, clear trends can be seen for supercritical runs (1-4): the selectivity of hydrogen decreases with temperature, while the selectivities of all other species increase with temperature. This shows that under super critical conditions, mostly hydrogen gas is produced for lower temperatures, while heavier gases are gradually being produced in larger amounts as the temperature increases. For sub-critical runs, a similar trend can be observed for heavier gases, whose selectivity also increases with temperature, but it is hard to determine a clear trend for the selectivity of hydrogen, as it first increases and then decreases. This somewhat odd behaviour may be linked to the fact that the experimental conditions were very unstable for sub-critical runs, especially for runs 5 and 6. It is also interesting to note the similarity between the selectivities of the products of runs 1 and 6, which seems to imply that an increase in pressure has a similar effect on the reaction as an increase in temperature. Further, the gas selectivities of all species show a good match between runs 3 and 4, which confirms the reliability and repeatability of the experimental procedure as a whole. Lastly, if summed together, the selectivities of

all products do not sum up to 100 %. This is thought to be due to the presence of vapours originating from the liquid products in the gas mixture, and will be further discussed in section 4.1.3.

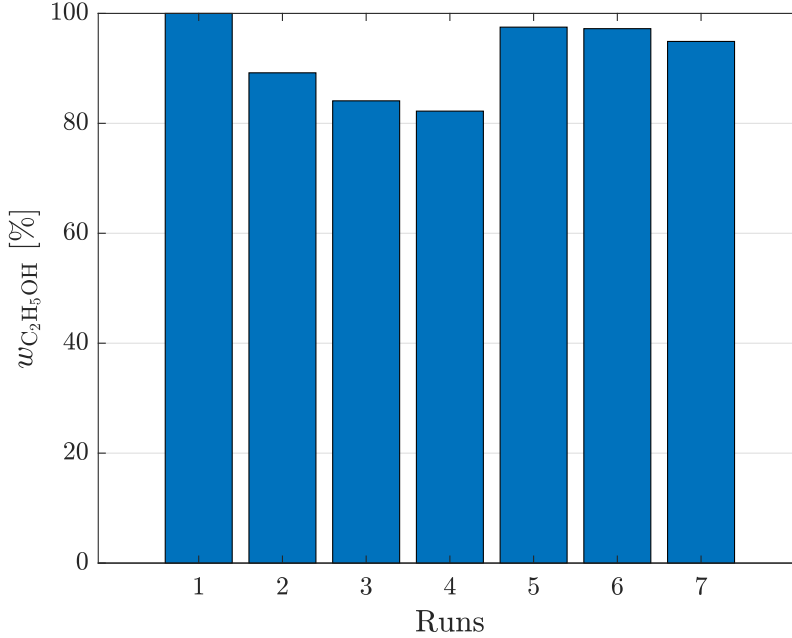


Figure 4.32: Mass fraction of ethanol in the collected liquid

Figure 4.32 shows the mass fraction of ethanol with respect to the total mass of liquid collected in the sample tank. It is defined as follows,

$$w_{C_2H_5OH} = \frac{m_{C_2H_5OH}}{m_l}, \quad (4.4)$$

where $m_{C_2H_5OH}$ is the mass of ethanol remaining after the reaction and m_l is the total mass of liquid collected in the sample tank. As can be seen on figure 4.32, the mass fraction of ethanol decreases with increasing temperature as well as with increasing pressure (except when comparing runs 1 and 5). The fact that the collected liquid is not entirely composed of ethanol firstly indicates that not only gas products, but also liquid products are formed by the thermal cracking of ethanol. Moreover, the aforementioned trend also indicates that more ethanol is consumed by the reaction at higher temperatures and pressures to form a larger amount of these liquid products. The fact that for run 1, $w_{C_2H_5OH} = 100$ %, is somewhat surprising when looking at the results for other runs, as it would be expected that the mass fraction of ethanol for run 1 be slightly lower than for run 5. Therefore, it is thought that measurement errors caused the value of $w_{C_2H_5OH}$ for run 1 to be slightly above its true value. Finally, when comparing runs 3 and 4, the mass fraction values agree to within a

few percent. This few percent difference is also thought to be due to measurement errors, and thus the ethanol mass fraction results for runs 3 and 4 are considered to agree with each other, further confirming the reliability and repeatability of the experimental procedure as a whole.

Figure 4.33 shows the relative peak area for the liquid products of the thermal cracking of ethanol. The relative peak area for each product is defined as

$$a = \frac{A_i - A_{0,i}}{A_{\text{C}_2\text{H}_5\text{OH}}}, \quad (4.5)$$

where A_i is the chromatogram peak area of product i , $A_{0,i}$ is the peak area of product i in pure solvent (see appendix B.1) and $A_{\text{C}_2\text{H}_5\text{OH}}$ is the peak area of ethanol. From figure 4.33, both water and acetaldehyde can be identified as liquid products of the thermal cracking of ethanol.

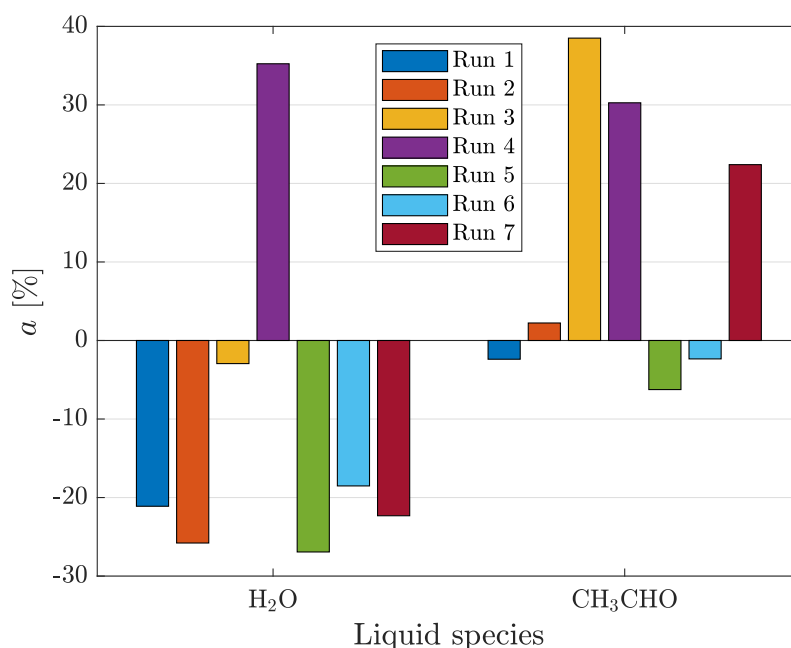


Figure 4.33: Relative peak area of the liquid products

For water, it is very hard to establish any trend as the results vary widely over all runs. This is due to the fact that the liquids were analysed with a GC-MS, which offers poor precision and repeatability for compounds having mass spectra where $m/z < 45$ u/e (see section 2.3.2), which is the case for water ($16 \leq m/z \leq 20$).

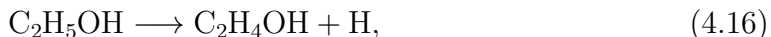
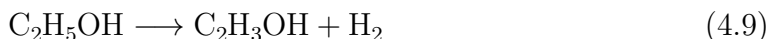
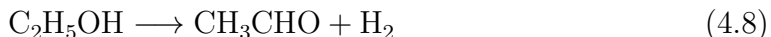
For acetaldehyde, although the results could not be properly quantified as for ethanol due to the lack of a calibration curve, a clear trend can be seen: the amount of acetaldehyde in the collected liquid increases with both temperature and pressure,

which coincides with the decrease of ethanol in the liquids with both temperature and pressure. The difference in the relative peak areas of acetaldehyde for runs 3 and 4 is probably due to the fact that the actual mass flow rate was a bit higher while the actual temperatures were a bit lower for run 4. This latter trend is similar to that of the gas yield for runs 3 and 4. The reason why no calibration curve could be made for acetaldehyde is a practical one. Indeed, the boiling temperature and vapour pressure (at room temperature) of acetaldehyde are respectively $T_b = 21\text{ }^\circ\text{C}$ and $p_{v,20^\circ\text{C}} = 99.18\text{ kPa}$ [13], making it very hard to handle in the laboratory, and thus making standard sample preparation very difficult.

4.1.3 Discussion

In this section, the results presented in section 4.1.2 will be discussed in detail and compared with existing literature in order to confirm their validity, as well as further understand the mechanisms behind the thermal cracking of ethanol.

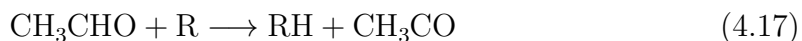
According to Park et al. [22], the main decomposition reactions of ethanol under combustion conditions are the following,



where reactions (4.6) and (4.7) are generally dominant, particularly at high temperatures. When comparing these reactions with the results presented in section 4.1.2, it seems that reactions (4.6) and (4.7) are not the main decomposition paths involved in the reaction, as rather little amounts of ethylene, methane and ethane (the latter two usually resulting of a recombination of the methyl radical) are present in the reaction products. The results presented in this study seem to indicate that

reactions (4.8) and (4.9) are the main paths involved in the thermal cracking reaction of ethanol at low temperatures and high pressures. Indeed, large amounts of hydrogen, as well as acetaldehyde are present in the reaction products, which could indicate that either ethanol decomposes directly into these two compounds (reaction (4.8)), or that it decomposes into vinyl alcohol and hydrogen (reaction (4.9)) only for the vinyl alcohol to then restructure itself to form acetaldehyde, or both. As the products also contain methane, ethylene, ethane and water, reactions (4.6), (4.7), (4.10), (4.11), (4.12) and (4.13) may act as secondary decomposition paths, with the large compounds involved further decomposing into smaller, lighter species.

Carbon monoxide on the other hand, may form through reaction (4.8) where the acetaldehyde (CH_3CHO) further decomposes as,



or through reaction (4.10) where the formaldehyde (CH_2O) further decomposes as,



as is suggested by Avedisian et al. [30]. The reaction patterns discussed above describe well how the products measured could have been formed from the thermal cracking of ethanol.

Further, when directly comparing the results with existing literature, a good concordance is observed. For example, Nishimoto previously conducted thermal cracking experiments of ethanol under supercritical conditions at the Tsue-Nakaya laboratory [21]. He obtained gas selectivities of about 80 % for hydrogen, 18 % for ethylene and 1 % for ethane from conducting thermal cracking experiments of ethanol at $T = 693 \text{ K}$, $\dot{V} = 23,31 \text{ cm}^3/\text{min}$ and $p = 7 \text{ MPaG}$. In addition, he also detected water and acetaldehyde as the products of the thermal cracking of ethanol at $T = 693 \text{ K}$, $\dot{V} = 31 \text{ cm}^3/\text{min}$ and $p = 7 \text{ MPaG}$.

Avedisian et al. conducted thermal cracking experiments of ethanol [30] as well, although their experiments were conducted for stationary cracking of ethanol under atmospheric pressure, thus under sub-critical conditions quite different from those presented in this study. The experiments were conducted for temperatures ranging from 600 to 1500 K. Their results also show hydrogen as the most abundant gas product, followed by carbon monoxide, methane, ethylene, ethane and CO_2 . Regarding liquid products, the detected compounds are, in order of abundance: acetaldehyde,

water, formaldehyde, 1,1-diethoxyethane and ethyl acetate, which agrees with the liquid products found in this study, as the three latter compounds were detected with extremely low molar fractions ($< 0.2 \%$).

Furthermore, an old study on the pyrolysis of ethanol by Barnard et al. [1] shows that the primary products of the pyrolysis of ethanol are acetaldehyde and hydrogen. Indeed, molar fractions of about 50 % for hydrogen, 5 % for carbon monoxide and 10 % for methane were obtained from the stationary thermal cracking of ethanol at $T = 576 \text{ }^{\circ}\text{C}$ and $p = 185 \text{ mmHg}$. Although the experimental conditions are quite different, these results also show that hydrogen is by far the most abundant gaseous product.

Hashemi et al. conducted a detailed study on the high-pressure pyrolysis and oxidation ethanol [8]. Unfortunately, they did not measure the amount of hydrogen produced by the reaction due to technical limitations. However, they did obtain quantitative results for methane, carbon monoxide, acetaldehyde, ethylene, ethane and formaldehyde. Their results showed mole fractions of about 5 % for acetaldehyde, 4 % for methane, 3 % for carbon monoxide, 2 % for ethylene, 0.4 % for formaldehyde and 0.3 % for ethane for flow-type pyrolysis experiments of ethanol at $p = 50 \text{ bar}$ and $T = 900 \text{ K}$. This shows a good general agreement with the results presented in section 4.1.2.

Finally, Ijima et al. also conducted a study on the flow-type thermal decomposition of bioethanol [9]. Their results are only qualitative, but show the presence of hydrogen as the sole product for $p = 7 \text{ MPaG}$ and $T = 650 \text{ K}$, and the presence of hydrogen, methane and ethylene as the reaction products for $p = 7 \text{ MPaG}$ and $T = 770 \text{ K}$. This further reinforces the reliability of the results obtained in this study, as there is a good qualitative matching between the former and the results proposed by Ijima et al.

As mentioned in section 4.1.2, the sum of the gas selectivities presented on figure 4.31 is never equal to 100 % for any run. In fact, these sums are equal to

$$\sum S_{g1,i} = 80.1 \% \quad (4.21)$$

$$\sum S_{g2,i} = 76.1 \% \quad (4.22)$$

$$\sum S_{g3,i} = 75.5 \% \quad (4.23)$$

$$\sum S_{g4,i} = 75.7 \% \quad (4.24)$$

$$\sum S_{g5,i} = 76.1 \% \quad (4.25)$$

$$\sum S_{g6,i} = 80.1 \% \quad (4.26)$$

$$\sum S_{g7,i} = 76.8 \% \quad (4.27)$$

for each run, respectively. This shows that some part of the gas products is not detected or measured properly. It is thought that this undetected part of the gas products corresponds to vapours generated by the liquid products, especially acetaldehyde. Indeed, any liquid in a closed container will vaporise until the pressure on the liquid surface reaches the liquid's vapour pressure, point at which an equilibrium is reached. In the case of a liquid mixture, the vapour pressure will depend on the vapour pressures of each species composing the mixture. Anyway, as water and ethanol have very low vapour pressures: $p_{v,\text{H}_2\text{O},20^\circ\text{C}} = 2.315 \text{ kPa}$ and $p_{v,\text{C}_2\text{H}_5\text{OH},20^\circ\text{C}} = 5.820 \text{ kPa}$ [13], they will not form a large amount of vapour. Acetaldehyde however, has a very high vapour pressure: $p_{v,\text{CH}_3\text{CHO},20^\circ\text{C}} = 99.18 \text{ kPa}$ [13], and will form a large amount of vapour, which could explain the missing amounts of gas indicated by equations (4.21)-(4.27).

4.2 Simulation work

This section presents the results of the two versions of the numerical simulation model, and discusses its validity. First, the results of the ideal gas version of the simulation model are presented in detail. Then, the same is done for the results of the real gas version of the model. Finally, the validity of the model is discussed by comparing the numerical results with the experimental ones shown in section 4.1.2.

4.2.1 Ideal gas version

Figures 4.34-4.41 show the selectivities of the main products of the cracking reaction of ethanol in function of reaction temperature for pressures of 5 MPaG and 7 MPaG. The selectivities shown below are directly calculated by Cantera, and are defined as

$$S_i = \frac{n_i}{n_{\text{tot}}}, \quad (4.28)$$

where n_i is the number of moles of substance i , and n_{tot} is the total number of moles of all species.

Figure 4.34 shows the selectivity of ethanol in function of reaction temperature for different pressures. The thermal cracking reaction starts occurring at a temperature of about 800 K, as that is when the selectivity of ethanol starts to decrease. As expected, the selectivity decreases with temperature, showing that a higher amount of ethanol is converted to products as the temperature increases. Cracking is com-

plete from about 1100 K, temperature at which the selectivity of ethanol reaches 0. The pressure does not seem to have a major effect on the selectivity of ethanol. Indeed, an increase in pressure only shifts the curve towards lower temperatures, showing that more ethanol reacts for a higher pressure at a given temperature.

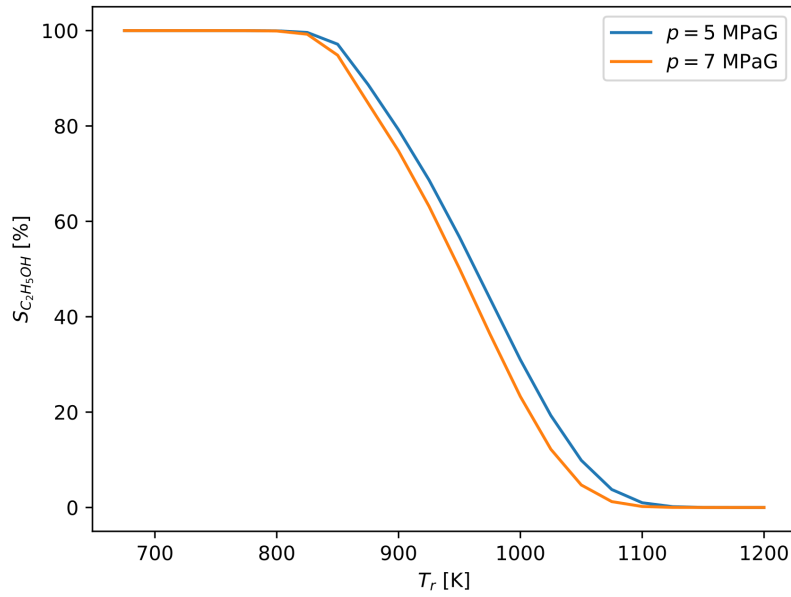


Figure 4.34: Ethanol selectivity in function of reaction temperature

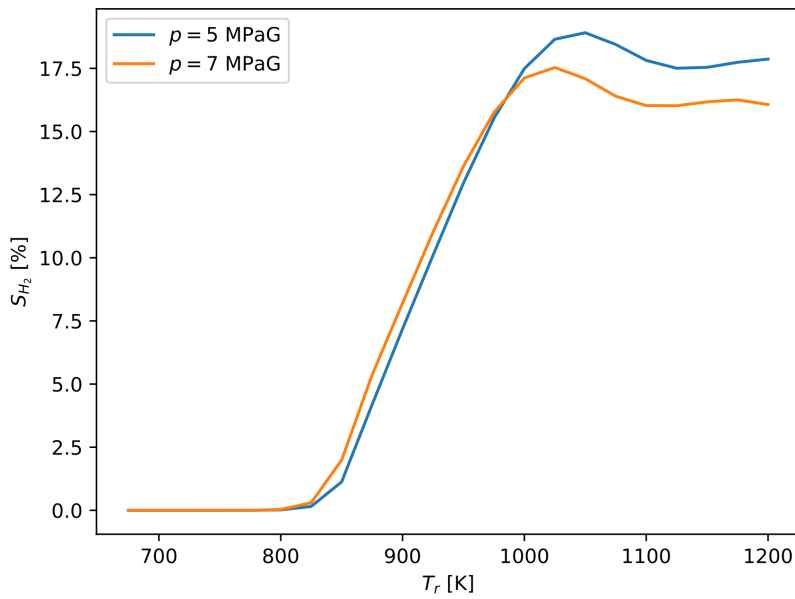


Figure 4.35: Hydrogen selectivity in function of reaction temperature

Figure 4.35 shows the selectivity of hydrogen in function of reaction temperature for different pressures. It can be seen that hydrogen is formed already at very low temperatures, as its selectivity starts to increase from about 800 K. This shows that it will be one of the first products to be formed when the cracking reaction starts, at low temperatures. In addition, figure 4.35 shows that the hydrogen selectivity reaches a maximum value at around 1050 K, which implies that above this temperature, some of the hydrogen formed by the reaction further reacts to form other products. Finally, a lower pressure seems to enhance the formation of hydrogen, because, even though hydrogen starts being formed at slightly higher temperatures, it reaches a maximum selectivity of about 19 % at 5 MPaG, which is about 2 % higher than its maximum selectivity at 7 MPaG.

Figure 4.36 shows the selectivity of carbon monoxide in function of reaction temperature for different pressures. Carbon monoxide starts forming at around 850 K, which is a bit later than hydrogen. It reaches a maximum selectivity of about 27 % at around 1100 K, and then shows a slight decrease in selectivity until 1200 K. This trend indicates that for most temperatures, carbon monoxide is formed as a reaction product in increasing amount. At very high temperatures (> 1100 K), however, a small amount of this carbon monoxide seems to further react and form other products. A higher pressure seems to enhance the formation of carbon monoxide for temperatures between 850 and 1150 K, but does not have any influence at very high temperatures (1150-1200 K).

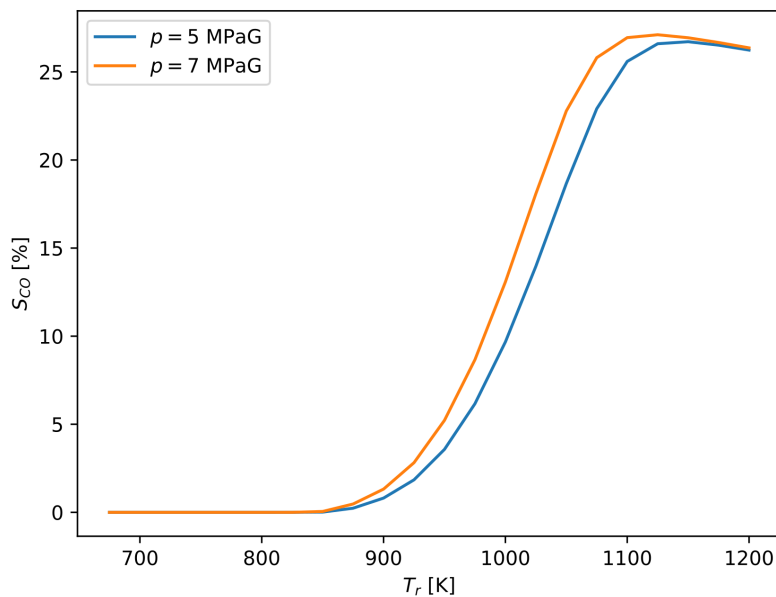


Figure 4.36: Carbon monoxide selectivity in function of reaction temperature

Figure 4.37 shows methane selectivity in function of reaction temperature for different pressures. Similarly to carbon monoxide, methane starts forming around 850 K. Its selectivity continuously increases with temperature, until reaching a maximum of about 30 % for $p = 7$ MPaG and 28 % for $p = 5$ MPaG at 1200 K. This shows that methane is always being formed as a reaction product for temperatures ranging from 850 to 1200 K. For all temperatures for which methane is formed, pressure enhances its formation, i.e. for a given temperature the methane selectivity increases with pressure.

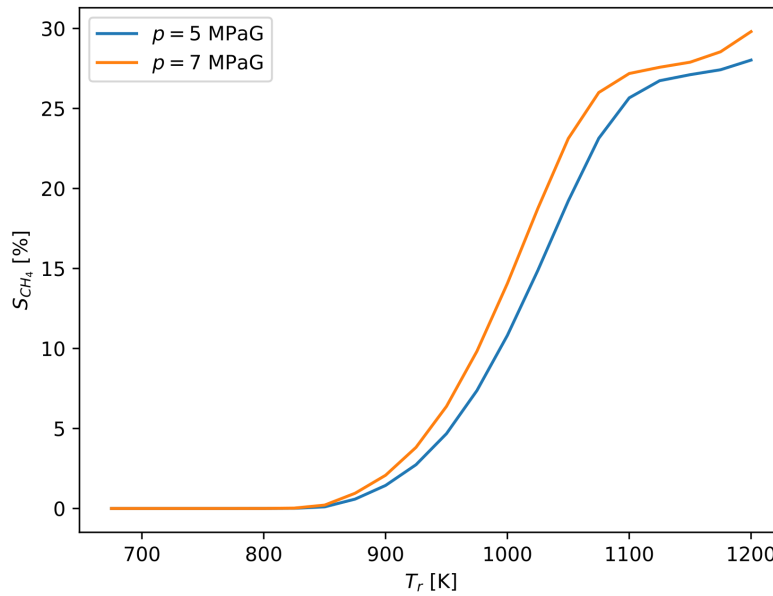


Figure 4.37: Methane selectivity in function of reaction temperature

Figure 4.38 shows the ethylene selectivity in function of reaction temperature for different pressures. Similarly to hydrogen, ethylene starts forming at relatively low temperature, about 800 K. In an interesting fashion, the selectivity of ethylene first increases until reaching a local maximum of about 5 % for $p = 5$ MPaG and 4.5 % for $p = 7$ MPaG at around 1000 K, before decreasing to reach a local minimum of about 4 % for $p = 5$ MPaG and 3 % for $p = 3$ MPaG at around 1100 K. Finally, the ethylene selectivity increases again to reach its absolute maximum of about 6 % for $p = 5$ MPaG and 5 % for $p = 7$ MPaG at 1200 K. This shows that ethylene is first formed as a reaction product for low temperatures, that then, at medium temperatures, part of that ethylene starts reacting itself to form other products, and that finally, at high temperatures, ethylene starts being formed again as a product. Pressure does not show a strong influence on the formation of ethylene for low

temperatures (800-950 K). However, an increased pressure inhibits the formation of ethylene for higher temperatures (950-1200 K).

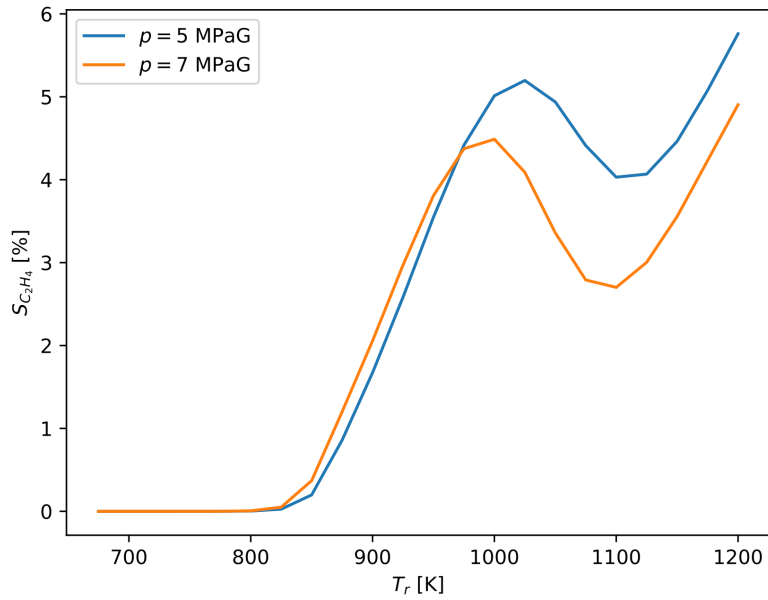


Figure 4.38: Ethylene selectivity in function of reaction temperature

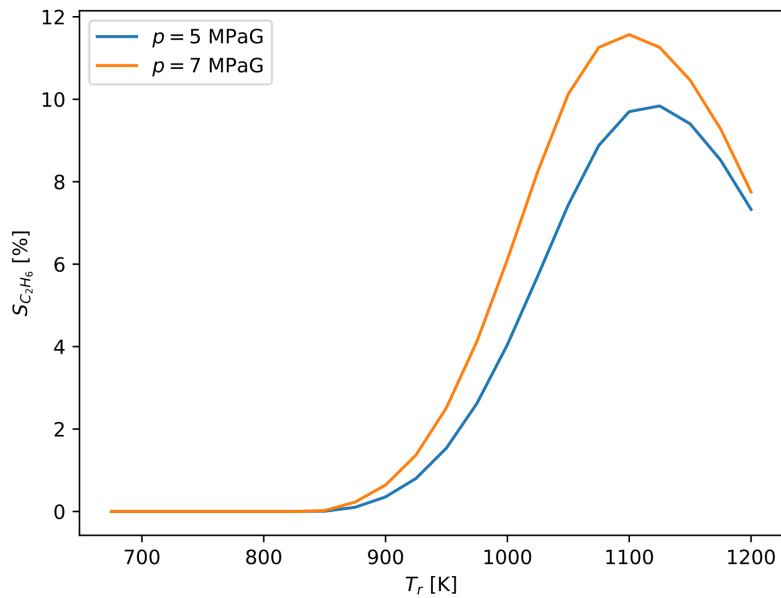


Figure 4.39: Ethane selectivity in function of reaction temperature

Figure 4.39 shows the selectivity of ethane in function of reaction temperature for different pressures. Ethane starts being formed, similarly to carbon monoxide

and methane, at around 850 K, before its selectivity increases to a maximum value of about 12 % for $p = 7$ MPaG and 10 % for $p = 5$ MPaG at around 1100 K. Then, for high temperatures (1100-1200 K), the ethane selectivity decreases, showing that, while ethane is formed as a reaction product with increasing abundance for temperatures ranging from 850 to 1100 K, at high temperatures, part of that ethane further reacts to form other products, such as ethylene, whose selectivity increases between 1100 and 1200 K. Pressure seems to generally enhance the formation of ethane, as a higher pressure implies a higher selectivity for all temperatures for which ethane is formed.

Figure 4.40 shows the selectivity of water as a function of reaction temperature. Water starts being formed at around 800 K, and its selectivity continuously increases until reaching a flat maximum of about 14 % at around 1100 K. This shows that water is a reaction product which is formed in increasing amount for temperatures ranging from 800 to 1100 K, and keeps being formed at a constant amount at high temperatures (1100-1200 K). Pressure does not show an important influence on the formation of water, as the selectivity curve is only slightly shifted to lower temperatures for higher pressure.

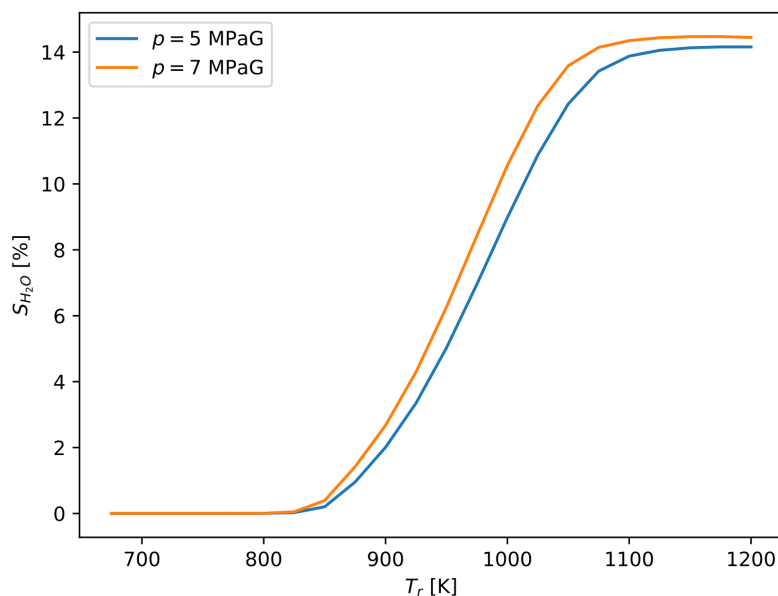


Figure 4.40: Water selectivity in function of reaction temperature

Figure 4.41 shows the selectivity of formaldehyde in function of reaction temperature. Formaldehyde is formed as a product for temperatures between 800 and 1150 K. However, its selectivity does not exceed 1 %, which makes it a very minor

product. Pressure does not show a big influence on its formation either.

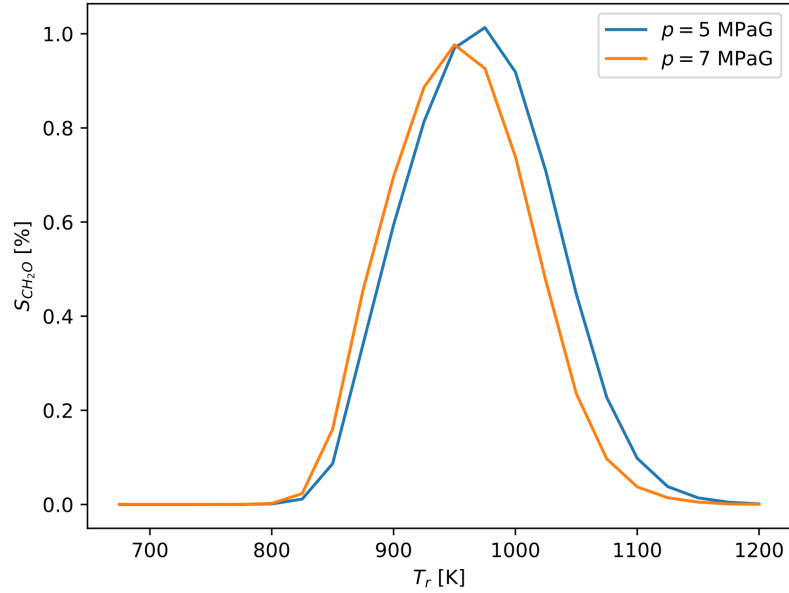


Figure 4.41: Formaldehyde selectivity in function of reaction temperature

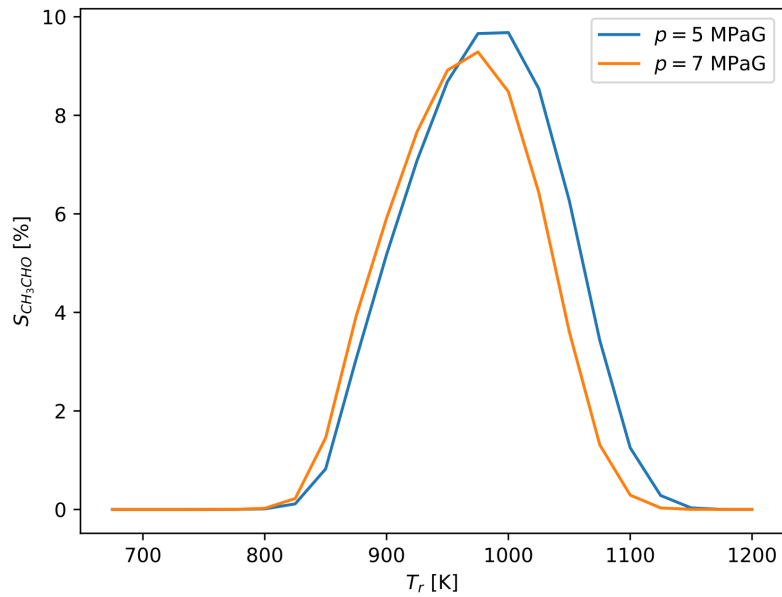


Figure 4.42: Acetaldehyde selectivity in function of reaction temperature

Figure 4.42 shows the selectivity of acetaldehyde as a function of reaction temperature. The selectivity of acetaldehyde, in an interesting fashion, shows a similar

pattern as that of formaldehyde, although at much higher values. Indeed, acetaldehyde is formed as a reaction product for temperatures between 800 and 1150 K, with a maximum selectivity of about 9 % at around 1000 K. At higher temperatures (1000-1200 K), either less acetaldehyde is formed, or some of the acetaldehyde formed decomposes to form smaller compounds. Pressure has little effect on the formation of acetaldehyde, a higher pressure slightly inhibits its formation.

Figure 4.43 shows the selectivity of vinyl alcohol as a function of reaction temperature. The selectivity of vinyl alcohol shows a similar pattern as that of acetaldehyde, although at much lower concentrations. Vinyl alcohol is formed between 800 and 1150 K, with a maximum selectivity of about 2 % at around 950 K. As vinyl alcohol is a isomer to acetaldehyde, it is thought that most of the vinyl alcohol formed restructures itself to acetaldehyde during of after the reaction, which explains its similar behaviour to acetaldehyde, although at much lower concentrations. Pressure does not show a great influence on the formation of acetaldehyde.

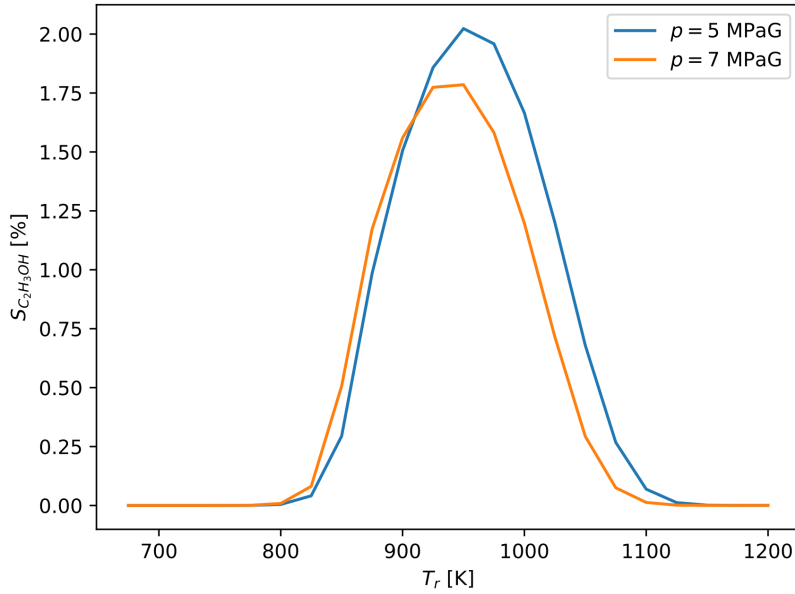


Figure 4.43: Vinyl alcohol selectivity in function of reaction temperature

Figure 4.44 shows the heat per unit mass absorbed by the thermal cracking reaction of ethanol. The heat per unit mass was calculated from an energy balance for the reactor as described below. The first law of thermodynamics for an open system with one inlet and one outlet states that:

$$\frac{dE}{dt} = \dot{Q} - \dot{W} + \dot{m}(h_1 - h_2 + \frac{1}{2}(u_1^2 - u_2^2) + g(z_1 - z_2)). \quad (4.29)$$

As the system is at steady state, no work is exchanged with the environment, and $z_1 = z_2$, equation (4.29) becomes

$$\dot{Q} = \dot{m}(h_2 - h_1 + \frac{1}{2}(u_2^2 - u_1^2)), \quad (4.30)$$

and thus the heat per unit mass can be expressed as

$$q = \frac{\dot{Q}}{\dot{m}} = h_2 - h_1 + \frac{1}{2}(u_2^2 - u_1^2), \quad (4.31)$$

where h_1 , h_2 , w_1 and w_2 are the enthalpies and velocities at the inlet and outlet respectively.

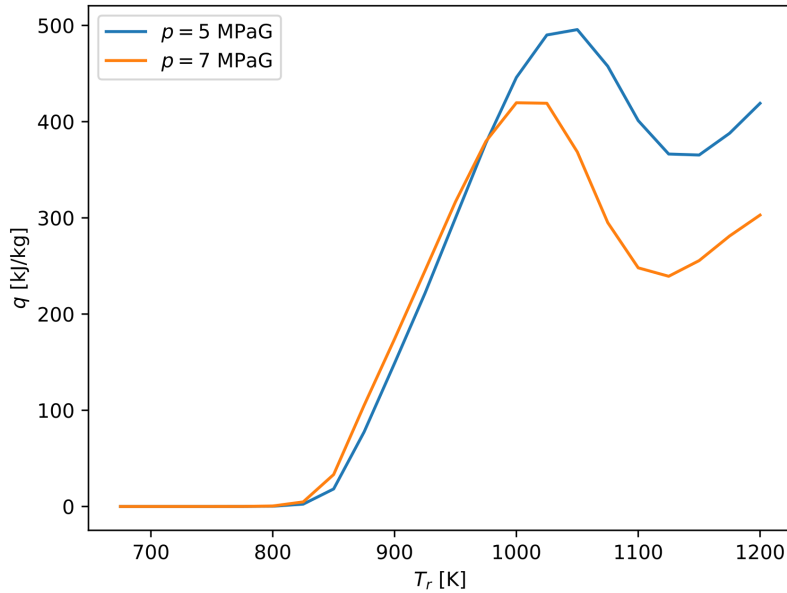


Figure 4.44: Heat per unit mass absorbed by the reaction

Figure 4.44 shows that, for low temperatures (800-1000 K) the heat per unit mass increases with temperature, which is expected, as the more the temperature increases, the more ethanol is broken down into products (see figure 4.34), which is the process that absorbs temperature. For these low temperatures, there is no major influence of pressure, as a pressure increase only shifts the curve slightly towards lower temperatures, which is a consequence of the reaction starting earlier at higher pressure. For medium temperatures (1000-1100 K), after reaching a maximum at around 1000 K, the heat per unit mass decreases with temperature, which is somewhat unexpected. This may be a consequence of the fact that, for these temperatures, smaller compounds, such as hydrogen or ethylene, stop being formed in

quantities as high as at 1000 K in favour of heavier compounds, such as ethane. This means that less molecular bonds are broken, and thus less energy is absorbed. This decrease in temperature could also be due to a change in reaction pathway, in the sense that, although about the same products are produced in similar amounts as for lower temperatures, the sequence of reactions leading to those products changes due to the increase in temperature. Therefore, as the heat per unit mass absorbed depends on the reactions involved in the decomposition of ethanol, this could in turn reduce the overall heat absorbed. For high temperatures (1100-1200 K), the heat per unit mass increases again with temperature. This could be due to mechanisms opposite to those mentioned before, i.e. more hydrogen and ethylene are formed instead of ethane, or the reaction pathway change again to a more heat absorbing one. Lastly, at medium and high temperatures, a lower pressure favours heat absorption. This could also be due to the fact that pressure influences the products formed, as well as the reaction pathways.

4.2.2 Real gas version

The results of the real gas version of the simulation model are extremely similar to those of the ideal gas version, and will therefore, in order to avoid redundancy, not be discussed in detail in this section. The figures showing products selectivities and the heat absorbed per unit mass are presented in appendix D.

The fact that the results of both versions are almost identical make the real gas version somewhat unnecessary. Indeed, the real gas version was expected to improve simulation accuracy at the cost of computing power and time. However, as it does not show improved results, the real gas version only bears disadvantages: it requires more computing power and time. Hence, it can be concluded that the Redlich-Kwong thermodynamic model does not bring any improvement for the numerical simulation of the thermal cracking of ethanol at the studied conditions. Nonetheless, under different conditions or for other reactions, switching from an ideal gas model to a Redlich-Kwong real gas one may bring significant improvements to the accuracy of the global simulation model.

4.2.3 Model validation

In this section, the validity of the model will be assessed by comparing the simulation results with the experimental ones. As the real gas version did not show any significant improvement with respect to the ideal gas one, only results from the latter will be discussed here. More specifically, six figures presenting the mass

fractions of each of the compounds which were measured experimentally will be discussed in detail. These mass fractions are defined as,

$$w_i = \frac{m_i}{m_{\text{tot}}}, \quad (4.32)$$

where m_i is the mass of compound i , and m_{tot} is the total mass of all the substances involved in the reaction (reactants and products).

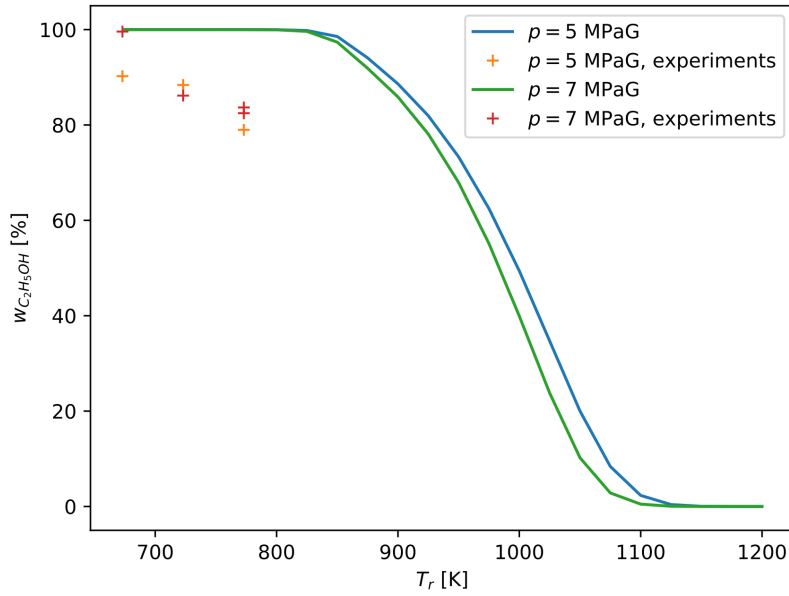


Figure 4.45: Mass fraction of ethanol in function of reaction temperature

Figure 4.45 shows the mass fraction of ethanol as a function of reaction temperature for two different pressures, where the lines show the simulation results, while the markers correspond to the experimental measurements. At first, it would seem that the model completely disagrees with the experimental results, implying that at least one of the two procedures contains some kind of error. However, in the experiments, the temperature is measured at the center of the reaction tube by the thermocouples, while the reaction happens on the hotter tube surface, whose temperature is the actual reaction temperature which is defined in the simulation model. Therefore, the experimental measurements are plotted in function of the temperature in the center of the tube, while the simulation results are plotted in function of the actual reaction temperature. Due to products being produced and phase change happening during the reaction, the thermal conductivity may change drastically along the tube's inner radius, and thus the tube surface temperature may be significantly higher than the temperature in the tube center. This means that

if the tube surface temperature were to be considered for the experimental results plotted on figure 4.45, the points would significantly shift to the right. Assuming that shift were to be of about 150 K, the experimental results would actually agree quite well with the simulation, as the decrease trend of the points is similar to that of the curves. This would then confirm the validity of the simulation model.

Figure 4.46 shows the mass fraction of hydrogen as a function of reaction temperature. Again, lines correspond to simulation results while points correspond to experimental measurements. Similarly to figure 4.45, it first seems that the experimental measurements and the simulation results disagree completely. However, if, for the same reasons as detailed above, the points were to be shifted of about 150 K to the right, a good agreement between experiments and simulation model would be obtained. Indeed, on this figure, even the points for $p = 7$ MPaG are always above those for $p = 5$ MPaG, which corresponds to what the simulation results show.

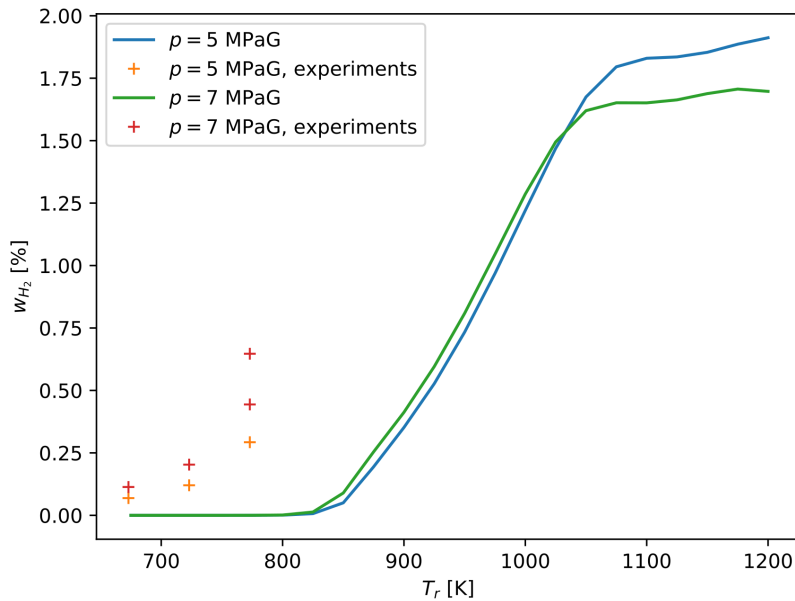


Figure 4.46: Mass fraction of hydrogen in function of reaction temperature

Figures 4.47-4.50 show the mass fractions of carbon monoxide, methane, ethylene and ethane in function of reaction temperature, respectively. As for figures 4.45 and 4.46, the lines show the simulation results, while the points represent experimental measurements. For these four figures, similar observations can be made as for figures 4.45 and 4.46, i.e. at first glance, the experimental results do not seem to agree with the numerical ones, but, when considering the temperature difference between tube center and tube wall, a shift of the experimental measurements to the right is

expected. Again, if this shift were to be of about 150 K, good agreement would be obtained between experiments and simulation model for all results, except for those of ethylene.

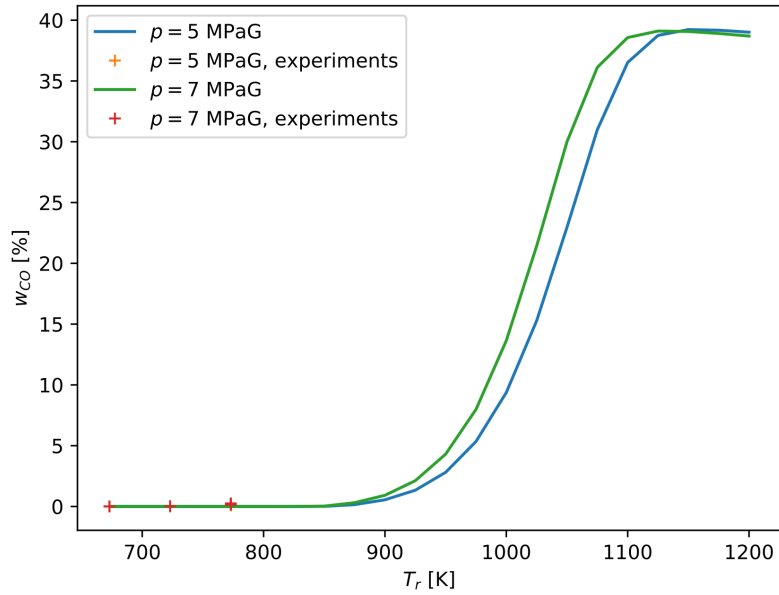


Figure 4.47: Mass fraction of carbon monoxide in function of reaction temperature

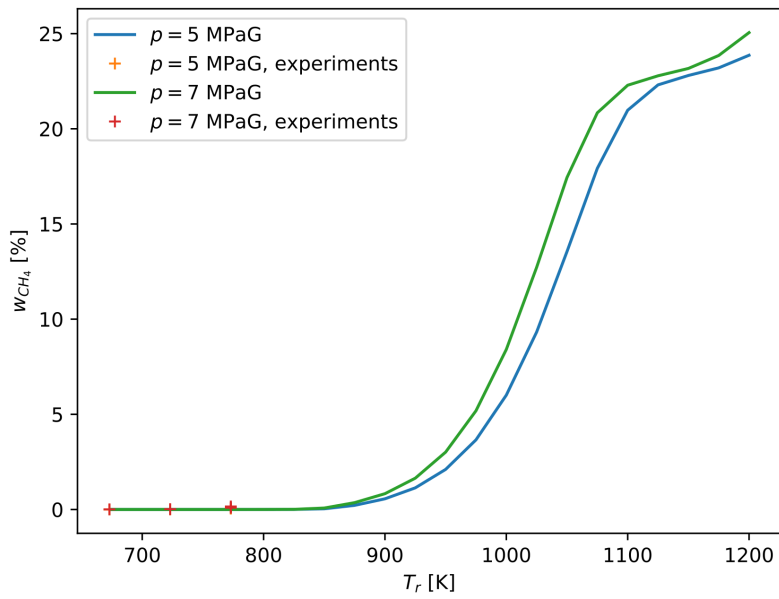


Figure 4.48: Mass fraction of methane in function of reaction temperature

Indeed, when looking at figure 4.49, even if the experimental points were to be shifted of about 150 K to the right, they would not coincide with the curve representing the numerical results, as the rate of increase of the mass fraction of ethanol appears to be much higher for the simulation results than for the experimental ones.

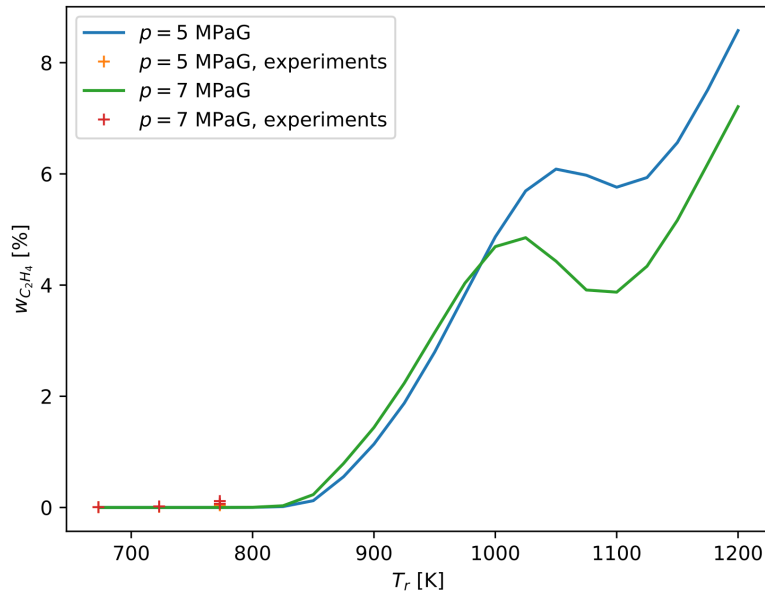


Figure 4.49: Mass fraction of ethylene in function of reaction temperature

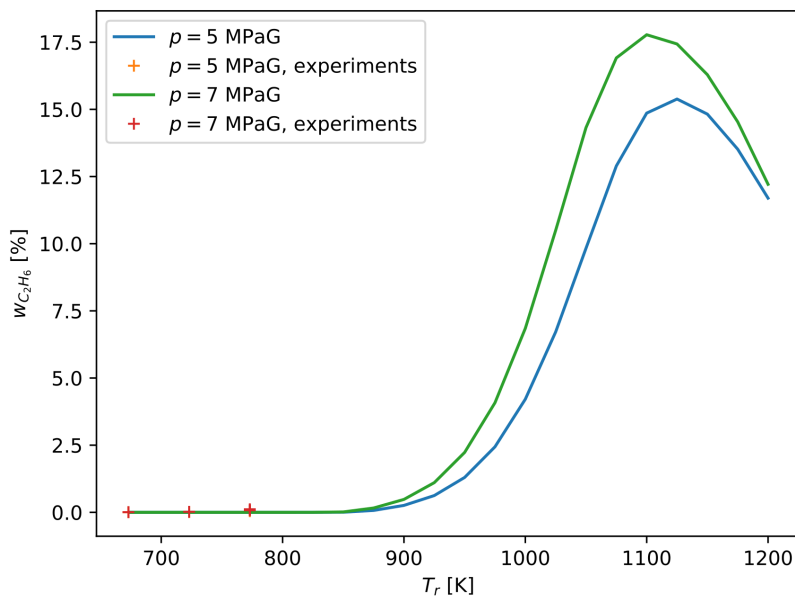


Figure 4.50: Mass fraction of ethane in function of reaction temperature

In conclusion, considering the data presented in this section, it seems that the simulation model developed in this study could be a valid model to simulate the thermal cracking of ethanol. However, due to the lack of sufficient data, such as tube surface temperature for the experiments, this model, although showing satisfying general trends, cannot be properly confirmed to be an accurate representation of the thermal cracking of ethanol. Further investigation is therefore necessary in order to actually determine whether or not this model is an accurate representation of the thermal cracking of ethanol, or if it contains major flaws that undermine its reliability. A first way to gain a better insight into the model's validity would be to conduct additional experiments where not only the temperature at the tube center, but also the one at the tube wall is measured. Another way to gain a better insight would be to calculate a simplified temperature profile for the inside of the reaction tube in order to estimate the tube surface temperature based on the central temperature. These further investigations are outside of the scope of this project, and left as future improvements for posterior research.

Chapter 5

Conclusion

5.1 Major outcomes

The experimental results obtained throughout this study lead to the following conclusions about the thermal cracking of ethanol.

- It can be difficult to accurately control the mass flow rate during the thermal cracking experiments with the setup used in this study, especially under sub-critical conditions, where oscillations may occur independently of the setup.
- With the correct settings and know-how, the reaction temperature can be controlled quite accurately thanks to the experimental setup.
- The thermal cracking reaction seems to start occurring at temperatures T_3 and T_4 around 400 °C, both for $p = 5$ MPaG and $p = 7$ MPaG.
- Conversion and gas yield both increase with temperature, while gas yield also increases with pressure.
- For all experimental conditions, hydrogen is the most abundant gaseous product (in terms of selectivity), while carbon monoxide, methane, ethylene and ethane make up the rest of the gas mixture.
- The selectivity of hydrogen decreases with temperature, while those of the other gases increase with temperature and pressure.
- The mass fraction of unreacted ethanol decreases with both temperature and pressure.
- Water and acetaldehyde make up the other liquid products, although their amount could not be quantified.

- The decomposition mechanism of ethanol is quite complicated and is made of primary and secondary reaction pathways. These pathways may change with temperature and pressure and can be composed of several sequential reactions.

The numerical results, on their side, lead to the conclusions about the thermal cracking of ethanol described below.

- The cracking reaction starts at a wall temperature of about 825 K, and is complete at around 1125 K.
- The selectivities of hydrogen and carbon monoxide increase with reaction temperature for low and medium temperatures before showing a slight decrease at high temperatures.
- The selectivities of methane and water increase with reaction temperature. Their rate of increase is strongest for low and medium temperatures, and drops at high temperatures.
- The selectivity of ethylene varies a lot with reaction temperature, showing both a local maximum and minimum, while that of ethane increases with reaction temperature for low and medium temperatures, before dropping significantly at high temperatures.
- The selectivities of formaldehyde, acetaldehyde and vinyl alcohol all show the same trend: a strong increase with reaction temperature at low temperatures, a maximum at medium temperature, and a decrease to zero at high temperatures.
- The abundance of all products is strongly dependent on reaction temperature, but only a few are significantly affected by pressure (hydrogen, ethylene, ethane).
- The heat per unit mass absorbed by the reaction is dependent both on reaction temperature and pressure. It shows a maximum at around 1050 K for $p = 5$ MPaG.
- The real gas version of the model does not yield any significant improvements with respect to the ideal gas one.
- The simulation model seems to show the same trend as the experimental results, but could not be properly validated due to the mismatch between flow and wall temperatures.

The aforementioned points summarise the major outcomes of this study, and provide a synthesised overview of the improved understanding of the thermal cracking reaction of ethanol, which was brought about by this study.

5.2 Future research possibilities

A few research ideas which exceed the scope of this project are proposed in this section as a reference for future studies and future researchers. As a development of this project, the influence of the mass flow rate on the thermal cracking of ethanol could, for example, be investigated. Other possible developments include, but are not limited to, the investigation of the cracking of a fuel mixture composed of ethanol blended with a more standard hydrocarbon, e.g. heptane or iso-octane, the investigation of the catalytic cracking of ethanol or of the possibility of steam reforming (in addition to the work already accomplished by Nishimoto [21]), or the investigation of the thermal cracking of other biofuels, such as methanol for example.

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Finally, I would like to thank my family and friends, who supported me throughout the entirety of this work, on good days as on bad days. I would especially like to thank my father and sister, who supported me all along this work, without fail, even throughout the distance.

Appendix A

User manuals

A.1 GC-TCD manual

Gas Chromatograph (GC-14B, C-R8A) User Manual

Last updated: 2022/03/29

Original author: Kinoshita Ryosuke

Translated and updated by: Rafael Pichler

Contents

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1 Preamble

This manual describes the procedure of use for the GC-14B gas chromatograph. The GC-14B is a gas chromatograph with a thermal conductivity detector (GC-TCD). Its purpose is the identification of lower hydrocarbon and atmospheric gases which result of the thermal decomposition of hydrocarbon fuels.

2 Required elements

The elements required to perform analyses are summarised below.

- Main unit (GC-14B)
- Data logger (C-R8A)
- Argon gas cylinder
- Gas sample injector syringe
- Flowmeter (SFM-1000)
- Aluminium bag(s)

It is preferable that the chromatograph be operated by 2 people, especially during sample injection.

3 Operation procedure

3.1 Prior preparations

1. Open the argon cylinder's main valve (argon is used as the carrier gas). In principle, do not move the regulator, it should be set to an appropriate pressure already (~ 0.6 MPa).



2. Turn on the main unit (frontside, bottom-right) and the data logger (backside, left).



3. Next, press the [MONIT] button on the logger to display the current status, and confirm that SPD: 10, ATT: 4. (There is also a [MONIT] button on the controller, but the logger's shall be used here).

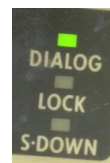


4. Enter the program settings (except the stop time, see table 1) on the controller of the main unit. The procedure for entering INIT TEMP is given as an example. Press the [INIT TEMP] button once, enter 40 with the numeric keypad, and finally press the [ENT] button. Thereby, the value of INIT TEMP has been set to 40 °C. To input TCD-T, press the [SHIFT DOWN] button before pressing the [DET-T / TCD-T] button.



5. Set the logger stop time by pressing [COMMAND] → [L], entering the desired value (in minutes), and pressing [ENTER] on the logger. The stop time should be adjusted according to the temperature program (see table 1), i.e. it should correspond to the total time necessary to complete the program.

6. Switch to dialog mode ([SHIFT DOWN] + [FILE / FUNC] → numeric keypad [1] → [ENT]) on the controller. In this mode, each setting value can be changed interactively. Confirm that the DIALOG lamp lights up.



7. By pressing [ENT] repeatedly, you can move to the parameter you want to set. Then, you can enter the desired value with the numeric keypad. Here, press [ENT] repeatedly until CMAX is displayed, and enter 310 with the numeric keypad ([3] [1] [0] [ENT]). This is the maximum temperature of the column and is a necessary operation to protect the column.
8. Normal input is not possible in dialog mode. Exit the dialog mode by pressing [SHIFT DOWN] → [ESCP].
9. Press [START] **twice** on the controller, and immediately after that, press [STOP]. As a consequence, the logger will start printing, so press the [START 1 / STOP 1] button to stop it.
10. Enter the program settings again in the same way as in step 4. LIMIT might be displayed on the controller's monitor and it may not be possible to input the set values normally, but all the values should be input without worrying about it (the memory of the main unit might be full, but this re-entry procedure is considered to be redundant, i.e. the previously set values still hold).
11. Check that the green button of HEATER at the bottom right of the main unit is lit. If not, press it to turn it on. This will start heating the main unit to the set parameters (INJ TEMP, etc).
12. Give the machine about 10 min to heat up. Once done, the READY lamp on the controller will light up.
13. While checking the value displayed on the logger monitor, adjust the voltage [μ V] with both knobs of the TCD (coarse adjustment (COARSE) on the bottom and fine adjustment (FINE) on the top). Set the voltage as close to 0 [μ V] as possible, at least within a range of ± 500 [μ V], but ideally within a range of ± 5 [μ V]. The value is unstable for a few hours after the main unit has been started. Complete the operations up to step 12 about 3h00 before the start of the analysis, and wait.



3.2 Sample injection and analysis

Important: Before analysing the actual sample, it is necessary to run analyses with air instead of the sample. Indeed, the first analyses tend to have an unstable baseline, which hinders the obtention of accurate results. Therefore, a few analyses need to be done with air, until the baseline becomes sufficiently stable. Once this is the case, the actual sample is analysed (see section 3.3.1).

1. Check the flow rate of argon with the flowmeter. Insert the tip of the flowmeter pipe into the two ports located at the top rear of the main unit's left side (see photo). Set the flow meter to N2 mode, and confirm that the flow rates are approximately 1: 66 ml/min (~170 kPa on the CARRIER 1 gauge), and 2: 60 ml/min. These values can be in a range of ± 2 -3 ml/min, without any problem. If necessary, adjust the values by using the [CARRIER 1] and [CARRIER 2] knobs on the right side of the main body.
2. One of the two operators (hereinafter A) holds the aluminium bag with both hands, and the other (hereinafter B) opens the bag's valve while applying the syringe to the bag's entrance with one hand.
3. When the valve opens, A squeezes the bag and blows out the gas. This pushes away the atmosphere near the bag's entrance and improves the accuracy of the analysis.
4. B holds the syringe with one hand so that it does not separate from the bag's entrance, and pulls the syringe's piston with the other hand to extract a sample. During this operation, the syringe should be filled to about 0.35 ml (depends on the gas composition and type of column).
If the injected sample is too large, the resulting peaks will widen, thus making it impossible to obtain an accurate component ratio.
5. B then presses the [START] button on the controller (the logger starts operating) and injects the sample into injection hole 1 of the main body (topside, left). Press the [START] button on the controller again as soon as the sample is injected (starts the analysis).



6. Note that the retention time (RT) [min] on the controller monitor and next to the peak (on the paper) is displayed in decimal notation after the comma. The correspondence between retention times and each component (peak) has been pre-calibrated (see table 2).
7. Wait until the analysis is completed. The analysis can be manually stopped at any time. To do this, press the [STOP] button on the controller to stop the main unit, and press the [START 1 / STOP 1] button to stop the logger.

3.3 Post-analysis operation

3.3.1 Analysis of another sample

1. Press the [FEED] button on the logger to make the thermal paper long enough, and cut it. Press once to feed, press again to stop.
2. Wait until the COOL lamp turns off and the READY lamp lights up (~10-30 min).
3. If you want to change a setting, press [COL], which will clear all settings. Then, enter the new settings as in section 3.1 step 4 (the setting's number corresponds to the analysis line/column).
4. After that, repeat the sample injection procedure (section 3.1 step 13, or 12 if new settings have been entered, to section 3.2 step 7).

3.3.2 End of use

1. Once the analysis is complete, cut out the thermal paper.
2. Press [COL] (clears all program settings), and enter the program settings again. However, now, all the settings whose unit is °C shall be set to **room temperature (27 °C)**. Further, PROG RATE and CURR shall be set to **0**, in order to keep the COOL lamp lit.
3. The current temperature in the column can be displayed by selecting [MONIT] → [INIT TEMP] on the controller. Wait until it has cooled to **room temperature** (about 30 min).
4. Once the column has cooled down completely, turn off both the main unit and logger.
5. Close the main plug of the argon cylinder. Leave the regulator open, i.e. do not move it.

4 Tables

Table 1: Program settings

Item [notation on controller]	Value (for N ₂ and O ₂ analysis)	Value (for hydrocarbon analysis)	Unit
Initial temperature [INIT TEMP]	30	40	°C
Initial time [INIT TIME]	5	5	min
Program rate [PROG RATE]	40	15	°C/min
Final temperature [FINAL TEMP]	200	300	°C
Final time [FINAL TIME]	3	5	min
Injector temperature [INJ]	200	300	°C
Detector temperature [DET-T]	200	300	°C
TCD temperature [TCD-T]	150	300	°C
Det [DET]	4	4	-
Pol [POL]	2	2	-
Current [CURR]	50	50	mA
Logger stop time [STOP.TM]	13	28	min

Table 2: Gas chromatograph calibration

Substance	Conversion formula <i>A</i> : area, <i>n</i> : amount [mol]	Retention time [min]
Oxygen (O ₂)	$n = 2.1 \cdot 10^{-10} \cdot A$	1.884
Nitrogen (N ₂)	$n = 2.4 \cdot 10^{-10} \cdot A$	2.033
Hydrogen (H ₂)	$n = 2.9 \cdot 10^{-11} \cdot A$	0.649
Carbon monoxide (CO)	$n = 2.6 \cdot 10^{-10} \cdot A$	2.289
Methane (CH ₄)	$n = 8.0 \cdot 10^{-11} \cdot A$	5.391
Carbon dioxide (CO ₂)	$n = 2.2 \cdot 10^{-10} \cdot A$	9.776
Ethylene (C ₂ H ₄)	$n = 9.6 \cdot 10^{-11} \cdot A$	14.609
Ethane (C ₂ H ₆)	$n = 7.5 \cdot 10^{-11} \cdot A$	15.871
Propylene (C ₃ H ₆)	$n = 1.1 \cdot 10^{-10} \cdot A$	21.961
Propane (C ₃ H ₈)	$n = 8.2 \cdot 10^{-11} \cdot A$	22.519

A.2 GC-MS manual

GC-MS Guidance Manual

Last updated: 2022/06/15

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Normal Use

1. Device start up

1.1. Main unit start up

1. Open the helium cylinder's main valve (the secondary pressure is normally pre-set to about 0.6 MPa; the flow rate is automatically controlled by the GC). Replace the cylinder when the main pressure drops to about 1-2 MPa.
2. Check that the switchboard (1P-6-1) is turned on.
3. Turn on the main power in the following order : GC (front side, bottom right), MS (backside, bottom left), and computer.
4. Start the program, by clicking the 【GCMS 分析】 desktop icon.
5. On the login screen, just click 【OK】 .

1.2. Vacuum pump start up

1. Click the 【真空系の起動・停止】 icon on the 【分析】 assistant bar.
2. Click 【自動起動】 (it takes a little while to vacuum the machine).
3. When 【完了】 is displayed, click 【閉じる】 .
4. Complete the operations up to this point one day before the analysis.
※ It takes one day to completely purge the inside of the carrier piping from the mixture of air and carrier gas. If this procedure is not followed, the baseline will not be stable during analysis, hence making peak detection difficult.

2. Analysis preparation

2.1. Vacuum leak check

1. Click the 【チューニング】 icon on the 【分析】 assistant bar.
2. Click the 【ピークモニタ】 icon on the 【チューニング】 assistant bar.
3. Select 【水,空気】 from the 【モニタグループ】 list.
4. Click the filament icon 【フィラメントの ON/OFF】 to turn on the filament.
5. Tune the 【検出器】 voltage such that the peak height of m/z 18 (water) is half the height of the display window.
6. Confirm that the peak height of m/z 28 (nitrogen) does not exceed twice the one of m/z 18 (water).
※ If this limit is exceeded, air might be leaking. Hence, check for vacuum leaks.
※ If it is only slightly exceeded, and the auto tuning result is normal, the analysis can still be performed.
7. Click the filament icon 【フィラメントの ON/OFF】 to turn off the filament.
8. Close the 【チューニング】 window by clicking on another tab. On the 【現在のチューニングファイルを保存しますか?】 message screen, click 【いいえ】 .

2.2. Method file creation

Good method files have been developed for the analysis of polarised and non-polarised compounds using the TC-BOND Q and SH-Rxi-1HT columns, respectively. These method files have each been declined into two versions, one for using diethyl ether and the other for using hexane as a solvent. They can be used without modification for the analysis of such compounds, using the previously mentioned columns and solvents. They are named 【 211104_pol_ether.qgm 】 , 【211104_pol_hexane.qgm】,【211027_np_ether.qgm】and【211027_np_hexane.qgm】, and can be found on the GC-MS computer in 【D:\211104】 and 【D:\211027】 or in 【\\BAIMAN\share\Research Groups\GC\GC-MS\Method files】 . These files should not be directly modified, but rather copied under a new name and then modified, if needed

1. Open the 【メソッド】 tab of the 【データエクスプローラ】 .
2. Open the method file you want to edit, by double-clicking it.
3. Click 【ファイル(F)】 → 【メソッドファイルに名前を付けて保存(A)】 .
4. Set the autosampler parameters (they're pre-set to default values, which can be used for analysis).
 - ・ 注入前の溶媒洗浄回数 : Number of times the inside of the syringe is automatically washed with solvent before sample injection.
 - ・ 注入後の溶媒洗浄回数 : Number of times the inside of the syringe is automatically washed with solvent after sample injection.
 - ・ 注入前の試料洗浄回数 : Number of times the inside of the syringe is co-washed with the sample before sample injection and after solvent washing.
5. Set the 【GC】 parameters with respect to the selected column.
 - ・ カラムオープン温度 : Initial temperature of the column oven, set it below the sample's boiling point (40-100 °C).
 - ・ 気化室温度 : The sample is vaporised before injection. Set the temperature above the sample's boiling point (200-300 °C).
 - ・ 注入モード : Injection mode, select 【スプリット】 or 【スプリットレス】 .
 - ※ スプリット : Split, best for samples having a concentration higher than 1 ppm.
 - ※ スプリットレス : Splitless, best for samples having a concentration lower than 1 ppm.
 - ※ When using the split setting, the detection peak becomes wider and the sensitivity drops.
 - ・ 制御モード : Select 【圧力】 or 【線速度】 .
 - ※ Selection of the carrier gas flow rate control method. In 【圧力】 , the back pressure is constant; and in【線速度】 , the carrier gas flows at a constant linear velocity in the column. When set to 【圧力】 , the holding time varies as the gas temperature rises. When set to 【線速度】 , the carrier gas always flows at a constant volume flow rate. Therefore, in general, it is better to select 【線速度】 .
 - ・ レート : Heating rate [°C/min]
 - ・ 温度 : Target temperature [°C]
 - ・ ホールド時間 : Time interval during which the sample is kept at the target temperature [min]

6. Set the **【MS】** parameters.
 - ・ 溶媒溶出時間 : Enter the solvent retention time.
 - ※ MS detectors deteriorate when high-concentration components are added. Since the solvent used for sample preparation inevitably has a high concentration, it is necessary to turn off the detector during the solvent's elution time. In order to avoid interference with other components, a substance having a short retention time is usually used as a solvent. The substance used as a solvent is analysed in advance using the same method as for a sample, and the holding time is measured (the detector won't be deteriorated by this single analysis). In the subsequent analyses, set the solvent elution time such that damage to the detector is avoided.
 - ・ 検出器電圧 : Select **【チューニング結果からの相対値】** .
 - ※ Tune within the range of 0.1-0.3 kV when the peak intensity is small. Peak intensity increases 2-4 times when increased by 0.1 kV.
 - ※ As mentioned in the point about the solvent elution time, if the sensitivity of the detector is increased and a high concentration substance is added, the detector will be damaged. The voltage should therefore be increased gradually from the smallest value, until it reaches a satisfactory value.
 - ・ 開始時間 : Time at which the detector is turned on.
 - ・ 終了時間 : Time at which the detector is turned off.
 - ・ 開始 : Minimum mass at which ions are measured.
 - ・ 終了 : Maximum mass at which ions are measured.
7. Set the similarity search parameters.
 - ・ Click **【メソッド(M)】** → **【定性処理パラメータ(L)】** .
 - ・ Select the **【シミラリティ検索パラメータ】** tab.
 - ・ Select both the NIST14s and NIST14 libraries, which are the ones used for similarity searches (location: C:/GCMSsolution/library).
8. Click the **【上書き保存】** icon.

2.3. Auto tuning

Start directly from step 4 if you just created the method file and it is still open in the program.

1. Click the **【データ採取】** icon on the **【分析】** assistant bar.
2. Click open **【開く】** on the toolbar.
3. Double-click the method file which will be used for analysis.
4. Click **【データ採取(A)】** → **【初期値を装置にダウンロード(I)】** .
 - ・ Configuration parameters are sent to the device.
 - ・ As soon as each parameter reaches the set value, **【GC : 準備完了】** and **【MS : 準備完了】** are highlighted in green. During the setting time, they are highlighted in yellow.
 - ・ Here, it takes some time for the vaporisation chamber and the detector temperatures to rise.

During this period, if the column oven temperature is manually raised to the maximum temperature used for analysis, the residue in the column can be washed. When the vaporisation chamber and detector temperatures reach the set values, select 【初期値を装置にダウンロード】 again to return the column oven temperature to the initially set values.

5. Click the 【チューニング】 icon on the 【分析】 assistant bar.
 6. Click the 【ピークモニタ】 icon on the 【チューニング】 assistant bar.
 7. Click 【ファイル(F)】 → 【チューニングファイルの新規作成(N)】 .
 - ・ On the 【チューニングモードの選択】 screen, select 【標準】. Here, the amount of current flowing through the detector is set (standard is sufficient for the samples used in the laboratory).
 8. Select the filament (フィラメント) to use.
 - ・ Select #1. The detector contains a set of electrodes, and the direction in which the current flows (the direction in which the voltage is applied) is defined by the selected one. This direction is also a parameter of the analysis, and if it is changed, different results will be obtained. Therefore, usually, keep #1 selected. However, electrodes have a limited lifetime, and if #1 is worn out, #2 shall be selected, which will thus change the current direction. Then, the electrode which is not worn out can still be used without replacement. Replace the part once both sides are exhausted.
 9. Click the 【オートチューニング開始】 icon on the 【チューニング】 assistant bar.
 10. Enter the file name and click 【保存】 .
 - ・ Auto tuning starts.
 - ・ A report will be shown once the tuning is completed (~10 minutes).
 11. Click the 【上書き保存】 button on the toolbar.
 12. Check the results of auto tuning.
 - ・ Check if each half width 【半値幅】 is in the range of 0.5 to 0.7.
 - ・ Check if the voltage of the detector 【検出器】 is 2 kV or less.
 - ・ Check if the relative strength ratio 【強度比】 of m/z 502 is 2% or more.
 - ・ Check if the peak intensity 【強度】 of m/z 69 is more than twice the peak intensity of m/z 28 (switch tabs to 【スペクトル】 and check).
- ※ If any of the above items are abnormal, the cause may be vacuum leakage, improper column mounting, or a dirty ion source.

2.4. Sample preparation

2.4.1. Gas samples

When preparing gas samples using extremely flammable and/or toxic gases, such as hydrogen (H₂) or carbon monoxide (CO), take proper care not to release those gases inside the experiment rooms. Use a purge system with nitrogen (N₂), or directly release those gases outside the building to ensure that they are released into the atmosphere and do not pose any safety hazards.

1. Prepare the required elements.
 - Sample gas (in a tank if unknown mixture, in a gas cylinder if standard sample)
 - Solvent gas (in a gas cylinder, usually N₂ or He)
 - Sample preparation tank (the one with 4 inlets/outlets, 5 shut valves and a needle valve)
 - Vacuum pump
 - Absolute pressure sensor
 - Teflon tubes (a flexible metal tube is necessary for extremely flammable gases such as H₂)
 - Short metal tubes
 - Small injection tank
 - Gauge pressure sensor
 - Two $\frac{1}{2} \times \frac{9}{16}$ inch spanners
 - One adjustable wrench
2. Connect the sample gas container to the sample preparation tank, on one of the inlets which are connected to the needle valve, with the appropriate tube.
3. Connect the vacuum pump to the sample preparation tank, on the other inlet which is connected to the needle valve, with a Teflon tube.
4. Attach the absolute pressure sensor to one of the remaining inlets, using a short metal tube.
5. Turn on the pressure sensor.
6. After checking that all the valves are in the appropriate position, vacuum the tank and the connection tube between the tank and the sample gas container.
7. Once the tank has been vacuumed as much as possible (i.e. $p < 1$ kPa), shut the valve leading to the vacuum pump and turn off the pump.
8. Fill the tank with sample gas to the desired pressure. Use the needle valve to control the flow rate and reach the desired pressure precisely.
9. Shut the valve leading to the sample gas container.
10. Disconnect the sample gas container and connect the solvent gas cylinder to the same inlet (with a Teflon tube). Be careful not to release any toxic or extremely flammable gas into the room.
11. Vacuum the tube connecting the solvent gas cylinder and the sample preparation tank.
12. Dilute the sample gas with the solvent gas to the desired concentration ($x_s = \frac{p_s}{p_{\text{tot}}}$). The total pressure must be higher than the atmospheric pressure, and should ideally be as high as possible in order to maximise the number of samples that can be taken from the tank. The current pressure sensor's range is 0-133 kPa, so $p_{\text{max}} = 133$ kPa and $p_{\text{atm}} < p_{\text{tot}} \leq p_{\text{max}}$. Again, use the needle valve to control the flow rate and reach the desired pressure precisely.
13. Shut all valves and disconnect the solvent gas cylinder, vacuum pump and pressure sensor from the tank.
14. Leave the tank and wait for diffusion to happen, in order to obtain a homogeneous mixture. Usually about 1 h is enough time for the mixture to become homogeneous.

15. Attach the gauge pressure sensor to the small injection tank (with a short metal tube). Be careful as they're a pair with one sensor for -100-100 kPaG and the other for 0-1 MPaG. Use the appropriate one (in general that is the first one).
 16. Attach the injection tank to one of the inlets of the sample preparation tank which is connected to the needle valve (using another short metal tube).
 17. Connect the vacuum pump to the other inlet which is connected to the needle valve.
 18. Vacuum the injection tank and the connection tubing.
 19. Fill the injection tank with about 10 kPaG of the gas mixture.
 20. Shut all valves and detach the small injection tank from the sample preparation tank.
- ※ If there is enough pressure remaining in the sample preparation tank after one sample has been prepared, steps 16-20 can be repeated to make additional samples.

2.4.2. Liquid samples

Samples should be prepared in the micro-gravity room, where ventilation is possible. Bring all the necessary materials there, and use proper ventilation to avoid breathing in solvent vapours. Depending on the volatility of the solvent used, it might be necessary to prepare the sample in a fume hood, while wearing an activated carbon mask against organic vapours. For example, diethyl ether is extremely volatile ($T_b = 35\text{ }^{\circ}\text{C}$, $p_{v,20^{\circ}\text{C}} = 59\text{ kPa}$), and produces toxic and flammable vapours, therefore, it should always be handled inside a fume hood while a mask against organic vapours is being worn.

1. Prepare the required elements.
 - Chemical safety goggles
 - Nitrile rubber gloves
 - Chemicals (reagent(s), solvent(s))
 - Sample(s) to be analysed
 - Micro pipette(s)
 - Micro tip(s)
 - Vial(s)
 - Vial septum(s)
 - Vial cap(s)
 - Paper towels
 - Glass pipette
 - Pipette's rubber sucker
2. Put on the goggles and gloves.
3. Put the chemicals into their dedicated glass recipients (these can be found in the large plastic box, new recipients can be found in the cardboard box on the shelf).
 - Pour a small amount of reagent into its dedicated recipient.
 - Pour the required amount of solvent into its dedicated recipient. Solvents such as diethyl ether and acetone are volatile and evaporate significantly, so about 20 ml shall be used. For

other standard sample preparations, the reagent can be taken with a micropipette, so about 10 ml is sufficient. The recipients have a volume of 50 ml.

※ Do not put a pipette (or other tool) directly into the reagent bottle. In general, handle special grade reagents with care.

4. Place the septum in the cap (**dark side inside**).
5. Place the vial and chemical recipients on top of a paper towel.
6. Weigh the empty vial and tare the scale.
7. Put the microtip on the micropipette.
8. Inject the sample into the vial using the micropipette.
 - ※ The target sample concentration is of tens to hundreds of ppm (thousands are also acceptable). Adjust little by little, while taking into account that the minimum weight the scale can detect is 1 mg.
9. Weigh the sample each time a chemical is injected (know the amount of each chemical).
10. Attach the pipette sucker to the pipette.
11. Inject the solvent into the vial.
 - ※ Depending on the sample concentration, fill the vial up to about 80%.
12. Weigh the sample and solvent (note that diethyl ether is very volatile).
13. Close the vial with a cap containing a septum.
14. Label the vial (contents, date, sample number, etc.) with a permanent marker.
15. Set the vial(s).
16. Check the remaining amount (large bottle closest to the injector port) of cleaning solvent (usually acetone) and refill if necessary.
17. Push the autosampler arm slightly and press the **【RESET】** button on the auto injector.
 - ※ The position of the vial is automatically fine-tuned. If you forget this operation, you will get an autosampler error when executing the batch.

2.5. Batch file creation

A batch file is only necessary in order to perform a sequential analysis (see section 3.2). If a single analysis (see section 3.1) will be performed, this section can be skipped.

1. Open the **【バッチ】** tab of the **【データエクスプローラ】**.
2. Double-click the batch file you want to edit.
3. Click **【ファイル(F)】** → **【バッチファイルに名前を付けて保存(A)】**.
4. Add **【行の追加】** or remove **【行の削除】** rows depending on the number of samples.
 - ・ Right-click to copy **【コピー】**, add **【追加】**, insert **【挿入】**, delete **【削除】** lines, etc.
5. Enter each item
 - ・ バイアル番号 : The vial number on the autosampler arm, starting from the vial closest to the solvent bottle. For standard samples, analysing each sample twice and averaging out improves precision.

- ・ サンプル名 : Enter a detailed name for each sample, including the date, contents, etc. (e.g. 171230Run13)
 - ・ サンプル ID : Short identifier for the sample, can be left blank.
 - ・ サンプルタイプ : Select the sample type: 【0 : 未知】 unknown sample, 【1 : 標準】 standard sample (used to make a calibration curve). When selecting 【1 : 標準】 , 3 options appear:
 - 検量線の初期化 : Calibration curve initialisation, i.e. the first sample of the curve, denoted as 【1 : 標準(I)】 .
 - 検量点の追加 (平均) : Addition of calibration points, i.e. the other samples used for making the curve, denoted as 【1 : 標準】 .
 - 検量点の置き換え : Replacement of calibration points, i.e. samples used to replace previous wrong or imprecise samples on the curve, denoted as 【1 : 標準(R)】 .
 - ・ 解析の種類 : Can be left as is.
 - ・ メソッドファイル : Select the method file which will be used for the analysis.
 - ・ データファイル : Enter the data file name to which the results will be saved. Name it such that you can see the date, contents, etc. (e.g. 171230Run13)
 - ・ レベル番号 : The level number corresponds to the concentration levels of standard samples, it can be left at 1 for unknown samples. It is easiest to assign the level numbers in order of increasing concentration.
 - ・ 注入量 : The injected volume, it depends on the sample concentration, but about 0.5 is usually enough.
 - ・ チューニングファイル : Leave blank (uses the latest auto-tuning result).
6. Click the 【上書き保存】 button.

3. Analysis

3.1. Single analysis

Single analyses are best suited for gas injection, which is performed with the gas sampler.

1. Click 【データ採取】 on the 【分析】 assistant bar.
2. Double click the method file to be used in the data explorer.
3. Click 【サンプル登録】 on the 【データ採取】 assistant bar.
4. Enter the sample info in the 【サンプル登録】 window, and click 【OK】 .
 - ・ サンプル名(S) : Sample name
 - ・ サンプル ID(I) : Sample ID
 - ・ データファイル(D) : Data file to which the results will be saved to
 - ・ バイアル番号(V) : Vial number (usually set to 1 as there is only one sample to be analysed)
 - ・ 注入量 : Injection volume
5. Click 【準備】 on the 【データ採取】 assistant bar. The sample information is sent to the device, and the device is prepared for analysis, which takes a few minutes. As soon as the device is ready,

【GC : 準備完了】 and 【MS : 準備完了】 are highlighted in green.

6. Make sure that the knob of the gas sampler is set to 【LOAD】 , and mount the injection tank onto the sampler's 【IN】 port.
 7. Open the tank valve and wait for the pressure to drop to atmospheric level. That will purge the carrier gas (and previous sample) from the sampler, and ensure that the sample is not diluted.
 8. Turn the knob to 【INJECT】 .
 9. Once the 【STATUS】 , 【TEMP】 and 【FLOW】 lights on the GC turn green, press 【START】 on the GC control panel.
- ※ Leave the sampler knob on 【INJECT】 during the analysis. Don't turn it back to 【LOAD】 .

3.2. Sequential analysis

Sequential analyses are best suited for liquid injection, which is performed with the auto-injector.

1. On the batch file edit screen, click the 【開始】 icon on the 【バッチ処理】 assistant bar.
2. The message 【分析終了後エコモードに入りますか】 is displayed, select 【はい/いいえ】 .
 - ・ エコモード : The eco-mode saves power and carrier gas consumption during standby, after the batch has been processed. To cancel, click 【解除】 on the 【エコロジーモード】 screen. After cancellation, the device returns to the settings preceding the eco-mode. You can also enter the eco-mode by clicking the eco-mode icon in the 【装置モニタ】 .
3. Press the 【START】 button on the auto-injector.

3.3. Qualitative analysis

3.3.1. Data file reading

1. Open the 【データ】 tab of the 【データエクスプローラ】 .
2. Double-click the data file you want to display.

3.3.2. Mass spectrum display

1. Drag the area you want to display to enlarge it.
 - ・ If you want to restore the original or the previous display, right-click and select 【拡大を元に戻す】 or 【拡大を初期状態に戻す】 .
 - ・ Magnify in a way that both the peak top and baseline fit within the window.
2. Place the mouse pointer on the peak top and double-click to display the pointer.
 - ・ To fine-tune the pointer position, click the 【スキャン】 arrows and move the pointer left or right.
 - ・ When the mass spectrum for the peak top is red, the peak is saturated. In this case, the intensity ratio is different from the target component's spectrum, so click the 【スキャン】 arrows to adjust the pointer position and select a mass spectrum which is entirely black.
3. Click the spectrum subtraction button 【スペクトルの減算】 on the toolbar.
4. Double-click in the analysis curve's background, far enough to the side of the peak.

3.3.3. Similarity search

1. Click the 【シミラリティ検索】 icon on the 【定性処理】 assistant bar.
2. Check the similarity search results.
 - Substances with high spectral intensity ratio similarity are displayed starting from the top (the larger the 【類似度】 number, the higher the similarity).
 - Since compounds have various names, there are times when you cannot find the name you usually use. You may check by enlarging the column width of 【化合物名】 , or by looking at the simple molecular structure diagram displayed in the lower mass spectrum window.
 - Check the desired compound when entering the search results in the spectrum processing table.
 - After confirmation, click the 【ターゲットスペクトルをスペクトル処理テーブルに登録】 button (register the target spectrum) in the spectrum processing table to register the mass spectrum.
 - Close the 【シミラリティ検索結果】 screen.

3.3.4. Spectrum processing table

1. Click the 【定性処理テーブル】 icon on the 【定性処理】 assistant bar.
2. Maximize the window.
3. Double-click 【完了】 in the first row of the spectrum processing table to open the 【シミラリティ検索結果】 screen for each spectrum.
4. After checking the table, close the 【シミラリティ検索結果】 screen.
 - To edit the compound name, select the line and click 【化合物名の編集】 in the 【編集】 menu of the 【定性処理テーブル】 . Enter the compound name on the displayed 【化合物名の編集】 screen and click 【OK】 .
5. Close the 【定性処理テーブル】 .

3.3.5. Data file saving

1. Click save 【上書き保存】 on the toolbar.
2. Repeat steps 3.2.1-3.2.5 for each sample.

3.4. Quantitative analysis

A general outline of the quantitative analysis is given below.

Firstly, perform a qualitative analysis on the sample containing the component to be quantified, and register the retention time and mass spectrum of the target component in the spectrum processing table. The same method file is used for both analyses, thus the analysis conditions are the same for both as well. Then, prepare 3 to 6 standard samples with different concentrations, depending on the accuracy of the calibration curve to be obtained. Next, create a calibration curve according to the correspondence between the different concentrations and the detection intensity (peak area/height). Finally, obtain the target component concentration in the unknown sample using the prepared calibration curve.

3.4.1. Compound table creation

A compound table is used to quantify samples which will be/have been collected using the MS in 【スキャン】 mode. For samples which have been collected in 【SIM】 mode (which yields higher precision results), a SIM table must be created instead (see section 3.3.2).

1. Start the 【GCMS 再解析】 program and click the 【化合物テーブル作成】 icon on the 【ポストラン】 assistant bar.
2. From the data explorer, double-click the data file that saved the spectrum processing table of the target component(s).
3. Click the 【新規作成ウィザード】 icon on the 【化合物テーブル】 assistant bar.
4. On the 【化合物テーブルウィザード 1/7】 screen, select 【現在のスペクトル処理テーブルを使う】 and click 【次へ】 .
5. On the 【化合物テーブルウィザード 2/7】 screen, click 【次へ】 .
6. On the 【化合物テーブルウィザード 3/7】 screen, select a row in the table, check the mass spectrum of each component, and click 【次へ】 .
7. On the 【化合物テーブルウィザード 4/7】 screen, enter parameters such as the type of calibration curve 【検量線の種類】 and quantification method 【定量法】 , and click 【次へ】 .
 - ・ 定量法(Q) : Select the absolute calibration curve method 【絶対検量線法】 . The internal standard method 【内部標準法】 can also be used.
 - ・ 使用データ(B) : Type of detection intensity data to be correlated with concentration, 【面積】 area, or 【高さ】 height. In general, area should be used.
 - ・ 最大レベル数(L) : Number of standard samples prepared, i.e. number of concentration levels for creating a calibration curve.
 - ・ 検量線の種類(C) : Curve type, 【直線】 straight line, 【折れ線】 broken line connecting all points, 【二次式】 parabola, 【三次式】 3rd order polynomial, 【平均係数】 average coefficients curve.
 - ・ 原点通過(O) : Passage through the origin, 【通さない】 do not force through the origin, 【原点を通す】 pass through the origin, 【原点を通す (折れ線)】 pass through the origin (broken line).
 - ・ 重み付け(R) : Weighting for the regression.

- ・ 濃度単位(U) : Concentration unit
 - ・ 濃度値のフォーマット(F) : Set the appropriate concentration value format by using one of the following two options: 【小数点以下桁数】 number of digits after the decimal point, 【有効桁数】 number of significant figures.
8. On the 【化合物テーブルウィザード 5/7】 screen, set the concentration 【濃度】 and measured ions, and click 【次へ】 .
 - ・ 標準試料量 : Concentrations of the standard samples. If it is different for each substance, it can be corrected even after creating the wizard.
 - ・ 確認イオン数 : Enter the number of confirmed ions used for peak identification (1-2).
 - ・ Remember the correspondence between the concentrations entered here and the level number. It is easy to remember if the concentrations are arranged in ascending order. Concentration and level number correspondence will be required later when creating a batch file for sequential analysis.
 9. On the 【化合物テーブルウィザード 6/7】 screen, set the type of each component 【ターゲット成分 (Target)/内部標準成分(I.S.)】 , compound name, target ion, and confirmation ion, enter the information for each compound, and click 【次へ】 .
 - ・ Switch the compound displayed by changing the compound ID 【化合物 ID(I)】 .
 - ・ To change the ion type, click the cell of the type you want to change and select target ion 【ターゲットイオン】 , confirmation ion 【確認イオン】 , or do not use 【使用しません】 .
 - ・ The table columns indicate the ion mass【質量】and relative intensity【相対強度】 , respectively.
 - ※ One of the heaviest ions shall be the target ion (parent ion), because the ions which have the highest mass usually offer the best precision. In addition, 1 or 2 confirmation ions (child ions) are needed for confirmation.
 - ※ If you select 【使用しません】 for unnecessary ions, the accuracy will increase.
 - ※ For example, when the relative intensities are 1: 100, 2: 66, 3: 34, 4: 33, as the 3rd and 4th intensities are similar, the 3rd ion does not need to be detected.
 - ※ Confirmation ions should be as high in mass as possible.
 10. On the 【化合物テーブルウィザード 7/7】 screen, click 【完了】 .
 11. Click 【表示】 (view) to exit the edit mode.
 - ・ The compound table goes into display mode. If you want to edit again, click 【編集】 to enter edit mode.
 - ・ The concentrations can be set a posteriori using the edit mode.
 12. Click the 【化合物テーブルの保存】 icon on the 【化合物テーブル】 assistant bar.
 - ・ The method file used for qualitative analysis is selected.
 13. Click 【保存】 .
 - ・ A quantitative method for scan mode is created.
 - ・ If you want to keep the method file for qualitative analysis as it is, save this file with a different name.

3.4.2. SIM table creation

A SIM table is used to quantify samples which will be/have been collected using the MS in **【SIM】** mode. The **【SIM】** mode allows for higher precision results than the **【スキャン】** mode. It is not necessary to create such a table if all samples will be/have been collected in **【スキャン】** mode.

1. Click the **【MS テーブルの自動作成[COAST]】** icon on the **【化合物テーブル】** assistant bar.
2. Enter the file name and click **【保存】** . [Method file name saved earlier]_SIM is fine.
3. Maximise the **【MS テーブルの自動作成(COAST)】** screen.
4. The SIM table will be created automatically, so check the chromatogram and SIM table, and if necessary, correct it by referring to the following correction procedure.
 - In order to obtain sufficient accuracy, it is necessary that there are 20 or less m/z elements in one row (group). Modify the SIM table as needed.
 - When dividing groups (e.g. group 3 is divided into two groups) :
 - i. Click the table's third row.
 - ii. Right-click on the table and select **【行の挿入】** .
 - iii. Click the inserted row and drag your mouse on the chromatogram to enlarge the part which you want to separate.
 - iv. Click the peak where the compound name is displayed in the vicinity of its centre to divide group 3 into two groups.
5. After finishing, click **【OK】** .

3.4.3. Calibration curve

If the standard samples have already undergone sequential analysis and the results have been saved to data files, the calibration curve can be created straightaway. Otherwise, go back to sections 2.5 and 3.1, create a batch file and perform a sequential analysis before creating a calibration curve as indicated below. When creating the batch file, make sure to select the method file containing the compound or SIM table created before.

1. Click the **【検量線作成】** icon on the **【ポストラン】** assistant bar.
2. Double-click the method file used in the sequential analysis, from the data explorer.
3. Select a compound in the compound table and click on the data file for each level.
 - Check the prepared calibration curve and chromatogram.
 - If peak identification/integration is bad, perform manual identification/integration.
 - If, for one or several of the concentration levels, the peak of the target ion is saturated (flat top, red colour), edit the compound table and select another ion which is not saturated (one of the verification ions can typically be used as a new target ion).
 - If the samples have been analysed before creating the table, the data files need to be manually added to their corresponding levels (right-click → **【追加(A)】**).
4. Click save on the toolbar once you have obtained the desired calibration curve to save the method

file.

3.4.4. Quantitative result

The steps written in *italic* below are only necessary to evaluate samples which have been analysed before the calibration curve was created, or to re-evaluate samples after the calibration curve has been modified. If the sample to be quantified has not yet been analysed, create a batch file (see section 2.5) which uses the method file containing the calibration curve created before, and run a sequential analysis (see section 3.1), before proceeding to step 8.

1. Click the **【バッチ処理】** icon on the **【ポストラン】** assistant bar.
2. Create a new batch file by clicking **【ファイル(F)】** → **【バッチファイルの新規作成(N)】** .
3. Click the **【データファイルの選択】** icon on the **【バッチ処理】** assistant bar.
4. Select the data files to be (re)evaluated and click  to add them to the list of files to be (re)evaluated. Once all the files which need to be (re)evaluated are on the list, click **【OK】** .
5. In the newly created batch file, make sure that the method file containing the calibration curve is assigned to the samples being (re)evaluated.
6. Save the batch file under a new name.
7. Click the **【開始】** icon on the **【バッチ処理】** assistant bar.
8. Click the **【定量処理】** icon on the **【ポストラン】** assistant bar.
9. Double-click the data file to be displayed.
10. Click the **【結果】** tab of the compound table view, the reagent concentrations in the evaluated sample are displayed in the **【濃度】** column.
11. Save the data file containing the results.

4. Device shut down

4.1. Vacuum pump shut down

1. Click the **【真空系の起動・停止】** icon on the **【分析】** assistant bar.
2. Click **【自動停止】** .
 - The ion source will be cooled down, this usually takes about 20-30 min.
3. Once **【完了】** is displayed, click **【閉じる】** .

4.1. Main body shut down

1. Close the **【GCMS 解析】** program, as well as any other open programs.
2. Turn off the computer, MS, and GC, in that specific order.
3. Close the helium supply.

Maintenance

1. Column replacement

The instructions written in *italic* below are only relevant if a new column is being installed for the first time. The items written in *italic* are also only needed in that case.

1. Prepare the required items.
 - Capillary column to be used
 - Acetone
 - Gauze (キムワイプ)
 - Chemical safety goggles
 - Nitrile rubber gloves
 - *Scissors (for the tape)*
 - The GCMS toolbox where the following items can be found
 - Spanner : $\frac{3}{16} \times \frac{1}{4}$ inch
 - *Vespel ferrules*
 - *Nuts*
 - *Yellow tape*
 - *Column mounting jig (for INJ, the short one)*
 - *Column mounting jig (for MS, the long one)*
 - *Column cutter*
2. Stop operating the GCMS, and turn it off.
3. Put the goggles and gloves.
 - ※ The GCMS' analysis accuracy can be affected even by trace amounts of sebum. Try to keep the apparatus as clean as possible.
4. Pull the lever in the lower right of the oven door to open the oven.
5. Use a $\frac{1}{4}$ inch spanner to remove the nut on the INJ side.
6. Use a $\frac{1}{4}$ inch spanner to remove the nut on the MS side.
7. Remove the installed column from its hanger and store it in its box.
8. *Pass the nut followed by the vespel ferrule through the INJ side of the column to be used.*
 - ※ *The column's orientation does not matter. Adjust it such that it fits nicely inside the GC.*
 - ※ *For the vespel ferrule, place the taper (narrow tip) towards the nut.*
9. *Pass the column through the column mounting jig (for INJ, the short one).*
10. *Tighten the column mounting jig with the column's tip protruding by at least 1 cm.*
 - ※ *Use a $\frac{1}{4}$ inch spanner and lightly tighten until the column does not move.*
 - ※ *The vespel ferrule is soft and easy to seal, but it needs to be retightened after heating due to heat shrinkage (described later).*
11. *Cut the protruding part of the column with the column cutter.*
12. *Stick tape to the end of the nut and the column to mark and fix the nut's position.*

- ※ *Use tape that does not leave adhesive components on the column whenever possible.*
- ※ *The jig's purpose is to make the distance between the nut and the connection part of the INJ or MS accurate. This length determination is important.*
- 13. *Remove the column and nut from the jig.*
- 14. *Pass the nut and ferrule on the MS side in the same way as on the INJ side.*
- 15. *Fix the column to the jig (for MS, the long one), cut the tip of the column in the same way as on the INJ side, and stick a positioning mark.*
- 16. *Wipe off the dirt on the tip of the column to be used (from tip to nut, on both sides) with gauze (キムワイプ) soaked in acetone.*
 - ※ *During this operation, the positioning mark is likely to shift, so be careful.*
- 17. *Attach the column to the device.*
 - ※ *Tighten the nuts with the positioning marks stuck against them.*
 - ※ *Tighten first by hand, then tighten one full revolution (360°) with a ¼ inch spanner.*
 - ※ *If the ferrule is already fixed to the column (when installing a used column), tighten first the nuts by hand, and then about 20° to 40° with a spanner.*
- 18. *Remove the positioning mark and close the oven.*
- 19. *Turn on the GC, MS, and computer.*
- 20. *Start the 【GCMS 分析】 program.*
- 21. *Click the 【環境設定】 icon on the 【分析】 assistant bar.*
- 22. *Double-click 【カラム】 in the 【分析に使用するユニット(U)】 column of the 【環境設定】 window.*
- 23. *To register a new column, first click the 【追加(A)】 button to create a blank row in the registered columns table. Then, enter the column information in the created row.*
 - ※ *To delete a registered column, select a row in the table and click the 【削除(D)】 button.*
- 24. *Select the newly installed column's row, click 【選択(S)】 to set it, and click 【OK】 to close the window.*
- 25. *Then, close the 【環境設定】 window by clicking 【設定(S)】 .*
- 26. *Anneal the column.*
 - ※ *The vespel ferrule may shrink because of the temperature changes in the column oven, causing leakage in the ferrule part. Therefore, raise the temperature of the column oven and sample vaporisation chamber to the analysis temperature, and after cooling, retighten the nuts on both sides with a ¼ inch spanner.*
 - *Make sure the oven door is tightly closed.*
 - *Open the main valve of helium.*
 - *Start the vacuum pump (see section 1.2).*
 - *Raise the 【カラム温度】 and 【気化室温度】 temperatures to the analysis temperature on the operation panel of the GC main unit. For the operation method, refer to GC Control Panel Operation Method.*
 - *After keeping the column at the analysis temperature for a certain period of time (~30min), cool it to room temperature.*

- *After confirming on the monitor that the column has cooled sufficiently, open the oven door and tighten the nuts. The vespel ferrule might be considerably loose, so be careful not to change the column position. If it changes, it is necessary to readjust it with a jig, which is troublesome.*
27. The column replacement operation is complete. However, if air leakage is confirmed either by the vacuum leak check or the auto-tuning results after the replacement operation, it is probable that the column mounting was inadequate. Leakage may happen even a while after replacement. Each time the vacuum system is stopped, annealing is performed, and, if leakage happens, the retightening operation should be repeated.

2. Replacement of consumables

The device counts the number of analyses, and automatically notifies you when consumables need to be replaced.

- Septum : See MS navigator.
- Glass insert : See MS navigator.

GC control panel operation method

※ Each of the GCMS settings is usually controlled by the **【GCMS】** program, but they can also be set through the control panel on the GC main unit. The panel is especially convenient to control the temperature while annealing (when replacing the column) or cleaning the column (while downloading the initial settings onto the device).

※ The upper lamp is a status indicator for each parameter. If it is green, it means that the analysis starts on standby, and if it is orange, it means that it cannot be set.



1. Confirmation of each parameter

1. Press the **【MONIT】** button.
2. The set values for each parameter are displayed on the monitor.

2. Temperature settings

1. Press the **【COL】** button to display the **【カラム温度】** setting screen.
2. Press the **【Arrows】** to move between the key settings. Set the desired heating program (curve) using the **【Numeric keys】** and the **【ENTER】** button.
3. Similarly, you can set the **【気化室温度】** by pressing the **【INJ】** button.

※ When the detector temperature is lowered to about room temperature, the detector turns off automatically. In that case, it can be turned on in the **【真空引き】** (vacuuming) item of the **【GCMS 分析】** program on the PC.

4. Press the **【START】** button to launch the heating program

3. Flow rate setting

1. Press the **【FLOW】** button to set the flow rate.
2. Normally, this setting is not changed here, but is controlled by the method file created above. However, if you want to purge the carrier line immediately, such as when starting up the device, set the flow rate through the control panel. Operation time can thereby be shortened.

※ The flow may be turned off when the device is running (check from the flow rate display value). In that case, you can turn it on by pressing the **【ON/OFF】** button on the **【FLOW】** tab.

A.3 GC-BID manual

GC-BID User Manual

Last updated: 2022/06/15

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Translated and updated by: Rafael Pichler

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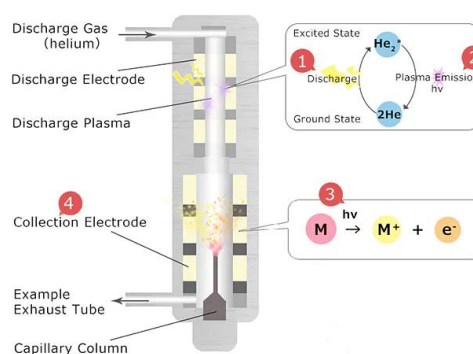
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1. BID (Dielectric Barrier Discharge Ionisation Detector) device

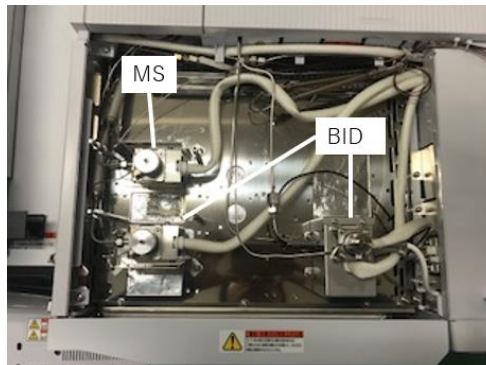
1.1. Short description

The BID is a gas chromatography detector which detects chemical compounds using a plasma discharge. Concretely, helium is first excited by an electric discharge, before returning to its ground state. When doing so, it releases a quantum of energy which will in turn ionise the compound to be detected. Since the emission energy of helium is very high, $E_{\text{em,He}} = 17.7 \text{ eV}$, any compound, except neon ($E_{i,\text{Ne}} = 21.6 \text{ eV}$) and helium itself ($E_{i,\text{He}} = 24.6 \text{ eV}$), can be ionised, because $E_{\text{em,He}} > E_i$, where E_i is the ionisation energy of the compound. Moreover, the detector's minimal detectable concentration is of the order of 0.1 ppm, which is extremely sensitive (100 times lower than that of TCD and half that of FID). Therefore, it is even possible to detect trace components.



1.2. Device connection

Separate lines for the GC-BID and GC-MS are prepared.





Unlike the GC-MS, the GC-BID has a generation line called a helium combustion tube. This combustion tube consists of a helium generation unit and an HP2.

In addition, **high-purity helium** is used for the GC-BID. Be careful because it is different from the helium used for the GC-MS!



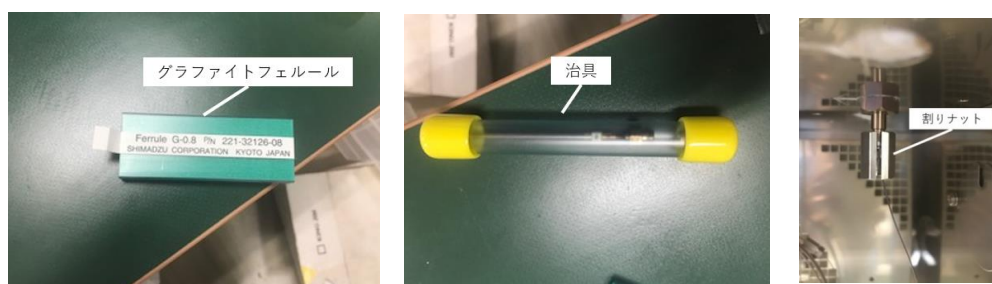
2. Preparation

2.1. Column installation

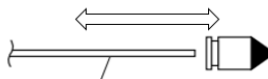
※ The steps written in *italic* below are only necessary when installing a new column for the first time. For columns on which graphite ferrules are already installed, they can be skipped.

※ The detailed installation manual is saved in [【\\Baiman\share\Research Groups\GC\GC-BID】](#), so please refer to it if you do not understand the procedure. In addition, more installation details are given in the maintenance guide (see section 2.4 on how to access it).

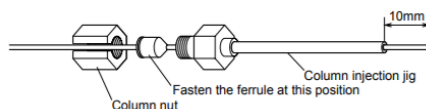
- ① *Prepare a column, two G-0.8 graphite ferrules 【グラファイトフェルール】, a jig 【治具】, and a split nut 【割りナット】 (pictured below).*



- ② *Remove the wire from the graphite ferrule, deburring 2-3 times through the ferrule.*



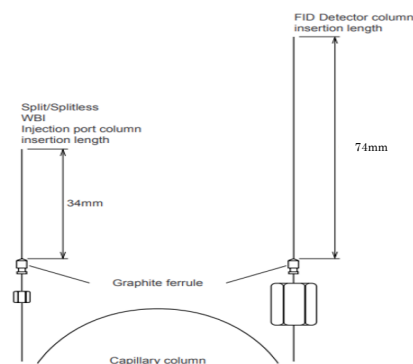
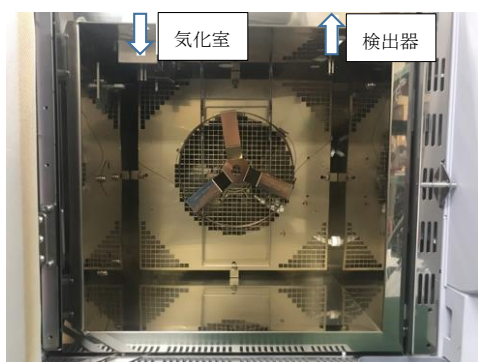
- ③ *Thread both ferrules on the column, with their pointed ends towards the column tips (see the figure in ⑤ below).*
- ④ *Fix the graphite ferrule to the column using a jig, a split nut, and spanners of 6 and 10 mm. The ferrule shall be tightened such that it does not move when the column is lightly shaken, but does move when pulled on by hand. On the video, Mr. Kubo of Shimadzu Access tightens about 60 to 90°, 11 times.*
- ⑤ *Position the ferrule on the vaporiser side at a distance of 34 mm from the column tip, and the one on the detector side such that it is at about the same distance from the tip as the jig length (74 mm).*



- ⑥ *Make sure that the MS detector column connection is sealed (N.B. This seal 【密栓】 can be used repeatedly).*



- ⑦ Remove the BID seal (made of a graphite ferrule and a split nut) from the BID vaporisation chamber 【気化室】 and detector 【検出器】 entrances using a 10 mm spanner. Store the removed ferrules (used for sealing) separately from the new ferrules.
- ⑧ Wipe the column tips (ahead of the ferrules) with a 【キムワイプ】 paper towel soaked in acetone.
- ⑨ Attach both sides of the column with split nuts. Tighten them as much as possible by hand, and then tighten an extra 90° with a 10 mm spanner.



↑This figure is slightly wrong: the vaporisation chamber also has a big nut.

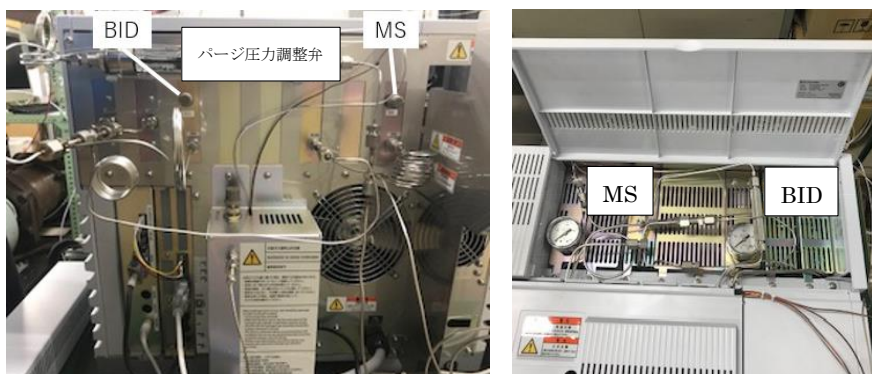
※ The BID uses a plot column, which is packed with particles, and is different from the columns for MS. If this column is used for MS, the particles will flow. Therefore, you cannot use BID columns for MS.

※ Two columns can be attached, but BID and MS columns should not be attached at the same time because they deteriorate quickly. When using BID, it is preferable to remove the MS column and use only the BID column, and when using MS, it is preferable to remove the BID column and attach only the MS column.

2.2. Preliminary operation

※ When the BID is in use, it is desirable to keep the HP2 and generation unit turned on, and the gas cylinder open. However, in order to reduce helium consumption, the gas supply is closed after use.

- ① Open the **G1 helium** gas cylinder, and set the secondary pressure to 0.6 MPa.
- ② Adjust the BID purge pressure with the purge pressure adjustment valve 【ページ圧力調整弁】 on the back of the GC. If the sample is a liquid, set it to 0 kPa, and if it is a gas, set it to 20 kPa during preliminary operation. After that, for the first analysis, it will be set to 100 kPa, and, if stable data can be obtained, it will be reduced again to about 20 kPa.
- ※ This purge gas is used to extrude the sample gas from the manual sampler.
- ③ Check that the MS purge gas pressure is set to 0 kPa, i.e. the MS purge adjustment valve on the back of the GC should be completely closed.



- ④ Wait for **at least 2 hours** before starting the generation unit.
- ⑤ If liquid samples are going to be analysed, the auto-injector needs to be installed on the BID injection port. If the auto-injector is installed on the MS injection port (which is usually the case), follow the instructions below to move it to the BID injection port.
- ⑥ Lift the auto-injector from its support sticks and put it on the MS.
- ⑦ Remove the GC's plastic cover.
- ⑧ Use an 8 mm spanner to remove the 4 support sticks from around the MS injection port and reattach them around the BID injection port. Be careful not to lose the washers that come with each stick.
- ⑨ Put back the plastic cover, and move the injection port cover from the BID port to the MS port.
- ⑩ Install the auto-injector on the BID injection port by sliding it onto the support sticks.

2.3. Device start up

※ Lab Solutions is the analysis software for the GC-BID. Do not launch it with the hardware for GC-MS. Make sure that the column is for GC-BID and is attached to the GC-BID path, as described above, before starting Lab Solutions.

- ① Turn on the GC, MS (because GC and PC are connected via the MS), and PC, in that order.
- ② Double-click the 【Lab Solutions】 icon on the desktop.

- ③ The login screen will appear, but leave the user ID as **【Admin】** and the password blank, and click **【OK】** to log in.
- ④ The main screen will open, click on the **【装置】** icon.
- ⑤ Double-click the icon of the device to be used (here, **【GCMS-BID】**). The computer communicates with the device, and an analysis **【分析】** program is launched.



2.4. Accessing the maintenance guide

- ① In the **【分析】** program, click **【メンテナンスガイド】** in the **【メイン】** assistant bar.
- ② **【島津 GC メンテナンスヘルプ】** will open, click on **【GC-2010/2010Plus】** .

After that, select the desired instructions. For example, column mounting is explained in detail.

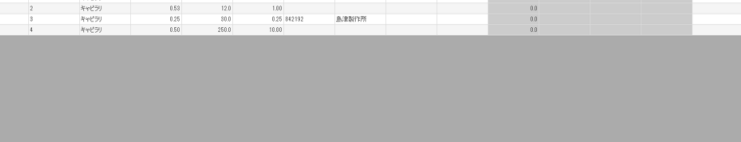
2.5. Column and analysis line settings

The device configuration, including column and analysis line settings, is set on the **【環境設定】** screen. The steps written in *italic* below are only necessary when a new column is installed for the first time.



- ① Click the **【環境設定】** icon on the **【メイン】** assistant bar. The **【環境設定】** window opens.
- ② Here, elements can be added to or removed from the analysis line. If liquid samples are going to be analysed, they will be injected using the auto-injector. Thus, the auto-injector must be added to the analysis line. This can be done by selecting the auto-injector **【オートサンプラー】** in the left **【有効なユニット(A)】** column, and clicking the blue arrow to add it to the right **【分析に使用するユニット(U)】** column.
- ③ Double-click **【カラム】**  **カラム** in the right column. The **【分析ライン 1】** window opens.
- ④ Click **【カラム一覧参照(R)】** . The **【カラム一覧】** window opens.
- ⑤ *Right-click, and click **【行の追加(W)】** .*
- ⑥ *Fill in each item in the newly added line. The entry method explained below uses the Micropacked ST column as an example.*
 - (a) 名称 : Name
 - (b) カラム No. : Column number
 - (c) タイプ : Type, select **【キャピラリー】** or **【パッキド】** . *Set it to **【キャピラリー】** when using a packed column with dummy settings.*
 - (d) 内径 : Inner diameter
 - (e) 長さ : Length
 - (f) 液相の膜厚 : Liquid phase film thickness

*Enter (d), (e) and (f) as described in the instruction manual. However, in the case of this column, they are written in **【Notes on device connection】** in the instruction manual. Note that you need to enter a value that is **different from the actual column size** as shown! Read the instruction manual properly!*



名前	材料ID	材料名	タイプ	Density (mm)	Elastic Modulus (GPa)	Poisson's Ratio	Thermal Expansion Coefficient (1/K)	Thermal Conductivity (W/mK)	Specific Heat (J/kgK)	Material Type	Material ID	Material Name	Material Type	Material ID	Material Name
1	CSP100K-118	CSP100K-118	Steel	0.00785	207.0	0.30	11.7	45.0	470.0	Steel	1	CSP100K-118	Steel	1	CSP100K-118
2	RT-100	RT-100	RT-100	0.00785	207.0	0.30	11.7	45.0	470.0	RT-100	2	RT-100	RT-100	2	RT-100
3	RT-100	RT-100	RT-100	0.00785	207.0	0.30	11.7	45.0	470.0	RT-100	3	RT-100	RT-100	3	RT-100
4	MECHPACKED	MECHPACKED	MECHPACKED	0.00785	207.0	0.30	11.7	45.0	470.0	MECHPACKED	4	MECHPACKED	MECHPACKED	4	MECHPACKED

- ## 2.6. GC-2010 start-up parameters

- ① Click **【環境設定】** on the **【メイン】** assistant bar, the **【環境設定】** window opens.
- ② Double-click **【GC-2010】** in the **【分析に使用するユニット】** column, the **【GC-2010】** window opens.
- ③ **【START TIME】** can be set. **【START TIME】** controls the temperature and flow rate at start-up, but if it is set to 0, the detector will be damaged, so the gas is purged first. The purge time is usually 10 to 15 minutes. If the machine is left running all night and you want make measurements on the next day, you can set it to 5 minutes.

- N.B. What is the start time? In order to prevent damage to the BID cell, the detector temperature does not rise immediately when the GC is started, but after the air in the BID cell is completely replaced with the carrier gas/detector gas.

Good method files have been developed for the analysis of various compounds. They can be used without modification for the analysis of these compounds, and potentially for others as well (validation test needed). The files have already been calibrated for certain compounds of interest, so check the existing calibration curve(s) within the relevant file before performing a new calibration. They are named according to the compounds they were developed for and can be found in

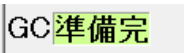
【[\\baiman\share\Research Groups\GC\GC-BID\Method_files](#)】 and on the GC computer in 【C:\Data\[The folder corresponding to their date of creation]】. These files should not be directly modified, but rather copied under a new name and then modified, if needed.

- ① Open the 【メソッド】 tab of the 【データエクスプローラ】.
- ② Open the method file you want to edit, by double-clicking it.
- ③ Click 【ファイル(F)】 → 【メソッドファイルに名前を付けて保存(A)】.
- ④ Make sure that 【詳細】 is selected in the device parameter view 【装置パラメータビュー】.
- ⑤ Right-click in the device parameter view and verify that 【オープン温度プログラム変更とデータ採取時間のリンク(L)】 is selected. Now, the detector turn-off time 【終了時間(M)】 (see 【BID1】 tab) will be automatically set according to the oven temperature program 【カラムオープン温度プログラム(U)】 (see 【カラム】 tab).
- ⑥ Set the column oven parameters in the 【カラム】 tab.
 - ・ カラム温度(T) : Initial temperature of the column oven
 - ・ カラムオープン温度プログラム(U) : This table allows the analysis temperature program to be set. Set the program in accordance with the column's characteristics and the target samples to be analysed. The following items need to be specified (several lines can be entered).
 - ・ レート : Heating rate [°C/min]
 - ・ 温度 : Target temperature [°C] (the first target temperature corresponds to the initial temperature)
 - ・ ホールド時間 : Time interval during which the sample is kept at the target temperature [min]
- ※ For more details about analysis temperature programs, refer to further literature (e.g. Shimadzu's Application Data Sheet (Chromatogram Micropacked ST.pdf), stored in 【[\\baiman\share\Research Groups\GC\GC-BID](#)】).
- ⑦ Set the detector parameters in the 【BID1】 tab.
 - ・ 検出器温度(T) : Detector (BID) temperature, set it between 150 °C and 300 °C, and at least as high as the maximum target temperature reached by the temperature program. For more details about the detector temperature, refer to other documents (e.g. Shimadzu's Application Data Sheet).
 - ・ 終了時間(M) : Detector turn-off time, it is automatically set in function of the temperature program if 【オープン温度プログラム変更とデータ採取時間のリンク(L)】 is selected.
 - ・ 遅れ時間 : Delay time, this allows you to start to save the analysis results from a later time than the beginning of the analysis. It can be useful, for example, to exclude the solvent peak from appearing in the resulting chromatogram. It is important to note, however, that this delay time only affects the time at which the results start to be saved, it does not turn off the detector.
 - ・ 流量プログラム(G) 放電ガス : This table allows a discharge gas flow rate program to be set, but the flow rate is usually kept constant at 50 mL/min.
- ⑧ Set the injector parameters in the 【SPL2】 tab.

- 気化室温度(T) : Vaporisation chamber (injector) temperature, not so important when injecting gases, as they do not need to be vaporised. It is usually set to 200 °C. However, when injecting liquids, make sure that this temperature is set above the sample's boiling point.
- 注入モード(M) : Injection mode, can be set to 【スプリット】 or 【スプリットレス】. Select 【スプリット】 for capillary columns.
- ※ A split consists in using only a part of the total carrier gas flow for analysis, while the rest is discarded. This is done because capillary columns have very small inner diameters. The split ratio, which is described later, is the discarding ratio. For example, if the split ratio is 30, 30 units are discarded for 1 which is let flowing.
- 制御モード(F) : Control mode, can be set to 【圧力】 (pressure) or 【線速度】 (linear velocity). In pressure control, the back pressure is kept constant, while in linear velocity control, the linear velocity in the column is kept constant and the carrier gas flows steadily. In pressure control, the holding time varies as the gas temperature changes during heating. However, when velocity is controlled, the carrier gas always flows at a constant volume flow rate. Therefore, in general, it is better to select 【線速度】 control.
- ※ Pressure control is used when, for example, the reference application sheet gives a pressure control program which keeps the flow rate constant.
- 圧力(P) : Pressure, it is determined by 【カラム流量(C)】 when in velocity control mode, and by the 【気化室プログラム(J) 圧力】 table when in pressure control mode, so leave it as is.
- 全流量(O) : Total flow rate, automatically calculated by 【カラム流量(C)】 + 【パージ流量(U)】 + 【カラム流量(C)】 × 【スプリット比(I)】 , so leave it as is. Once the settings are complete, it must be **higher than 15 mL/min**.
- カラム流量(C) : Column flow rate, linked to 【線速度(L)】 , so set either one or the other.
- 線速度(L) : Linear velocity, linked to 【カラム流量(C)】 , so set either one or the other. The linear velocity is the speed at which the gas travels through the column. It should be **between 20 and 40 cm/sec**.
- パージ流量(U) : Purge flow rate, it is set to 3 mL/min and does not change. The purge flow prevents sample gas leaking through the septum towards the detector from being unintentionally detected and affecting the analysis.
- スプリット比(I) : Split ratio
- 気化室プログラム(J) 圧力 : In pressure control mode, this table allows the pressure program to be set. This program should be set in accordance with the temperature program, in order to maintain a constant flow rate throughout the analysis. Moreover, the total times of both programs should match. This is typically done by referring to a reference application sheet. The following items need to be specified (several lines can be entered).
- レート : Pressure increase rate [kPa/min]
- 圧力 : Target pressure [kPa]
- ホールド時間 : Time interval during which the sample is kept at the target pressure [min]

- ⑨ Click the **【上書き保存】** icon.
- ⑩ Click **【ダウンロード】** on the right side of the device parameters view to send the method file to the device.

2.8. GC startup procedure

- ① Click the **【GC 起動】** button in the **【データ採取】** assistant bar.
- ② Wait for the GC's status to be **【準備完】**. 
- ③ Check that the BID settings are correct, and that the detector gas does not contain any impurities (④ to ⑦).



- ④ Press the **【DET】** key on the GC main unit operation panel multiple times to display the BID detector setting screen. Make sure the temperature of the detector is above 150 °C.
- ⑤ Check that the plasma is turned on. If not, turn on the plasma by pressing the **【PF1】** button, which should show **【点灯】** above it.
- ⑥ Remove the screw on the front of the detector.
- ⑦ Look into the detector through the screw holes in ④ and confirm that the plasma is lit on the line. Immediately after replacing the cylinder, this plasma may be blurred. It is highly possible that impurities were mixed in the original line, and the problem is solved by changing the plasma gas flow rate from 50 ml/min to 100 ml/min and continuing the flow for about 1 hour.



2.9. Sample preparation

2.9.1. Gas samples

When preparing gas samples using extremely flammable and/or toxic gases, such as hydrogen (H₂) or carbon monoxide (CO), take proper care not to release those gases inside the experiment rooms. Use a purge system with nitrogen (N₂), or directly release those gases outside the building to ensure that

they are released into the atmosphere and do not pose any safety hazards.

- ① Prepare the required elements.
 - Sample gas (in a tank if unknown mixture, in a gas cylinder if standard sample)
 - Solvent gas (in a gas cylinder, usually N₂ or He)
 - Sample preparation tank (the one with 4 inlets/outlets, 5 shut valves and a needle valve)
 - Vacuum pump
 - Absolute pressure sensor
 - Teflon tubes (a flexible metal tube is necessary for extremely flammable gases such as H₂)
 - Short metal tubes
 - Small injection tank
 - Gauge pressure sensor
 - Two ½ × 9/16 inch spanners
 - One adjustable wrench
- ② Connect the sample gas container to the sample preparation tank, on one of the inlets which are connected to the needle valve, with the appropriate tube.
- ③ Connect the vacuum pump to the sample preparation tank, on the other inlet which is connected to the needle valve, with a Teflon tube.
- ④ Attach the absolute pressure sensor to one of the remaining inlets, using a short metal tube.
- ⑤ Turn on the pressure sensor.
- ⑥ After checking that all the valves are in the appropriate position, vacuum the tank and the connection tube between the tank and the sample gas container.
- ⑦ Once the tank has been vacuumed as much as possible (i.e. $p < 1$ kPa), shut the valve leading to the vacuum pump and turn off the pump.
- ⑧ Fill the tank with sample gas to the desired pressure. Use the needle valve to control the flow rate and reach the desired pressure precisely.
- ⑨ Shut the valve leading to the sample gas container.
- ⑩ Disconnect the sample gas container and connect the solvent gas cylinder to the same inlet (with a Teflon tube). Be careful not to release any toxic or extremely flammable gas into the room.
- ⑪ Vacuum the tube connecting the solvent gas cylinder and the sample preparation tank.
- ⑫ Dilute the sample gas with the solvent gas to the desired concentration ($x_s = \frac{p_s}{p_{\text{tot}}}$). The total pressure must be higher than the atmospheric pressure, and should ideally be as high as possible in order to maximise the number of samples that can be taken from the tank. The current pressure sensor's range is 0-133 kPa, so $p_{\text{max}} = 133$ kPa and $p_{\text{atm}} < p_{\text{tot}} \leq p_{\text{max}}$. Again, use the needle valve to control the flow rate and reach the desired pressure precisely.
- ⑬ Shut all valves and disconnect the solvent gas cylinder, vacuum pump and pressure sensor from the tank.
- ⑭ Leave the tank and wait for diffusion to happen, in order to obtain a homogeneous mixture.

Usually about 1 h is enough time for the mixture to become homogeneous.

- ⑮ Attach the gauge pressure sensor to the small injection tank (with a short metal tube). Be careful as they're a pair with one sensor for -100-100 kPaG and the other for 0-1 MPaG. Use the appropriate one (in general that is the first one).
- ⑯ Attach the injection tank to one of the inlets of the sample preparation tank which is connected to the needle valve (using another short metal tube).
- ⑰ Connect the vacuum pump to the other inlet which is connected to the needle valve.
- ⑱ Vacuum the injection tank and the connection tubing.
- ⑲ Fill the injection tank with about 10 kPaG of the gas mixture.
- ⑳ Shut all valves and detach the small injection tank from the sample preparation tank.
- ※ If there is enough pressure remaining in the sample preparation tank after one sample has been prepared, steps ⑯-⑳ can be repeated to make additional samples.

2.9.2. Liquid samples

Samples should be prepared in the micro-gravity room, where ventilation is possible. Bring all the necessary materials there, and use proper ventilation to avoid breathing in solvent vapours. Depending on the volatility of the solvent used, it might be necessary to prepare the sample in a fume hood, while wearing an activated carbon mask against organic vapours. For example, diethyl ether is extremely volatile ($T_b = 35\text{ }^{\circ}\text{C}$, $p_{v,20^{\circ}\text{C}} = 59\text{ kPa}$), and produces toxic and flammable vapours, therefore, it should always be handled inside a fume hood while a mask against organic vapours is being worn.

- ① Prepare the required elements.
 - Chemical safety goggles
 - Nitrile rubber gloves
 - Chemicals (reagent(s), solvent(s))
 - Sample(s) to be analysed
 - Micro pipette(s)
 - Micro tip(s)
 - Vial(s)
 - Vial septum(s)
 - Vial cap(s)
 - Paper towels
 - Glass pipette
 - Pipette's rubber sucker
- ② Put on the goggles and gloves.
- ③ Put the chemicals into their dedicated glass recipients (these can be found in the large plastic box, new recipients can be found in the cardboard box on the shelf).
 - Pour a small amount of reagent into its dedicated recipient.
 - Pour the required amount of solvent into its dedicated recipient. Solvents such as diethyl

ether and acetone are volatile and evaporate significantly, so about 20 ml shall be used. For other standard sample preparations, the reagent can be taken with a micropipette, so about 10 ml is sufficient. The recipients have a volume of 50 ml.

※ Do not put a pipette (or other tool) directly into the reagent bottle. In general, handle special grade reagents with care.

- ④ Place the septum in the cap (**dark side inside**).
- ⑤ Place the vial and chemical recipients on top of a paper towel.
- ⑥ Weigh the empty vial and tare the scale.
- ⑦ Put the microtip on the micropipette.
- ⑧ Inject the sample into the vial using the micropipette.
 - ※ The target sample concentration is of tens to hundreds of ppm (thousands are also acceptable). Adjust little by little, while taking into account that the minimum weight the scale can detect is 1 mg.
- ⑨ Weigh the sample each time a chemical is injected (know the amount of each chemical).
- ⑩ Attach the pipette sucker to the pipette.
- ⑪ Inject the solvent into the vial.
 - ※ Depending on the sample concentration, fill the vial up to about 80%.
- ⑫ Weigh the sample and solvent (note that diethyl ether is very volatile).
- ⑬ Close the vial with a cap containing a septum.
- ⑭ Label the vial (contents, date, sample number, etc.) with a permanent marker.
- ⑮ Set the vial(s).
- ⑯ Check the remaining amount (large bottle closest to the injector port) of cleaning solvent (usually acetone) and refill if necessary.
- ⑰ Push the autosampler arm slightly and press the **【RESET】** button on the auto injector.
 - ※ The position of the vial is automatically fine-tuned. If you forget this operation, you will get an autosampler error when executing the batch.

2.10. Batch file creation

A batch file is only necessary in order to perform a sequential analysis (see section 3.2). If a single analysis (see section 3.1) will be performed, this section can be skipped.

- ① Click the **【バッチ分析】** button on the **【メイン】** assistant bar.
- ② Click the **【ウィザード】** button on the **【バッチ分析】** assistant bar to launch the batch file creation wizard.
- ③ In the **【バッチテーブルウィザード】** window, enter the items listed below and click **【次へ(N)】**.
 - ・ バッチテーブル(B) : Batch table, **【新規作成】** create new, or **【追加】** add (to the existing table)
 - ・ メソッドファイル(M) : Select the method file which shall be used for the analysis.
 - ・ グループ数(G) : Number of sample groups (usually 1)
 - ・ 未知試料のみ(U) : Unknown samples only

- ・ 標準試料のみ(S) : Standard samples only
 - ・ 標準試料 & 未知試料(K) : Both standard and unknown samples
 - ・ 挟み込みキャリブレーション(C) : Bracket calibration
- ④ In the 【バッチテーブルウィザード – ライン 1 標準試料】 window, enter the items listed below for the standard samples, and click 【次へ(N)】 . Select 【自動番号】 next to the corresponding entries to auto-increment numbers at the end of sample names, IDs and data file names.
- ・ サンプル名(S) : Sample name, enter a detailed name for each sample, including the date, contents, etc. (e.g. 171230Run13).
 - ・ サンプル ID(I) : Sample ID, short identifier for the sample, can be left blank
 - ・ データファイル名 : The name of the data file to which the results should be saved to, choose it such that you can see the date, contents, etc. (e.g. 171230Run13).
 - ・ 検量線のレベル数(N) : The number of concentration levels used for the calibration curve. It is easiest to assign the level numbers in order of increasing concentration.
 - ・ 各レベルの標準試料のバイアル数(L) : The number of samples for each concentration level
 - ・ 同じバイアルからの注入回数(R) : The number of injections (analyses) per vial, analysing each sample twice and averaging out improves precision.
 - ・ バイアル番号(V) : Allows you to set the three following settings for each vial
 - ・ 検量線初期化(A) : Initialisation of the calibration curve
 - ・ レポートの印刷(P) : Print report
 - ・ レポートフォーマットファイル(F) : The name of the file to which the report will be printed
- ⑤ In the 【バッチテーブルウィザード – ライン 1 未知試料】 window, enter the items listed below for the unknown samples, and click 【次へ(N)】 . Select 【自動番号】 next to the corresponding entries to auto-increment numbers at the end of sample names, IDs and data file names.
- ・ サンプル名(S) : Sample name, enter a detailed name for each sample, including the date, contents, etc. (e.g. 171230Run13).
 - ・ サンプル ID(I) : Sample ID, short identifier for the sample, can be left blank
 - ・ データファイル名 : The name of the data file to which the results should be saved to, choose it such that you can see the date, contents, etc. (e.g. 171230Run13).
 - ・ 各グループの未知試料のバイアル数(R) : The number of samples in each group (usually 1)
 - ・ 同じバイアルからの注入回数(R) : The number of injections (analyses) per vial
 - ・ バイアル番号(V) : Allows you to set the two following settings for each vial
 - ・ レポートの印刷(P) : Print report
 - ・ レポートフォーマットファイル(F) : The name of the file to which the report will be printed
- ⑥ In the 【バッチテーブルウィザード – サマリーレポート】 window, the settings for printing a summary report can be entered. Usually, such a report is not necessary, so just click 【次へ(N)】 .
- ⑦ In the 【バッチテーブルウィザード – そのほかの設定】 window, the auto-conditioning settings listed below can be entered. They are usually not necessary, so just click 【次へ(N)】 .
- ・ スタートアップ(S) : Start-up

- ・ ベースラインチェック(C) : Baseline check
 - ・ シャットダウン(H) : Shut-down
- ⑧ In the **【バッチテーブルウィザード – バッチテーブルの保存】** window, enter the items listed below and click **【完了】** .
- ・ バッチファイルを保存する(S) : Check the box to save the batch file
 - ・ バッチファイル名(B) : Enter the name of the newly created batch file, or select the file to be edited.
- ⑨ The batch table created by the wizard is displayed on the screen. However, it may still contain errors, such as two different samples having the same name. Therefore, it is necessary to verify that the following entries are correct for each sample.
- ・ バイアル番号 : The vial number on the autosampler arm, starting from the vial closest to the solvent bottle.
 - ・ サンプル名 : Sample name
 - ・ サンプル ID : Sample ID
 - ・ サンプルタイプ : Sample type, **【0 : 未知】** unknown sample, **【1 : 標準】** standard sample. When **【1 : 標準】** is selected, there are 3 sub-options:
 - 1 : 標準(I) : Calibration curve initialisation, i.e. the first sample of the curve.
 - 1 : 標準 : Addition of calibration points, i.e. the other samples used for making the curve.
 - 1 : 標準(R) : Replacement of calibration points, i.e. samples used to replace previous wrong or imprecise samples on the curve.
 - ・ メソッドファイル : The method file which will be used for the analysis.
 - ・ データファイル : The data file to which the results will be saved (must be different for each sample).
 - ・ レベル番号 : The level number, it corresponds to the concentration levels of standard samples.
- ⑩ Click the **【上書き保存】** button.
- ※ You can add **【行の追加】** or remove **【行の削除】** rows to/from the batch table if necessary.
- ・ Right-click to copy **【コピー】** , add **【追加】** , insert **【挿入】** , delete **【削除】** lines, etc.

3. Analysis

3.1. Single analysis

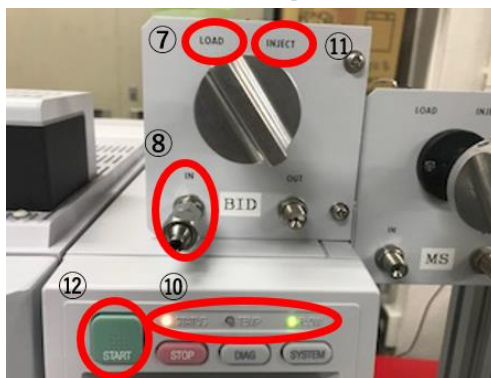
Single analyses are best suited for gas injection, which is performed with the gas sampler. The BID analyses gases at ppm level, therefore samples should be diluted with nitrogen or helium down to a concentration of a few percent.

※ For the **first few analyses** after starting the GC-BID, set the purge pressure to **100 kPa**. Once stable data is obtained, the purge pressure can be lowered to 20 kPa.

- ① Check that both the 【BID1 検出器】 and 【BID プラズマ】 control items are ON in the GC items on the right side of the PC screen.

GC 分析中			
項目	ステータ	単位	制御
SPL2 温度	200.0	℃	
SPL2 圧力	400.0	kPa	
全流量	38.0	mL/min	
パージ流量	3.0	mL/min	☒ ON ☐ OFF
一次圧	596	kPa	
カラム 温度	265.0	℃	
カラムID			
BID1 温度	280.0	℃	
BID1 放電力	50.0	mL/min	
BID1 検出器			☒ ON ☐ OFF
BID1 プラズマ			☒ ON ☐ OFF
キャリアガス	He		☒ ON ☐ OFF

- ② Click the【シングル分析の開始】icon on the【データ採取】assistant bar. The single analysis condition setting window opens.
- ③ Enter the sample name and ID under 【サンプル名】 and 【サンプル ID】 , respectively
- ④ Select the method file to be used under 【メソッドファイル(M)】 .
- ⑤ Under 【データファイル(D)】 , specify the name and save location of the data file which will contain the analysis results.
- ⑥ Enter a number other than 0 in 【バイアル(V)】 . If you enter "0" here, the analysis will only register the baseline, so be careful not to set it to "0".
- ⑦ Click 【OK】 .
- ⑧ Confirm that the window 【データ採取の開始】 is open.



- ⑨ Make sure that the knob of the gas sampler is set to **【LOAD】** , and mount the injection tank onto the sampler's **【IN】** port.
- ⑩ Open the tank valve and wait for the pressure to drop to atmospheric level. That will purge the carrier gas (and previous sample) from the sampler, and ensure that the sample is not diluted.
- ⑪ Turn the knob to **【INJECT】** .
- ⑫ Wait for the **【STATUS】** , **【TEMP】** and **【FLOW】** lights on the GC to turn green.
- ⑬ Click on **【開始】** , the analysis starts.
- ※ Leave the sampler knob on **【INJECT】** during the analysis. Don't turn it back to **【LOAD】** .
- ※ You can go back and forth between the method file view and the chromatogram-only view by pressing **【装置パラメータの表示/非表示】**

3.1.1. End time modification during data collection

- ① Click **【データ採取(A)】** .
- ② Click **【分析時間の変更(C)】** .
- ③ A window for changing the analysis time will open. Enter a new analysis time and click **【OK】** .

3.1.2. Stopping during data collection

- ① Click the **【中止】** icon on the **【データ採取】** assistant bar.

3.1.3. Automatic zero point adjustment using the GC control panel

- ① Press the **【MONIT】** key to display the following monitor main screen.
- ② Press the **【PF3】** key to automatically move the baseline to the zero point.
- ③ Press the **【8】** key to enlarge the graph and the **【2】** key to reduce the graph.
- ④ Use the **【6】** key to advance the graph display time, and the **【4】** key to delay the time.

3.2. Sequential analysis

Sequential analyses are best suited for liquid injection, which is performed with the auto-injector.

- ① Click the **【バッチ分析の開始】** icon on the **【バッチ分析】** assistant bar.
- ※ It is possible to analyse only part of the batch table. To do so, select the rows to be analysed, click the **【バッチ分析の開始】** icon, check **【選行】** , and click **【開始】** .

3.3. Data analysis

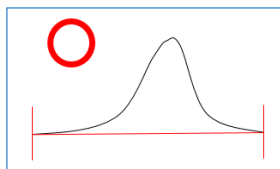
- ① Click the **【解析ツール】** icon in the Lab Solutions main window.
- ② Click the **【再解析】** icon in the analysis tool window.
- ③ Select the data file you want to analyse from the data explorer screen and double-click it, the file's chromatogram is displayed.
- ④ The displayed chromatogram has undergone peak waveform processing, as indicated by the red lines.

- ⑤ Left-click to select a range and enlarge it to check if the waveform processing is performed correctly. By the way, to return from the enlarged display to the original size display, right-click and select **【拡大を元に戻す(U)】**.

※ The procedure to follow when waveform processing is not good is described below (⑥ to ⑧).

- ⑥ Click **【編集】** in **【メソッドビュー】** at the bottom right of the screen.
- ⑦ Click the **【波形処理】** tab.
- ⑧ Change the value of **【Slope (S)】** as necessary. **【Slope】** is the slope of the chromatogram, and the peak is recognized from the time when it exceeds the value specified by **【Slope】** to the time when it drops below it. You can check the processing result when you change the value of **【Slope】** by changing from **【編集】** mode to **【表示】** mode in **【メソッドビュー】**.

The rough processing result is illustrated below.



- ⑨ Click the **【ピークテーブル】** tab in **【結果ビュー】**.
- ⑩ Check if all the target components are detected in the peak table.
- ⑪ Click **【表示】** in **【メソッドビュー】**.
- ⑫ Next, create a compound table. First, click the **【ウィザード】** icon on the **【データ解析】** assistant bar.
- ⑬ The **【化合物テーブルウィザード 1/5】** window opens. In principle, the parameters displayed here are not changed, so just click **【次へ(N)】**.
- ⑭ The **【化合物テーブルウィザード 2/5】** window opens. Select the **【処理】** column of the target compound(s) and click **【次へ(N)】**.
- ⑮ The **【化合物テーブルウィザード 3/5】** window opens. Select the desired quantitative method from **【定量法(Q)】**. The external standard method **【外部標準法】**, which is commonly used, is described here. Set the parameters listed below.
- ・ 使用データ(B) : Type of measured data to be correlated with concentration, **【面積】** area, or **【高さ】** height. In general, area should be used.
 - ・ 最大レベル数(L) : Number of concentration levels used for creating a calibration curve.
 - ・ 検量線の種類(C) : Curve type, **【直線】** straight line, **【折れ線】** broken line connecting all points, **【二次式】** parabola, **【三次式】** 3rd order polynomial, **【平均係数】** average coefficients curve.
 - ・ 原点通過(O) : Passage through the origin, **【通さない】** do not force through the origin, **【原点を通す】** pass through the origin, **【原点を通す (折れ線)】** pass through the origin (broken line).
 - ・ 重み付け(W) : Weighting for the regression.
 - ・ 検量線表示の X 軸(X) : Variable to be displayed on the x-axis of the calibration curve, **【濃度】** concentration, or **【面積/高さ】** area/height. Usually, concentration is selected.

- ・ 濃度単位(U) : Concentration unit
 - ・ 濃度値のフォーマット(F) : Set the appropriate concentration value format by using one of the following two options: 【小数点以下桁数】 number of digits after the decimal point, 【有効桁数】 number of significant figures.
- ⑩ Click 【次へ(N)】 .
 - ⑪ The【化合物テーブルウィザード 4/5】window opens. Here, the identification processing parameters are set, but they are usually not tampered with, so just click 【次へ(N)】 .
 - ⑫ The 【化合物テーブルウィザード 5/5】 window opens. Enter the compound name(s) in the 【化合物名】 column and the concentrations in the 【濃度(1)】 , 【濃度(2)】 , 【濃度(3)】 , etc. columns. It is easiest to enter the concentrations in order, from lowest to highest. The retention time(s) are displayed in the 【保持時間】 column.
 - ⑬ Click 【完了】 .
 - ⑭ Click 【ファイル(F)】 → 【データファイルとメソッドファイルを上書き保存(N)】 .

3.4. Manual calibration curve creation

- ① Click the 【検量線】 icon on the 【メイン】 assistant bar of the 【再解析】 program.
- ② Drag and drop the method file from the 【データエクスプローラ】 screen to the 【検量線ビュー】 window. You can also just double-click the method file in the 【データエクスプローラ】 .
- ③ Click on the 【Data】 tab in the 【データエクスプローラ】 screen.
- ④ Drag and drop the standard sample data file from the 【データエクスプローラ】 screen to the desired level in the 【データファイル】 tree view. However, pay attention to the levels (1, 2, ...), which are ordered from lowest to highest concentration. By the way, you can delete them by right-clicking 【削除】 .
- ⑤ The calibration curve is displayed.
- ⑥ Click 【ファイル(F)】 → 【メソッドファイルを上書き保存(S)】 .

3.5. Compound table retention time change

As the column gets dirty, the retention time changes and the compound's peak time becomes shorter. In this case, it is possible to edit the chromatogram such that the peak happens at the originally expected retention time.

- ① Click 【編集】 in 【メソッドビュー】 to switch to edit mode.
- ② Click the 【化合物】 tab in 【メソッドビュー】 , and click the 【保持時間】 cell to be changed.
- ③ Select the peak whose retention time is to be changed. The change in retention time is automatically registered in the compound table.
- ④ Click 【表示】 in 【メソッドビュー】 .

※ On the contrary, if the compound's peak time is longer than expected, then there is a high possibility that a leak is happening somewhere in the line.

4. Shutdown operation

- ① Click the 【GC 停止】 icon in the 【データ採取】 assistant bar of the 【分析】 program.
- ② Click 【はい(Y)】 .
- ③ Wait until the temperature drops below 100 °C before closing the PC software (Lab Solutions), it takes about 30-45 min.
- ④ Once the temperature has dropped, turn off the PC, MS and GC. However, do not turn off the generation unit.
- ⑤ Close the GC-BID pressure regulator (on the back of the GC).

5. Switching from GC-BID to GC-MS

- ① Turn off the helium generation unit (HP2) and remove the plug from the outlet.
- ② Wait 2 hours for the helium generation unit to cool down.
- ③ Close the high purity helium cylinder.
- ④ On the back of the GC, completely close the GC-BID regulator (7 revolutions).
- ⑤ Remove the column for BID.
- ⑥ Close the BID inlet and outlet by attaching two 0.8 mm graphite ferrules (on a core) onto them with the nuts.
- ⑦ Attach the column for GC-MS to the GC-MS interface. For installation details, refer to the 【GCMS_manual】 stored in 【[\\baiman\share\Research Groups\GC\GC-MS](#)】 .
- ⑧ Attach the helium regulator to the helium cylinder for MS.
- ⑨ Open the helium cylinder for MS and set the secondary pressure to about 0.6 MPa.
- ⑩ On the back of the GC, open the GC-MS regulator, such that the pressure reaches 50 kPa.
- ⑪ Turn on, in that order, the GC, MS, and PC.
- ⑫ Launch the 【GCMS 分析】 program.
- ⑬ Click 【OK】 .
- ⑭ On the 【分析】 assistant bar, click the 【真空系の起動・停止】 icon to turn on the vacuum pump.
※ If the carrier line 1 does not flow immediately after replacing the column, it is because it may take time to start the turbo molecular pump.

From here, follow the GC-MS manual.

6. Switching from GC-MS to GC-BID

- ① Close the helium cylinder for MS.
- ② Close the GC-MS regulator located on the back of the GC.
- ③ Remove the column for MS.
- ④ Close the MS interface (vaporised chamber outlet and detector inlet), and attach a column for BID to the BID interface according to section 2.1.
- ⑤ Attach the helium regulator to the high purity helium cylinder (G1) for BID.

Refer to section 2.2 to finish the procedure.

7. Notes

- ① Do not launch the BID hardware and the GCMS software 【GCMS 分析】 simultaneously.
- ② Similarly, the GCMS hardware and BID software should not be launched simultaneously.
- ③ Replace the helium tank if its pressure lowers to 1.5-2.0 MPa.
- ④ If the GC-BID is not used for more than a month, the HP2 and generation unit may be turned off. When doing so, the HP2 and generation unit are turned off, and, after about 2 hours, the cylinder is closed.
- ⑤ If the GC-BID has not been used for a while, open the gas cylinder, wait for about 2 hours, and start the HP2 and generation unit.

Trick: In Shimadzu's software, 【F1】 is usually the shortcut to open the help screen.

8. Troubleshooting

8.1. Unstable baseline corrective action

This issue can have various causes, such as the conditioning of columns for BID detectors and helium combustion tubes, or leaks happening along the flowpath. Therefore, a BID analysis is performed, and the chromatogram is checked.

A-1 If N₂ and O₂ peaks appear, leakage is probably occurring somewhere in the flow path.

A-2 When multiple peaks appear, column conditioning is probably the problem.

A-3 If any of the above does not apply (A-1, A-2), follow the instructions below.

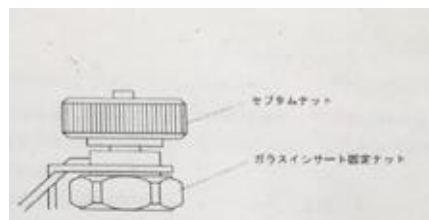
i. Verification of the column installation and vaporiser, detector. Check that the ferrule looseness and the tip length (ahead of the ferrule) are as described in section 2.1.

ii. Septum replacement

It is usually not a problem unless the liquid sample is directly injected into the vaporiser, however the septum might be deteriorated or dirty.

- ① Check that the temperature of the vaporisation chamber is lower than 50 °C, and that the GC is turned off.

- ② Remove the GC's top cover.
- ③ Remove the septum nut.



- ④ Replace the septum.

iii. Glass insert cleaning or replacement

- ① Check that the temperature of the vaporisation chamber is lower than 50 °C, and that the GC is turned off.
- ② Remove the glass insert fixing nut with the INJ spanner.
- ③ Lift the end of the glass insert with tweezers.
※ If the O-ring is stuck, turn the O-ring with tweezers first, and then lift the glass insert. If you pull the glass insert too strongly, you might damage the glass.



- ④ After removing the silica wool, wash the glass insert with acetone.
- ⑤ Cut a new silica wool and reinstall the insert.
※ Silica wool cannot be reused.

iv. Column conditioning

If liquid is detected to also be eluting from the column, it may cause baseline destabilisation. In that case, conditioning is necessary.

- ① Make sure that the GC is turned off.
- ② Remove the column from the detector inlet. Seal the inlet with a split nut and a sealing ferrule.
- ③ Start the GC, MS, PC, and software, in that order.
- ④ Select the method file which uses the column you want to condition (see section 2.7).
- ⑤ Click **【GC 起動(N)】** in the **【装置(I)】** menu of the taskbar.

- ⑥ Wait for the GC's status to be **【準備完】**. **GC準備完**

- ⑦ The column temperature is held at a temperature of 30 °C below the maximum temperature of the GC-BID 2010 Plus (**【MONIT】** button → **【温度 MONIT】**).

Appendix B

Chemical data sheets

B.1 Acetone [5]

2022/06/07

Distributed by FUJIFILM Wako Pure Chemical Corporation

Manufactured by FUJIFILM Wako Pure Chemical Corporation

Code No.01-0034

SPECIFICATION

Acetone

Guaranteed Reagent

REQUIREMENT	SPECIFICATION
* Appearance	Colorless clear liquid
Assay (CH ₃ COCH ₃) (GC)	min.99.5%(mass/mass)
Solubility in water	to pass test
Density (20°C)	0.789~0.792g/ml
Refractive index 20°C	1.358~1.360
Water	max.0.3%(mass/mass)
Residue after evaporation	max.5ppm(mass/mass)
Acidity (as CH ₃ COOH)	max.0.002%(mass/mass)
Alkalinity (as NH ₃)	max.0.001%(mass/mass)
Aldehydes (as HCHO)	max.0.002%(mass/mass)
Methanol (CH ₃ OH)	max.0.05%(mass/mass)
Substances reducing permanganate (as O)	max.2ppm(mass/mass)

JIS K 8034:2006 *:Additional test performed by Wako but not required by JIS

B.2 Ethanol [6]

2022/07/15

Distributed by FUJIFILM Wako Pure Chemical Corporation

Manufactured by FUJIFILM Wako Pure Chemical Corporation

Code No.05-0045

SPECIFICATION

Ethanol (99.5)

Guaranteed Reagent

REQUIREMENT	SPECIFICATION
* Appearance	Colorless clear liquid
Assay (C ₂ H ₅ OH) (GC)	min.99.5%(mass/mass)
Density (20°C)	0.789~0.791g/ml
Water	max.0.2%(mass/mass)
** Residue after evaporation	max.5ppm(mass/mass)
Acidity (as CH ₃ COOH)	max.0.002%(mass/mass)
Alkalinity (as NH ₃)	max.1ppm(mass/mass)
Aldehydes and ketones (as CH ₃ COCH ₃)	max.0.001%(mass/mass)
Methanol (CH ₃ OH)	max.0.02%(mass/mass)
2-Propanol [(CH ₃) ₂ CHOH]	max.0.01%(mass/mass)
1-Propanol (CH ₃ CH ₂ CH ₂ OH)	max.0.005%(mass/mass)
1-Butanol [CH ₃ (CH ₂) ₂ CH ₂ OH]	max.0.005%(mass/mass)
Substances reducing permanganate	to pass test
Substances darkened by sulfuric acid	to pass test

JIS K 8101:2006(*:Additional test performed by Wako but not required by JIS)(**:The specification is originally set by Wako not JIS)

Appendix C

Simulation model source code

C.1 Ideal gas version

```
#####
# Ethanol Thermal Cracking Ideal Gas Simulation Model
#####
# This program simulates the thermal cracking behaviour of ethanol
#   modelled as
# an ideal gas in a plug flow reactor (PFR).

# Import the necessary packages
import sys
import cantera as ct
import numpy as np
import matplotlib.pyplot as plt

#####
# Input parameters
#####

T_r = np.linspace(675, 1200, 22) # reaction temperature [K]
p = np.array([5, 7]) # reaction pressure [MPaG]
composition_0 = 'C2H5OH:1' # Fuel composition (relative mole fractions)
length = 0.77 # approximate reactor length [m]
mass_flow_rate = 20 * 1e-3/60 # mass flow rate [kg/s]
d = 2e-3 # reactor inner diameter [m]
area = np.pi * d**2 / 4 # reactor cross-sectional area [m**2]
constant_tube_temperature = True # set to False if the heat flux across
    the tube is constant instead of the temperature
heating = True # set to False if the fuel is being cooled rather than
    heated

# Input file containing the reaction mechanism
ct.add_directory('D:/UTokyo/Research/Simulation model/Ethanol chemical
    mechanism - Galway')
reaction_mechanism = 'galway_ethanol.yaml'
```

```

# Resolution: The PFR will be simulated by a chain of 'n_steps' stirred
    reactors.
n_steps = 1000
#####

#####
# Solving method: Chain of Reactors
#####
# The plug flow reactor is represented by a linear chain of
    zero-dimensional
# reactors. The gas at the inlet to the first one has the specified inlet
# composition, and for all others the inlet composition is fixed at the
# composition of the reactor immediately upstream. Since in a PFR model
    there
# is no diffusion, the upstream reactors are not affected by any
    downstream
# reactors, and therefore the problem may be solved by simply marching
    from
# the first to last reactor, integrating each one to steady state.
# (This approach is analogous to the one presented in 'surf_pfr.py', which
# additionally includes surface chemistry)

# Import the gas and metal models
gas = ct.Solution(reaction_mechanism)
metal = ct.Solution('steel.yaml') # Steel SUS316SC, which is the reaction
    tube metal, is modelled here

# Define selectivity, specific enthalpy change, heat absorbed per unit
    mass, and cooling power matrices
Xf_C2H5OH = np.zeros((np.size(p), np.size(T_r)))
Xf_H2 = np.zeros((np.size(p), np.size(T_r)))
Xf_CH4 = np.zeros((np.size(p), np.size(T_r)))
Xf_C2H4 = np.zeros((np.size(p), np.size(T_r)))
Xf_C2H6 = np.zeros((np.size(p), np.size(T_r)))
Xf_H2O = np.zeros((np.size(p), np.size(T_r)))
Xf_CO = np.zeros((np.size(p), np.size(T_r)))
Xf_CH2O = np.zeros((np.size(p), np.size(T_r)))
Xf_CH3OH = np.zeros((np.size(p), np.size(T_r)))
Xf_C2H3OH = np.zeros((np.size(p), np.size(T_r)))
Xf_CH3CHO = np.zeros((np.size(p), np.size(T_r)))

delta_h = np.zeros((np.size(p), np.size(T_r)))
q = np.zeros((np.size(p), np.size(T_r)))
Q_dot = np.zeros((np.size(p), np.size(T_r)))

Yf_C2H5OH = np.zeros((np.size(p), np.size(T_r)))
Yf_H2 = np.zeros((np.size(p), np.size(T_r)))
Yf_CH4 = np.zeros((np.size(p), np.size(T_r)))

```

```
Yf_C2H4 = np.zeros((np.size(p), np.size(T_r)))
Yf_C2H6 = np.zeros((np.size(p), np.size(T_r)))
Yf_CO = np.zeros((np.size(p), np.size(T_r)))

# Run the simulation for various flow rates and reaction temperatures,
# and analyse the results
for i in range(np.size(p)):
    for j in range(np.size(T_r)):

        # Set the reaction pressure and temperature
        pressure = p[i]*1e6 + ct.one_atm
        T_0 = T_r[j]
        print('-'*50)
        print(f'p = {p[i]:.1g} MPaG and T_0 = {T_0:.4g} K')

        # Set the gas and metal's initial conditions
        gas.TPX = T_0, pressure, composition_0
        metal.TP = T_0, ct.one_atm
        dz = length / n_steps
        r_vol = area * dz
        r_wall_surf = np.pi * d * dz

        #####
        # Calculate the convection coefficient between the tube and the
        # fuel.
        #####
        # The parameters are all evaluated at the reactor entrance.
        rho = gas.density # density of the fuel
        u_0 = mass_flow_rate / (rho * area) # flow velocity
        nu = gas.viscosity / rho # kinematic viscosity
        k_f = gas.thermal_conductivity # thermal conductivity of the fuel

        Re = u_0 * d / nu # Reynolds number
        Pr = nu * rho * gas.cp_mass / k_f # Prandtl number
        print(f'Re = {Re:.4g} and Pr = {Pr:.3g}')

        # Calculate the Nusselt number based on the above values of Re and
        # Pr, and the boundary conditions.
        if Re < 2300 and constant_tube_temperature:
            Nu = 3.66
            print('Laminar flow with a constant wall temperature')
        elif Re < 2300 and not constant_tube_temperature:
            Nu = 4.36
            print('Laminar flow with a constant heat flux')
        elif Re > 10000 and 0.7 <= Pr <= 160:
            if heating:
                n = 0.4
                print('heating')
            else:
```

```

        n = 0.3
        print('cooling')
        Nu = 0.023 * Re**(4/5) * Pr**n
        print('Turbulent flow with Re>10000')
    elif 3000 < Re <= 5e6 and 0.5 <= Pr <= 3000:
        f = (0.790 * np.log(Re) - 1.64)**(-2)
        Nu = f/8 * (Re - 1000) * Pr / (1 + 12.7*(f/8)**(1/2) *
            (Pr**(2/3) - 1))
        print('Turbulent flow with Re<5e6')
    else:
        sys.exit('Failed to calculate the convection coefficient h')

h = k_f/d * Nu # convection coefficient [W/m**2/K]
#####

#####
# Create a reactor network
#####
# Create a new reactor
r = ct.IdealGasReactor(gas)
r.volume = r_vol

# Create a reservoir to represent the reactor immediately upstream.
# Note that the gas object is set already to the state of the
    upstream reactor.
upstream = ct.Reservoir(gas, name='upstream')

# Create a reservoir for the reactor to exhaust into.
# The composition of this reservoir is irrelevant.
downstream = ct.Reservoir(gas, name='downstream')

# Create a reservoir to model the metal tube
tube = ct.Reservoir(metal, name='tube')

# The mass flow rate into the reactor will be fixed by using a
    MassFlowController object.
m = ct.MassFlowController(upstream, r, mdot=mass_flow_rate)

# We need an outlet to the downstream reservoir. This will
    determine the
# pressure in the reactor. The value of K will only affect the
    transient
# pressure difference. A too small value of K might make the
    pressure
# controller's transient response too stiff, which can result in a
    numerical
# error when computing sim.advance_to_steady_state()
v = ct.PressureController(r, downstream, master=m, K=1e-5) # the
    cantera example uses K=1e-5

```

```
# Create a wall to model the interface between the tube and the
    wall,
# through which the heat transfer happens.
interface = ct.Wall(tube, r, name='interface', A=r_wall_surf, U=h)

sim = ct.ReactorNet([r])
#####

# Define time, space, and other information vectors
z = (np.arange(n_steps) + 1) * dz
t_r = np.zeros_like(z) # residence time in each reactor
u = np.zeros_like(z)
t = np.zeros_like(z)
states = ct.SolutionArray(r.thermo)
# Iterate through the PFR cells
sim.rtol = 1e-7 # relative error tolerance used for the
    integration of the reactor equations, default rtol=1e-9
for n in range(n_steps):
    # Set the state of the reservoir to match that of the previous
        reactor
    gas.TDY = r.thermo.TDY
    upstream.syncState()
    # Integrate the reactor forward in time until steady state is
        reached
    sim.reinitialize()
    # noinspection PyArgumentList
    residuals = sim.advance_to_steady_state(return_residuals=True)
    # print(residuals)
    # Compute velocity and transform into time
    u[n] = mass_flow_rate / area / r.thermo.density
    t_r[n] = r.mass / mass_flow_rate # residence time in this
        reactor
    t[n] = np.sum(t_r)
    # Write output data
    states.append(r.thermo.state)

# Collect temperature, selectivity, mass selectivity and heat
    transfer data, as well as the final reaction time
T = states.T

X_C2H5OH = states.X[:, gas.species_index('C2H5OH')]
X_H2 = states.X[:, gas.species_index('H2')]
X_CH4 = states.X[:, gas.species_index('CH4')]
X_C2H4 = states.X[:, gas.species_index('C2H4')]
X_C2H6 = states.X[:, gas.species_index('C2H6')]
X_H2O = states.X[:, gas.species_index('H2O')]
X_CO = states.X[:, gas.species_index('CO')]
X_CH2O = states.X[:, gas.species_index('CH2O')]
```

```

X_CH3OH = states.X[:, gas.species_index('CH3OH')]
X_C2H3OH = states.X[:, gas.species_index('C2H3OH')]
X_CH3CHO = states.X[:, gas.species_index('CH3CHO')]

Y_C2H5OH = states.Y[:, gas.species_index('C2H5OH')]
Y_H2 = states.Y[:, gas.species_index('H2')]
Y_CH4 = states.Y[:, gas.species_index('CH4')]
Y_C2H4 = states.Y[:, gas.species_index('C2H4')]
Y_C2H6 = states.Y[:, gas.species_index('C2H6')]
Y_CO = states.Y[:, gas.species_index('CO')]

Xf_C2H5OH[i, j] = X_C2H5OH[n_steps - 1]
Xf_H2[i, j] = X_H2[n_steps - 1]
Xf_CH4[i, j] = X_CH4[n_steps - 1]
Xf_C2H4[i, j] = X_C2H4[n_steps - 1]
Xf_C2H6[i, j] = X_C2H6[n_steps - 1]
Xf_H2O[i, j] = X_H2O[n_steps - 1]
Xf_CO[i, j] = X_CO[n_steps - 1]
Xf_CH2O[i, j] = X_CH2O[n_steps - 1]
Xf_CH3OH[i, j] = X_CH3OH[n_steps - 1]
Xf_C2H3OH[i, j] = X_C2H3OH[n_steps - 1]
Xf_CH3CHO[i, j] = X_CH3CHO[n_steps - 1]

delta_h[i, j] = states.h[n_steps - 1] - states.h[0]
q[i, j] = delta_h[i, j] + u[n_steps - 1]**2 / 2 - u[0]**2 / 2
Q_dot[i, j] = mass_flow_rate * q[i, j]

Yf_C2H5OH[i, j] = Y_C2H5OH[n_steps - 1]
Yf_H2[i, j] = Y_H2[n_steps - 1]
Yf_CH4[i, j] = Y_CH4[n_steps - 1]
Yf_C2H4[i, j] = Y_C2H4[n_steps - 1]
Yf_C2H6[i, j] = Y_C2H6[n_steps - 1]
Yf_CO[i, j] = Y_CO[n_steps - 1]

#####

#####
# Compare Results in matplotlib
#####
# Plot temperature as a function of distance for each reaction
plt.figure()
plt.plot(z, T)
plt.xlabel('$z$ [m]')
plt.ylabel('$T$ [K]')
# plt.legend(loc=0)
plt.savefig(f'Figures/temperature_{p[i]:.1g}_{T_0:.4g}.svg')
# plt.show()
plt.close()

```

```
# Plot selectivity as a function of time for each reaction
plt.figure()
plt.plot(t, 100*X_C2H5OH, label='$C_2H_5OH$')
plt.plot(t, 100*X_H2, label='$H_2$')
plt.plot(t, 100*X_CO, label='$CO$')
plt.plot(t, 100*X_CH4, label='$CH_4$')
plt.plot(t, 100*X_C2H4, label='$C_2H_4$')
plt.plot(t, 100*X_C2H6, label='$C_2H_6$')
plt.plot(t, 100*X_H2O, label='$H_2O$')
plt.plot(t, 100*X_CH2O, label='$CH_2O$')
# plt.plot(t, 100*X_CH3OH, label='$CH_3OH$')
plt.plot(t, 100*X_C2H3OH, label='$C_2H_3OH$')
plt.plot(t, 100*X_CH3CHO, label='$CH_3CHO$')
plt.xlabel('$t$ [s]')
plt.ylabel('$S$ [%]')
plt.legend(loc=0)
plt.savefig(f'Figures/selectivity_{p[i]:.1g}_{T_0:.4g}.svg')
# plt.show()
plt.close()

# Print heat transfer information for each reaction
print(f'$\Delta h = \{delta\_h[i,j]:.3g\}$ J/kg')
print(f'$q = \{q[i,j]:.3g\}$ J/kg')
print(f'$Q\_dot = \{Q\_dot[i,j]:.3g\}$ W')
print('-'*50, '\n')

# Calculate the sum of the selectivities of all selected products for
each reaction

X = Xf_C2H5OH + Xf_H2 + Xf_CH4 + Xf_C2H4 + Xf_C2H6 + Xf_H2O + Xf_CO +
    Xf_CH2O + Xf_CH3OH + Xf_C2H3OH + Xf_CH3CHO
print('-'*50)
print('Sum of the selectivities of all products')
print(100*X)
print('-'*50, '\n')

# Import the experimental results

T_e5 = np.array([673, 723, 773])
T_e7 = np.array([673, 723, 773])
Ye_1 = np.array([0.995864172971780, 0.00113408223142351,
    8.06410422058261e-05, 6.37699813226576e-05, 5.97402612263109e-05,
    6.85294097824104e-05])
Ye_2 = np.array([0.861571534622899, 0.00203027555649921,
    0.000236741962474945, 0.000157407847277041, 0.000196542204489472,
    0.000196253164706947])
Ye_3 = np.array([0.836726140750115, 0.00646868174856772,
    0.00254219989455658, 0.00156755187171071, 0.00115602232494968,
    0.00114628047203331])
```

```

Ye_4 = np.array([0.824704593672230, 0.00443946507134414,
 0.00150765381084637, 0.000922169981577700, 0.000668006611575007,
 0.000781919498849072])
Ye_5 = np.array([0.902284009534334, 0.000690084381997280, 0, 0,
 5.31360461052594e-05, 5.06334534022401e-05])
Ye_6 = np.array([0.883904594317558, 0.00120343408035326,
 9.02680457035527e-05, 5.77050776249629e-05, 0.000109801009766264,
 0.000101096026606494])
Ye_7 = np.array([0.789808972621428, 0.00292701957873701,
 0.000812510633084490, 0.000492800380863692, 0.000384429809679403,
 0.000432125301902871])

Ye5_C2H5OH = np.array([Ye_5[0], Ye_6[0], Ye_7[0]])
Ye7_C2H5OH = np.array([Ye_1[0], Ye_2[0], Ye_3[0], Ye_4[0]])
Ye5_H2 = np.array([Ye_5[1], Ye_6[1], Ye_7[1]])
Ye7_H2 = np.array([Ye_1[1], Ye_2[1], Ye_3[1], Ye_4[1]])
Ye5_CO = np.array([Ye_5[2], Ye_6[2], Ye_7[2]])
Ye7_CO = np.array([Ye_1[2], Ye_2[2], Ye_3[2], Ye_4[2]])
Ye5_CH4 = np.array([Ye_5[3], Ye_6[3], Ye_7[3]])
Ye7_CH4 = np.array([Ye_1[3], Ye_2[3], Ye_3[3], Ye_4[3]])
Ye5_C2H4 = np.array([Ye_5[4], Ye_6[4], Ye_7[4]])
Ye7_C2H4 = np.array([Ye_1[4], Ye_2[4], Ye_3[4], Ye_4[4]])
Ye5_C2H6 = np.array([Ye_5[5], Ye_6[5], Ye_7[5]])
Ye7_C2H6 = np.array([Ye_1[5], Ye_2[5], Ye_3[5], Ye_4[5]])

# Plot final selectivity as a function of pressure and reaction
# temperature for each relevant species
plt.figure()
for i in range(np.size(p)):
    plt.plot(T_r, 100*Xf_C2H5OH[i, :], label=f'$p = {p[i]:.1g}$ MPaG')
# plt.plot(T_r, X_CH3OH, label='$CH_3OH$')
plt.xlabel('$T_r$ [K]')
plt.ylabel('$S_{C_2H_5OH}$ [%]')
plt.legend(loc=0)
plt.savefig('Figures/selectivity_C2H5OH.svg')
plt.show()

plt.figure()
for i in range(np.size(p)):
    plt.plot(T_r, 100*Xf_H2[i, :], label=f'$p = {p[i]:.1g}$ MPaG')
plt.xlabel('$T_r$ [K]')
plt.ylabel('$S_{H_2}$ [%]')
plt.legend(loc=0)
plt.savefig('Figures/selectivity_H2.svg')
plt.show()

plt.figure()
for i in range(np.size(p)):
    plt.plot(T_r, 100*Xf_CH4[i, :], label=f'$p = {p[i]:.1g}$ MPaG')

```

```
plt.xlabel('$T_r$ [K]')
plt.ylabel('$S_{CH_4}$ [%]')
plt.legend(loc=0)
plt.savefig('Figures/selectivity_CH4.svg')
plt.show()

plt.figure()
for i in range(np.size(p)):
    plt.plot(T_r, 100*Xf_C2H4[i, :], label=f'$p = {p[i]:.1g}$ MPaG')
plt.xlabel('$T_r$ [K]')
plt.ylabel('$S_{C_2H_4}$ [%]')
plt.legend(loc=0)
plt.savefig('Figures/selectivity_C2H4.svg')
plt.show()

plt.figure()
for i in range(np.size(p)):
    plt.plot(T_r, 100*Xf_C2H6[i, :], label=f'$p = {p[i]:.1g}$ MPaG')
plt.xlabel('$T_r$ [K]')
plt.ylabel('$S_{C_2H_6}$ [%]')
plt.legend(loc=0)
plt.savefig('Figures/selectivity_C2H6.svg')
plt.show()

plt.figure()
for i in range(np.size(p)):
    plt.plot(T_r, 100*Xf_H2O[i, :], label=f'$p = {p[i]:.1g}$ MPaG')
plt.xlabel('$T_r$ [K]')
plt.ylabel('$S_{H_2O}$ [%]')
plt.legend(loc=0)
plt.savefig('Figures/selectivity_H2O.svg')
plt.show()

plt.figure()
for i in range(np.size(p)):
    plt.plot(T_r, 100*Xf_CO[i, :], label=f'$p = {p[i]:.1g}$ MPaG')
plt.xlabel('$T_r$ [K]')
plt.ylabel('$S_{CO}$ [%]')
plt.legend(loc=0)
plt.savefig('Figures/selectivity_CO.svg')
plt.show()

plt.figure()
for i in range(np.size(p)):
    plt.plot(T_r, 100*Xf_CH2O[i, :], label=f'$p = {p[i]:.1g}$ MPaG')
plt.xlabel('$T_r$ [K]')
plt.ylabel('$S_{CH_2O}$ [%]')
plt.legend(loc=0)
plt.savefig('Figures/selectivity_CH2O.svg')
```

```

plt.show()

plt.figure()
for i in range(np.size(p)):
    plt.plot(T_r, 100*Xf_CH3OH[i, :], label=f'$p = {p[i]:.1g}$ MPaG')
plt.xlabel('$T_r$ [K]')
plt.ylabel('$S_{CH_3OH}$ [%]')
plt.legend(loc=0)
plt.savefig(f'Figures/selectivity_CH3OH.svg')
plt.show()

plt.figure()
for i in range(np.size(p)):
    plt.plot(T_r, 100*Xf_C2H3OH[i, :], label=f'$p = {p[i]:.1g}$ MPaG')
plt.xlabel('$T_r$ [K]')
plt.ylabel('$S_{C_2H_3OH}$ [%]')
plt.legend(loc=0)
plt.savefig(f'Figures/selectivity_C2H3OH.svg')
plt.show()

plt.figure()
for i in range(np.size(p)):
    plt.plot(T_r, 100*Xf_CH3CHO[i, :], label=f'$p = {p[i]:.1g}$ MPaG')
plt.xlabel('$T_r$ [K]')
plt.ylabel('$S_{CH_3CHO}$ [%]')
plt.legend(loc=0)
plt.savefig(f'Figures/selectivity_CH3CHO.svg')
plt.show()

# Plot heat absorbed per unit mass as a function of pressure and reaction
# temperature
plt.figure()
for i in range(np.size(p)):
    plt.plot(T_r, q[i, :] * 1e-3, label=f'$p = {p[i]:.1g}$ MPaG')
plt.xlabel('$T_r$ [K]')
plt.ylabel('$q$ [kJ/kg]')
plt.legend(loc=0)
# plt.ticklabel_format(style='sci', axis='y', scilimits=(0, 0),
# useOffset=False)
plt.savefig(f'Figures/heat_per_unit_mass.svg')
plt.show()

# Plot cooling power as a function of pressure and reaction temperature
plt.figure()
for i in range(np.size(p)):
    plt.plot(T_r, Q_dot[i, :], label=f'$p = {p[i]:.1g}$ MPaG')
plt.xlabel('$T_r$ [K]')
plt.ylabel('$\dot{Q}$ [W]')
plt.legend(loc=0)

```

```
plt.savefig(f'Figures/power.svg')
plt.show()

# Plot mass fraction as a function of pressure and reaction temperature
# for each relevant species
plt.figure()
for i in range(np.size(p)):
    plt.plot(T_r, 100*Yf_C2H5OH[i, :], label=f'$p = {p[i]:.1g}$ MPaG')
    if p[i] == 5:
        plt.plot(T_e5, 100*Ye5_C2H5OH, '+', label=f'$p = {p[i]:.1g}$ MPaG,
            experiments')
    elif p[i] == 7:
        plt.plot(T_e7, 100*Ye7_C2H5OH, '+', label=f'$p = {p[i]:.1g}$ MPaG,
            experiments')
# plt.plot(T_r, X_CH3OH, label='$CH_3OH$')
plt.xlabel('$T_r$ [K]')
plt.ylabel('$w_{C_2H_5OH}$ [%]')
plt.legend(loc=0, ncol=1)
plt.savefig(f'Figures/mass_selectivity_C2H5OH.svg')
plt.show()

plt.figure()
for i in range(np.size(p)):
    plt.plot(T_r, 100*Yf_H2[i, :], label=f'$p = {p[i]:.1g}$ MPaG')
    if p[i] == 5:
        plt.plot(T_e5, 100*Ye5_H2, '+', label=f'$p = {p[i]:.1g}$ MPaG,
            experiments')
    elif p[i] == 7:
        plt.plot(T_e7, 100*Ye7_H2, '+', label=f'$p = {p[i]:.1g}$ MPaG,
            experiments')
plt.xlabel('$T_r$ [K]')
plt.ylabel('$w_{H_2}$ [%]')
plt.legend(loc=0, ncol=1)
plt.savefig(f'Figures/mass_selectivity_H2.svg')
plt.show()

plt.figure()
for i in range(np.size(p)):
    plt.plot(T_r, 100*Yf_CO[i, :], label=f'$p = {p[i]:.1g}$ MPaG')
    if p[i] == 5:
        plt.plot(T_e5, 100*Ye5_CO, '+', label=f'$p = {p[i]:.1g}$ MPaG,
            experiments')
    elif p[i] == 7:
        plt.plot(T_e7, 100*Ye7_CO, '+', label=f'$p = {p[i]:.1g}$ MPaG,
            experiments')
plt.xlabel('$T_r$ [K]')
plt.ylabel('$w_{CO}$ [%]')
plt.legend(loc=0, ncol=1)
plt.savefig(f'Figures/mass_selectivity_CO.svg')
```

```
plt.show()

plt.figure()
for i in range(np.size(p)):
    plt.plot(T_r, 100*Yf_CH4[i, :], label=f'$p = {p[i]:.1g}$ MPaG')
    if p[i] == 5:
        plt.plot(T_e5, 100*Ye5_CH4, '+', label=f'$p = {p[i]:.1g}$ MPaG,
                experiments')
    elif p[i] == 7:
        plt.plot(T_e7, 100*Ye7_CH4, '+', label=f'$p = {p[i]:.1g}$ MPaG,
                experiments')
plt.xlabel('$T_r$ [K]')
plt.ylabel('$w_{CH_4}$ [%]')
plt.legend(loc=0, ncol=1)
plt.savefig(f'Figures/mass_selectivity_CH4.svg')
plt.show()

plt.figure()
for i in range(np.size(p)):
    plt.plot(T_r, 100*Yf_C2H4[i, :], label=f'$p = {p[i]:.1g}$ MPaG')
    if p[i] == 5:
        plt.plot(T_e5, 100*Ye5_C2H4, '+', label=f'$p = {p[i]:.1g}$ MPaG,
                experiments')
    elif p[i] == 7:
        plt.plot(T_e7, 100*Ye7_C2H4, '+', label=f'$p = {p[i]:.1g}$ MPaG,
                experiments')
plt.xlabel('$T_r$ [K]')
plt.ylabel('$w_{C_2H_4}$ [%]')
plt.legend(loc=0, ncol=1)
plt.savefig(f'Figures/mass_selectivity_C2H4.svg')
plt.show()

plt.figure()
for i in range(np.size(p)):
    plt.plot(T_r, 100*Yf_C2H6[i, :], label=f'$p = {p[i]:.1g}$ MPaG')
    if p[i] == 5:
        plt.plot(T_e5, 100*Ye5_C2H6, '+', label=f'$p = {p[i]:.1g}$ MPaG,
                experiments')
    elif p[i] == 7:
        plt.plot(T_e7, 100*Ye7_C2H6, '+', label=f'$p = {p[i]:.1g}$ MPaG,
                experiments')
plt.xlabel('$T_r$ [K]')
plt.ylabel('$w_{C_2H_6}$ [%]')
plt.legend(loc=0, ncol=1)
plt.savefig(f'Figures/mass_selectivity_C2H6.svg')
plt.show()
```

#####

C.2 Real gas version

```
#####
# Ethanol Thermal Cracking Real Gas Simulation Model
#####
# This program simulates the thermal cracking behaviour of ethanol
#   modelled as
# a real gas in a plug flow reactor (PFR).

# Import the necessary packages
import sys
import cantera as ct
import numpy as np
import matplotlib.pyplot as plt

#####
# Input parameters
#####

T_r = np.linspace(675, 1200, 22) # reaction temperature [K]
p = np.array([5, 7]) # reaction pressure [MPaG]
composition_0 = 'C2H5OH:1' # Fuel composition (relative mole fractions)
length = 0.77 # approximate reactor length [m]
mass_flow_rate = 20 * 1e-3/60 # mass flow rate [kg/s]
d = 2e-3 # reactor inner diameter [m]
area = np.pi * d**2 / 4 # reactor cross-sectional area [m**2]
constant_tube_temperature = True # set to False if the heat flux across
#   the tube is constant instead of the temperature
heating = True # set to False if the fuel is being cooled rather than
#   heated

# Input file containing the reaction mechanism
ct.add_directory('D:/UTokyo/Research/Simulation model/Ethanol chemical
#   mechanism - Galway')
reaction_mechanism = 'galway_ethanol_real_gas.yaml'

# Resolution: The PFR will be simulated by a chain of 'n_steps' stirred
#   reactors.
n_steps = 1000
#####

#####
# Solving method: Chain of Reactors
#####
# The plug flow reactor is represented by a linear chain of
#   zero-dimensional
# reactors. The gas at the inlet to the first one has the specified inlet
# composition, and for all others the inlet composition is fixed at the
```

```

# composition of the reactor immediately upstream. Since in a PFR model
  there
# is no diffusion, the upstream reactors are not affected by any
  downstream
# reactors, and therefore the problem may be solved by simply marching
  from
# the first to last reactor, integrating each one to steady state.
# (This approach is analogous to the one presented in 'surf_pfr.py', which
# additionally includes surface chemistry)

# Import the gas and metal models
gas = ct.Solution(reaction_mechanism)
ct.add_directory('D:/UTokyo/Research/Simulation model/Ethanol ideal gas')
metal = ct.Solution('steel.yaml') # Steel SUS316SC, which is the reaction
  tube metal, is modelled here

# Define selectivity, specific enthalpy change, heat absorbed per unit
  mass, and cooling power matrices
Xf_C2H5OH = np.zeros((np.size(p), np.size(T_r)))
Xf_H2 = np.zeros((np.size(p), np.size(T_r)))
Xf_CH4 = np.zeros((np.size(p), np.size(T_r)))
Xf_C2H4 = np.zeros((np.size(p), np.size(T_r)))
Xf_C2H6 = np.zeros((np.size(p), np.size(T_r)))
Xf_H2O = np.zeros((np.size(p), np.size(T_r)))
Xf_CO = np.zeros((np.size(p), np.size(T_r)))
Xf_CH2O = np.zeros((np.size(p), np.size(T_r)))
Xf_CH3OH = np.zeros((np.size(p), np.size(T_r)))
Xf_C2H3OH = np.zeros((np.size(p), np.size(T_r)))
Xf_CH3CHO = np.zeros((np.size(p), np.size(T_r)))

delta_h = np.zeros((np.size(p), np.size(T_r)))
q = np.zeros((np.size(p), np.size(T_r)))
Q_dot = np.zeros((np.size(p), np.size(T_r)))

Yf_C2H5OH = np.zeros((np.size(p), np.size(T_r)))
Yf_H2 = np.zeros((np.size(p), np.size(T_r)))
Yf_CH4 = np.zeros((np.size(p), np.size(T_r)))
Yf_C2H4 = np.zeros((np.size(p), np.size(T_r)))
Yf_C2H6 = np.zeros((np.size(p), np.size(T_r)))
Yf_CO = np.zeros((np.size(p), np.size(T_r)))

# Run the simulation for various flow rates and reaction temperatures,
  and analyse the results
for i in range(np.size(p)):
    for j in range(np.size(T_r)):

        # Set the reaction pressure and temperature
        pressure = p[i]*1e6 + ct.one_atm
        T_0 = T_r[j]

```

```
print('-'*50)
print(f'p = {p[i]:.1g} MPaG and T_0 = {T_0:.4g} K')

# Set the gas and metal's initial conditions
gas.TPX = T_0, pressure, composition_0
metal.TP = T_0, ct.one_atm
dz = length / n_steps
r_vol = area * dz
r_wall_surf = np.pi * d * dz

#####
# Calculate the convection coefficient between the tube and the
# fuel.
#####
# The parameters are all evaluated at the reactor entrance.
rho = gas.density # density of the fuel
u_0 = mass_flow_rate / (rho * area) # flow velocity
nu = gas.viscosity / rho # kinematic viscosity
k_f = gas.thermal_conductivity # thermal conductivity of the fuel

Re = u_0 * d / nu # Reynolds number
Pr = nu * rho * gas.cp_mass / k_f # Prandtl number
print(f'Re = {Re:.4g} and Pr = {Pr:.3g}')

# Calculate the Nusselt number based on the above values of Re and
# Pr, and the boundary conditions.
if Re < 2300 and constant_tube_temperature:
    Nu = 3.66
    print('Laminar flow with a constant wall temperature')
elif Re < 2300 and not constant_tube_temperature:
    Nu = 4.36
    print('Laminar flow with a constant heat flux')
elif Re > 10000 and 0.7 <= Pr <= 160:
    if heating:
        n = 0.4
        print('heating')
    else:
        n = 0.3
        print('cooling')
    Nu = 0.023 * Re**(4/5) * Pr**n
    print('Turbulent flow with Re>10000')
elif 3000 < Re <= 5e6 and 0.5 <= Pr <= 3000:
    f = (0.790 * np.log(Re) - 1.64)**(-2)
    Nu = f/8 * (Re - 1000) * Pr / (1 + 12.7*(f/8)**(1/2) *
        (Pr**(2/3) - 1))
    print('Turbulent flow with Re<5e6')
else:
    sys.exit('Failed to calculate the convection coefficient h')
```

```

h = k_f/d * Nu # convection coefficient [W/m**2/K]
#####

#####
# Create a reactor network
#####
# Create a new reactor
r = ct.Reactor(gas)
r.volume = r_vol

# Create a reservoir to represent the reactor immediately upstream.
# Note that the gas object is set already to the state of the
  upstream reactor.
upstream = ct.Reservoir(gas, name='upstream')

# Create a reservoir for the reactor to exhaust into.
# The composition of this reservoir is irrelevant.
downstream = ct.Reservoir(gas, name='downstream')

# Create a reservoir to model the metal tube
tube = ct.Reservoir(metal, name='tube')

# The mass flow rate into the reactor will be fixed by using a
  MassFlowController object.
m = ct.MassFlowController(upstream, r, mdot=mass_flow_rate)

# We need an outlet to the downstream reservoir. This will
  determine the
# pressure in the reactor. The value of K will only affect the
  transient
# pressure difference. A too small value of K might make the
  pressure
# controller's transient response too stiff, which can result in a
  numerical
# error when computing sim.advance_to_steady_state()
v = ct.PressureController(r, downstream, master=m, K=1e-5) # the
  cantera example uses K=1e-5

# Create a wall to model the interface between the tube and the
  wall,
# through which the heat transfer happens.
interface = ct.Wall(tube, r, name='interface', A=r_wall_surf, U=h)

sim = ct.ReactorNet([r])
#####

# Define time, space, and other information vectors
z = (np.arange(n_steps) + 1) * dz
t_r = np.zeros_like(z) # residence time in each reactor

```

```
u = np.zeros_like(z)
t = np.zeros_like(z)
states = ct.SolutionArray(r.thermo)
# Iterate through the PFR cells
if p[i] == 5 and T_0 == 675:
    sim.rtol = 1e-8 # relative error tolerance used for the
                    # integration of the reactor equations, default rtol=1e-9
elif p[i] == 7 and T_0 == 675:
    sim.rtol = 1e-6
else:
    sim.rtol = 1e-9
for n in range(n_steps):
    # Set the state of the reservoir to match that of the previous
    # reactor
    gas.TDY = r.thermo.TDY
    upstream.syncState()
    # Integrate the reactor forward in time until steady state is
    # reached
    sim.reinitialize()
    # noinspection PyArgumentList
    residuals = sim.advance_to_steady_state(return_residuals=True)
    # print(residuals)
    # Compute velocity and transform into time
    u[n] = mass_flow_rate / area / r.thermo.density
    t_r[n] = r.mass / mass_flow_rate # residence time in this
    # reactor
    t[n] = np.sum(t_r)
    # Write output data
    states.append(r.thermo.state)

# Collect temperature, selectivity and heat transfer data
T = states.T

X_C2H5OH = states.X[:, gas.species_index('C2H5OH')]
X_H2 = states.X[:, gas.species_index('H2')]
X_CH4 = states.X[:, gas.species_index('CH4')]
X_C2H4 = states.X[:, gas.species_index('C2H4')]
X_C2H6 = states.X[:, gas.species_index('C2H6')]
X_H2O = states.X[:, gas.species_index('H2O')]
X_CO = states.X[:, gas.species_index('CO')]
X_CH2O = states.X[:, gas.species_index('CH2O')]
X_CH3OH = states.X[:, gas.species_index('CH3OH')]
X_C2H3OH = states.X[:, gas.species_index('C2H3OH')]
X_CH3CHO = states.X[:, gas.species_index('CH3CHO')]
Xf_CH3CHO[i, j] = X_CH3CHO[n_steps - 1]

Y_C2H5OH = states.Y[:, gas.species_index('C2H5OH')]
Y_H2 = states.Y[:, gas.species_index('H2')]
Y_CH4 = states.Y[:, gas.species_index('CH4')]
```

```

Y_C2H4 = states.Y[:, gas.species_index('C2H4')]
Y_C2H6 = states.Y[:, gas.species_index('C2H6')]
Y_CO = states.Y[:, gas.species_index('CO')]

Xf_C2H5OH[i, j] = X_C2H5OH[n_steps - 1]
Xf_H2[i, j] = X_H2[n_steps - 1]
Xf_CH4[i, j] = X_CH4[n_steps - 1]
Xf_C2H4[i, j] = X_C2H4[n_steps - 1]
Xf_C2H6[i, j] = X_C2H6[n_steps - 1]
Xf_H2O[i, j] = X_H2O[n_steps - 1]
Xf_CO[i, j] = X_CO[n_steps - 1]
Xf_CH2O[i, j] = X_CH2O[n_steps - 1]
Xf_CH3OH[i, j] = X_CH3OH[n_steps - 1]
Xf_C2H3OH[i, j] = X_C2H3OH[n_steps - 1]

delta_h[i, j] = states.h[n_steps - 1] - states.h[0]
q[i, j] = delta_h[i, j] + u[n_steps - 1]**2 / 2 - u[0]**2 / 2
Q_dot[i, j] = mass_flow_rate * q[i, j]

Yf_C2H5OH[i, j] = Y_C2H5OH[n_steps - 1]
Yf_H2[i, j] = Y_H2[n_steps - 1]
Yf_CH4[i, j] = Y_CH4[n_steps - 1]
Yf_C2H4[i, j] = Y_C2H4[n_steps - 1]
Yf_C2H6[i, j] = Y_C2H6[n_steps - 1]
Yf_CO[i, j] = Y_CO[n_steps - 1]
#####

#####
# Compare Results in matplotlib
#####
# Plot temperature as a function of distance for each reaction
plt.figure()
plt.plot(z, T)
plt.xlabel('$z$ [m]')
plt.ylabel('$T$ [K]')
# plt.legend(loc=0)
plt.savefig(f'Figures/temperature_{p[i]:.1g}_{T_0:.4g}.svg')
# plt.show()
plt.close()

# Plot selectivity as a function of time for each reaction
plt.figure()
plt.plot(t, 100*X_C2H5OH, label='$C_2H_5OH$')
plt.plot(t, 100*X_H2, label='$H_2$')
plt.plot(t, 100*X_CO, label='$CO$')
plt.plot(t, 100*X_CH4, label='$CH_4$')
plt.plot(t, 100*X_C2H4, label='$C_2H_4$')
plt.plot(t, 100*X_C2H6, label='$C_2H_6$')
plt.plot(t, 100*X_H2O, label='$H_2O$')

```

```
plt.plot(t, 100*X_CH2O, label='$CH_2O$')
# plt.plot(t, 100*X_CH3OH, label='$CH_3OH$')
plt.plot(t, 100*X_C2H3OH, label='$C_2H_3OH$')
plt.plot(t, 100*X_CH3CHO, label='$C_2H_3OH$')
plt.xlabel('$t$ [s]')
plt.ylabel('$S$ [%]')
plt.legend(loc=0)
plt.savefig(f'Figures/selectivity_{p[i]:.1g}_{T_0:.4g}.svg')
# plt.show()
plt.close()

# Print heat transfer information for each reaction
print(f'$\Delta h$ = {delta_h[i,j]:.3g} J/kg')
print(f'$q$ = {q[i,j]:.3g} J/kg')
print(f'$Q_{dot}$ = {Q_dot[i,j]:.3g} W')
print('-'*50, '\n')

# Calculate the sum of the selectivities of all selected products for
each reaction

X = Xf_C2H5OH + Xf_H2 + Xf_CH4 + Xf_C2H4 + Xf_C2H6 + Xf_H2O + Xf_CO +
    Xf_CH2O + Xf_CH3OH + Xf_C2H3OH + Xf_CH3CHO
print('-'*50)
print('Sum of the selectivities of all products')
print(100*X)
print('-'*50, '\n')

# Import the experimental results

T_e5 = np.array([673, 723, 773])
T_e7 = np.array([673, 723, 773])
Ye_1 = np.array([0.995864172971780, 0.00113408223142351,
    8.06410422058261e-05, 6.37699813226576e-05, 5.97402612263109e-05,
    6.85294097824104e-05])
Ye_2 = np.array([0.861571534622899, 0.00203027555649921,
    0.000236741962474945, 0.000157407847277041, 0.000196542204489472,
    0.000196253164706947])
Ye_3 = np.array([0.836726140750115, 0.00646868174856772,
    0.00254219989455658, 0.00156755187171071, 0.00115602232494968,
    0.00114628047203331])
Ye_4 = np.array([0.824704593672230, 0.00443946507134414,
    0.00150765381084637, 0.000922169981577700, 0.000668006611575007,
    0.000781919498849072])
Ye_5 = np.array([0.902284009534334, 0.000690084381997280, 0, 0,
    5.31360461052594e-05, 5.06334534022401e-05])
Ye_6 = np.array([0.883904594317558, 0.00120343408035326,
    9.02680457035527e-05, 5.77050776249629e-05, 0.000109801009766264,
    0.000101096026606494])
```

```

Ye_7 = np.array([0.789808972621428, 0.00292701957873701,
                 0.000812510633084490, 0.000492800380863692, 0.000384429809679403,
                 0.000432125301902871])

Ye5_C2H5OH = np.array([Ye_5[0], Ye_6[0], Ye_7[0]])
Ye7_C2H5OH = np.array([Ye_1[0], Ye_2[0], Ye_3[0], Ye_4[0]])
Ye5_H2 = np.array([Ye_5[1], Ye_6[1], Ye_7[1]])
Ye7_H2 = np.array([Ye_1[1], Ye_2[1], Ye_3[1], Ye_4[1]])
Ye5_CO = np.array([Ye_5[2], Ye_6[2], Ye_7[2]])
Ye7_CO = np.array([Ye_1[2], Ye_2[2], Ye_3[2], Ye_4[2]])
Ye5_CH4 = np.array([Ye_5[3], Ye_6[3], Ye_7[3]])
Ye7_CH4 = np.array([Ye_1[3], Ye_2[3], Ye_3[3], Ye_4[3]])
Ye5_C2H4 = np.array([Ye_5[4], Ye_6[4], Ye_7[4]])
Ye7_C2H4 = np.array([Ye_1[4], Ye_2[4], Ye_3[4], Ye_4[4]])
Ye5_C2H6 = np.array([Ye_5[5], Ye_6[5], Ye_7[5]])
Ye7_C2H6 = np.array([Ye_1[5], Ye_2[5], Ye_3[5], Ye_4[5]])

# Plot final selectivity as a function of pressure and reaction
# temperature for each relevant species
plt.figure()
for i in range(np.size(p)):
    plt.plot(T_r, 100*Xf_C2H5OH[i, :], label=f'$p = {p[i]:.1g}$ MPaG')
# plt.plot(T_r, X_CH3OH, label='$CH_3OH$')
plt.xlabel('$T_r$ [K]')
plt.ylabel('$S_{C_2H_5OH}$ [%]')
plt.legend(loc=0)
plt.savefig('Figures/selectivity_C2H5OH.svg')
plt.show()

plt.figure()
for i in range(np.size(p)):
    plt.plot(T_r, 100*Xf_H2[i, :], label=f'$p = {p[i]:.1g}$ MPaG')
plt.xlabel('$T_r$ [K]')
plt.ylabel('$S_{H_2}$ [%]')
plt.legend(loc=0)
plt.savefig('Figures/selectivity_H2.svg')
plt.show()

plt.figure()
for i in range(np.size(p)):
    plt.plot(T_r, 100*Xf_CH4[i, :], label=f'$p = {p[i]:.1g}$ MPaG')
plt.xlabel('$T_r$ [K]')
plt.ylabel('$S_{CH_4}$ [%]')
plt.legend(loc=0)
plt.savefig('Figures/selectivity_CH4.svg')
plt.show()

plt.figure()
for i in range(np.size(p)):

```

```
plt.plot(T_r, 100*Xf_C2H4[i, :], label=f'$p = {p[i]:.1g}$ MPaG')
plt.xlabel('$T_r$ [K]')
plt.ylabel('$S_{C_2H_4}$ [%]')
plt.legend(loc=0)
plt.savefig('Figures/selectivity_C2H4.svg')
plt.show()

plt.figure()
for i in range(np.size(p)):
    plt.plot(T_r, 100*Xf_C2H6[i, :], label=f'$p = {p[i]:.1g}$ MPaG')
plt.xlabel('$T_r$ [K]')
plt.ylabel('$S_{C_2H_6}$ [%]')
plt.legend(loc=0)
plt.savefig('Figures/selectivity_C2H6.svg')
plt.show()

plt.figure()
for i in range(np.size(p)):
    plt.plot(T_r, 100*Xf_H2O[i, :], label=f'$p = {p[i]:.1g}$ MPaG')
plt.xlabel('$T_r$ [K]')
plt.ylabel('$S_{H_2O}$ [%]')
plt.legend(loc=0)
plt.savefig('Figures/selectivity_H2O.svg')
plt.show()

plt.figure()
for i in range(np.size(p)):
    plt.plot(T_r, 100*Xf_CO[i, :], label=f'$p = {p[i]:.1g}$ MPaG')
plt.xlabel('$T_r$ [K]')
plt.ylabel('$S_{CO}$ [%]')
plt.legend(loc=0)
plt.savefig('Figures/selectivity_CO.svg')
plt.show()

plt.figure()
for i in range(np.size(p)):
    plt.plot(T_r, 100*Xf_CH2O[i, :], label=f'$p = {p[i]:.1g}$ MPaG')
plt.xlabel('$T_r$ [K]')
plt.ylabel('$S_{CH_2O}$ [%]')
plt.legend(loc=0)
plt.savefig('Figures/selectivity_CH2O.svg')
plt.show()

plt.figure()
for i in range(np.size(p)):
    plt.plot(T_r, 100*Xf_CH3OH[i, :], label=f'$p = {p[i]:.1g}$ MPaG')
plt.xlabel('$T_r$ [K]')
plt.ylabel('$S_{CH_3OH}$ [%]')
plt.legend(loc=0)
```



```

plt.savefig(f'Figures/selectivity_CH3OH.svg')
plt.show()

plt.figure()
for i in range(np.size(p)):
    plt.plot(T_r, 100*Xf_C2H3OH[i, :], label=f'$p = {p[i]:.1g}$ MPaG')
plt.xlabel('$T_r$ [K]')
plt.ylabel('$S_{C_2H_3OH}$ [%]')
plt.legend(loc=0)
plt.savefig(f'Figures/selectivity_C2H3OH.svg')
plt.show()

plt.figure()
for i in range(np.size(p)):
    plt.plot(T_r, 100*Xf_CH3CHO[i, :], label=f'$p = {p[i]:.1g}$ MPaG')
plt.xlabel('$T_r$ [K]')
plt.ylabel('$S_{CH_3CHO}$ [%]')
plt.legend(loc=0)
plt.savefig(f'Figures/selectivity_CH3CHO.svg')
plt.show()

# Plot heat absorbed per unit mass as a function of pressure and reaction
# temperature
plt.figure()
for i in range(np.size(p)):
    plt.plot(T_r, q[i, :] * 1e-3, label=f'$p = {p[i]:.1g}$ MPaG')
plt.xlabel('$T_r$ [K]')
plt.ylabel('$q$ [kJ/kg]')
plt.legend(loc=0)
# plt.ticklabel_format(style='sci', axis='y', scilimits=(0, 0),
# useOffset=False)
plt.savefig(f'Figures/heat_per_unit_mass.svg')
plt.show()

# Plot cooling power as a function of pressure and reaction temperature
plt.figure()
for i in range(np.size(p)):
    plt.plot(T_r, Q_dot[i, :], label=f'$p = {p[i]:.1g}$ MPaG')
plt.xlabel('$T_r$ [K]')
plt.ylabel('$\dot{Q}$ [W]')
plt.legend(loc=0)
plt.savefig(f'Figures/power.svg')
plt.show()

# Plot mass fraction as a function of pressure and reaction temperature
# for each relevant species
plt.figure()
for i in range(np.size(p)):
    plt.plot(T_r, 100*Yf_C2H5OH[i, :], label=f'$p = {p[i]:.1g}$ MPaG')

```

```
if p[i] == 5:
    plt.plot(T_e5, 100*Ye5_C2H5OH, '+', label=f'$p = {p[i]:.1g}$ MPaG,
             experiments')
elif p[i] == 7:
    plt.plot(T_e7, 100*Ye7_C2H5OH, '+', label=f'$p = {p[i]:.1g}$ MPaG,
             experiments')
# plt.plot(T_r, X_CH3OH, label='$CH_3OH$')
plt.xlabel('$T_r$ [K]')
plt.ylabel('$w_{C_2H_5OH}$ [%]')
plt.legend(loc=0, ncol=1)
plt.savefig(f'Figures/mass_selectivity_C2H5OH.svg')
plt.show()

plt.figure()
for i in range(np.size(p)):
    plt.plot(T_r, 100*Yf_H2[i, :], label=f'$p = {p[i]:.1g}$ MPaG')
    if p[i] == 5:
        plt.plot(T_e5, 100*Ye5_H2, '+', label=f'$p = {p[i]:.1g}$ MPaG,
                 experiments')
    elif p[i] == 7:
        plt.plot(T_e7, 100*Ye7_H2, '+', label=f'$p = {p[i]:.1g}$ MPaG,
                 experiments')
plt.xlabel('$T_r$ [K]')
plt.ylabel('$w_{H_2}$ [%]')
plt.legend(loc=0, ncol=1)
plt.savefig(f'Figures/mass_selectivity_H2.svg')
plt.show()

plt.figure()
for i in range(np.size(p)):
    plt.plot(T_r, 100*Yf_CO[i, :], label=f'$p = {p[i]:.1g}$ MPaG')
    if p[i] == 5:
        plt.plot(T_e5, 100*Ye5_CO, '+', label=f'$p = {p[i]:.1g}$ MPaG,
                 experiments')
    elif p[i] == 7:
        plt.plot(T_e7, 100*Ye7_CO, '+', label=f'$p = {p[i]:.1g}$ MPaG,
                 experiments')
plt.xlabel('$T_r$ [K]')
plt.ylabel('$w_{CO}$ [%]')
plt.legend(loc=0, ncol=1)
plt.savefig(f'Figures/mass_selectivity_CO.svg')
plt.show()

plt.figure()
for i in range(np.size(p)):
    plt.plot(T_r, 100*Yf_CH4[i, :], label=f'$p = {p[i]:.1g}$ MPaG')
    if p[i] == 5:
        plt.plot(T_e5, 100*Ye5_CH4, '+', label=f'$p = {p[i]:.1g}$ MPaG,
                 experiments')
```

```

elif p[i] == 7:
    plt.plot(T_e7, 100*Ye7_CH4, '+', label=f'$p = {p[i]:.1g}$ MPaG,
            experiments')
plt.xlabel('$T_r$ [K]')
plt.ylabel('$w_{CH_4}$ [%]')
plt.legend(loc=0, ncol=1)
plt.savefig(f'Figures/mass_selectivity_CH4.svg')
plt.show()

plt.figure()
for i in range(np.size(p)):
    plt.plot(T_r, 100*Yf_C2H4[i, :], label=f'$p = {p[i]:.1g}$ MPaG')
    if p[i] == 5:
        plt.plot(T_e5, 100*Ye5_C2H4, '+', label=f'$p = {p[i]:.1g}$ MPaG,
                experiments')
    elif p[i] == 7:
        plt.plot(T_e7, 100*Ye7_C2H4, '+', label=f'$p = {p[i]:.1g}$ MPaG,
                experiments')
plt.xlabel('$T_r$ [K]')
plt.ylabel('$w_{C_2H_4}$ [%]')
plt.legend(loc=0, ncol=1)
plt.savefig(f'Figures/mass_selectivity_C2H4.svg')
plt.show()

plt.figure()
for i in range(np.size(p)):
    plt.plot(T_r, 100*Yf_C2H6[i, :], label=f'$p = {p[i]:.1g}$ MPaG')
    if p[i] == 5:
        plt.plot(T_e5, 100*Ye5_C2H6, '+', label=f'$p = {p[i]:.1g}$ MPaG,
                experiments')
    elif p[i] == 7:
        plt.plot(T_e7, 100*Ye7_C2H6, '+', label=f'$p = {p[i]:.1g}$ MPaG,
                experiments')
plt.xlabel('$T_r$ [K]')
plt.ylabel('$w_{C_2H_6}$ [%]')
plt.legend(loc=0, ncol=1)
plt.savefig(f'Figures/mass_selectivity_C2H6.svg')
plt.show()

```

```
#####
```

C.3 Steel modelling code

description: |-

This file simulates the thermodynamic response of steel SUS316SC, which
 ↪ is the steel alloy used for the reactor tube.

The data is taken from the NASA thermodynamic database, see
 ↪ `nasa_condensed.yaml`

```

phases:
- name: steel
  thermo: constant-density
  elements: [Cr, Fe, Ni]
  species: [Cr(cr), Fe(a), Ni(cr)]
  state:
    T: 300.0
    P: 1.01325e+05
    Y: {Cr(cr): 17, Fe(a): 71, Ni(cr): 12}

species:
- name: Cr(cr)
  composition: {Cr: 1}
  thermo:
    model: NASA7
    temperature-ranges: [200.0, 1000.0, 311.5]
    data:
      - [7.84826024, -0.11627602, 8.12369251e-04, -2.30807086e-06,
        ↪ 2.35328142e-09,
        -898.013946, -27.5733139]
      - [0.0, 0.0, 0.0, 0.0, 0.0, 0.0, 0.0]
  equation-of-state:
    model: constant-volume
    density: 7.190 g/cm^3
- name: Fe(a)
  composition: {Fe: 1}
  thermo:
    model: NASA7
    temperature-ranges: [200.0, 1000.0, 1042.0]
    data:
      - [2.41337476, -1.57780744e-03, 2.14701339e-05, -3.80171438e-08,
        ↪ 2.20426984e-11,
        -774.380998, -10.6560296]
      - [4690.80173, -9.90659991, 2.69427446e-03, 5.54445321e-06,
        ↪ -3.01659823e-09,
        -1.41547586e+06, -2.49294387e+04]
  equation-of-state:
    model: constant-volume
    density: 7.874 g/cm^3
- name: Ni(cr)
  composition: {Ni: 1}
  thermo:
    model: NASA7
    temperature-ranges: [200.0, 1000.0, 631.0]
    data:

```

```
- [3.92097614, -0.0234184719, 1.34230145e-04, -2.75971639e-07,  
  ↪ 1.98530861e-10,  
   -862.387206, -15.6856186]  
- [0.0, 0.0, 0.0, 0.0, 0.0, 0.0, 0.0]  
equation-of-state:  
  model: constant-volume  
  density: 8.908 g/cm^3
```

Appendix D

Real gas results – extra figures

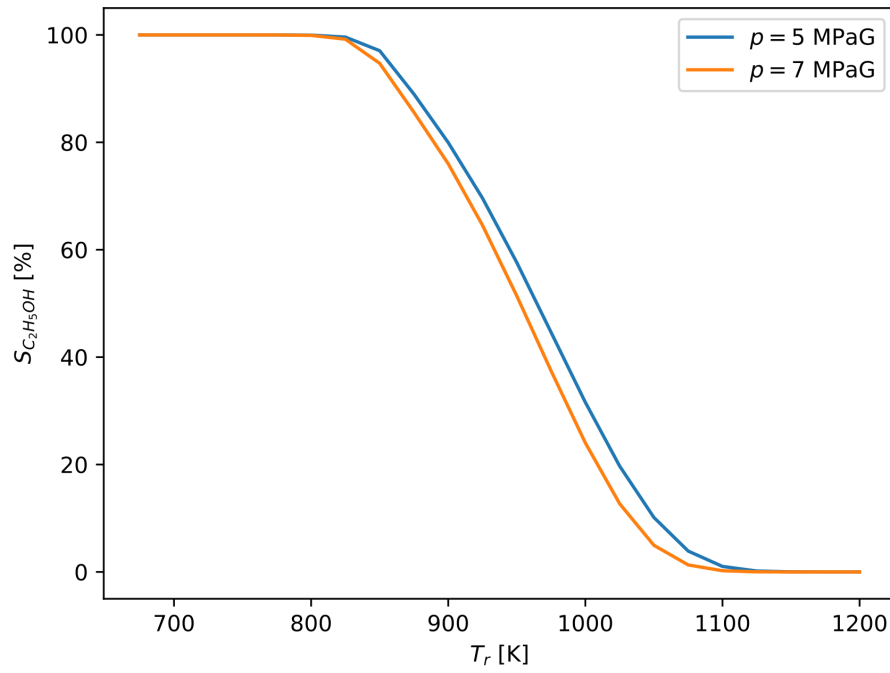


Figure D.1: Ethanol selectivity (real gas version)

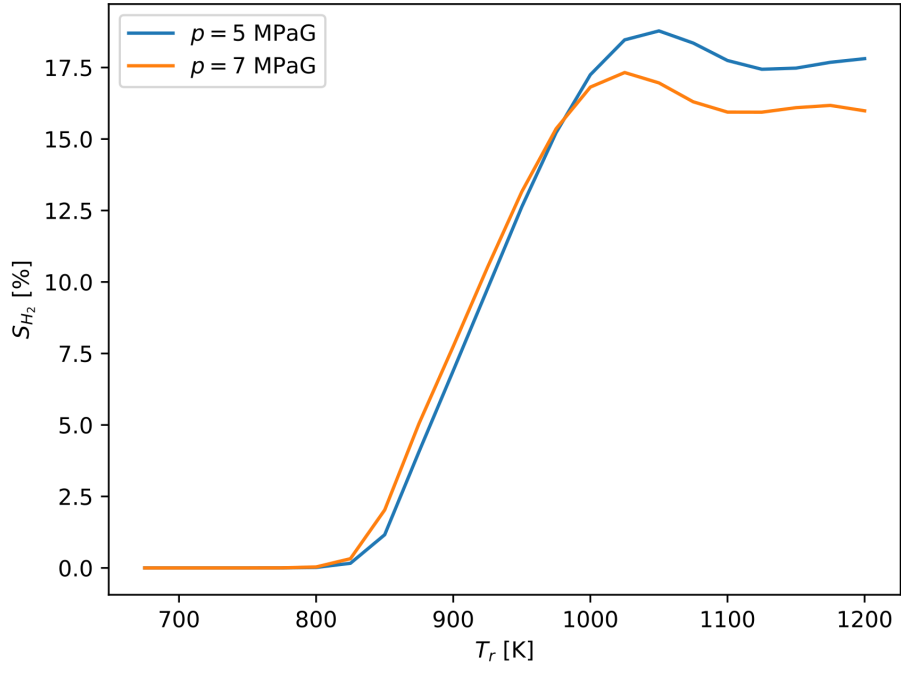


Figure D.2: Hydrogen selectivity (real gas version)

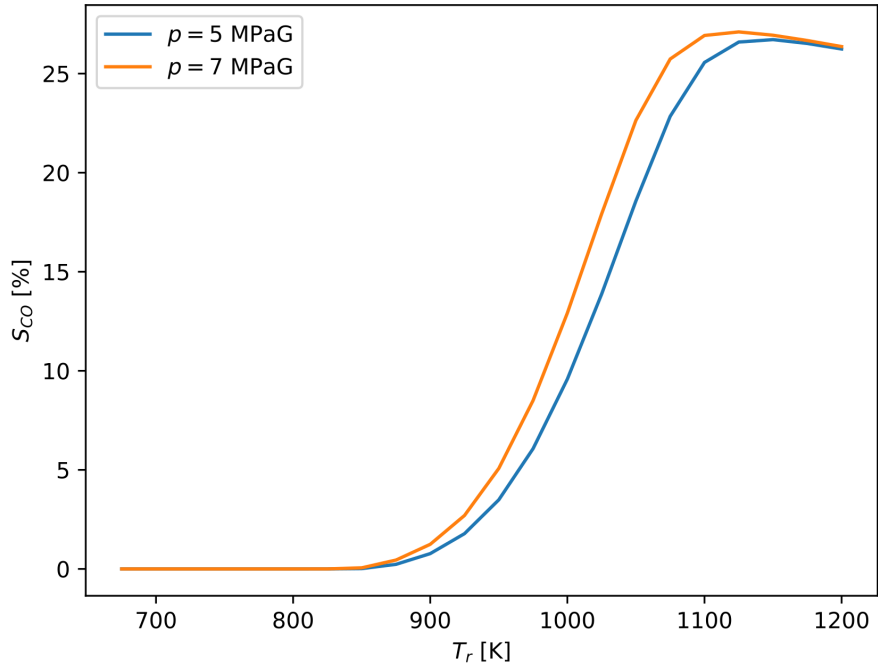


Figure D.3: Carbon monoxide (real gas version)

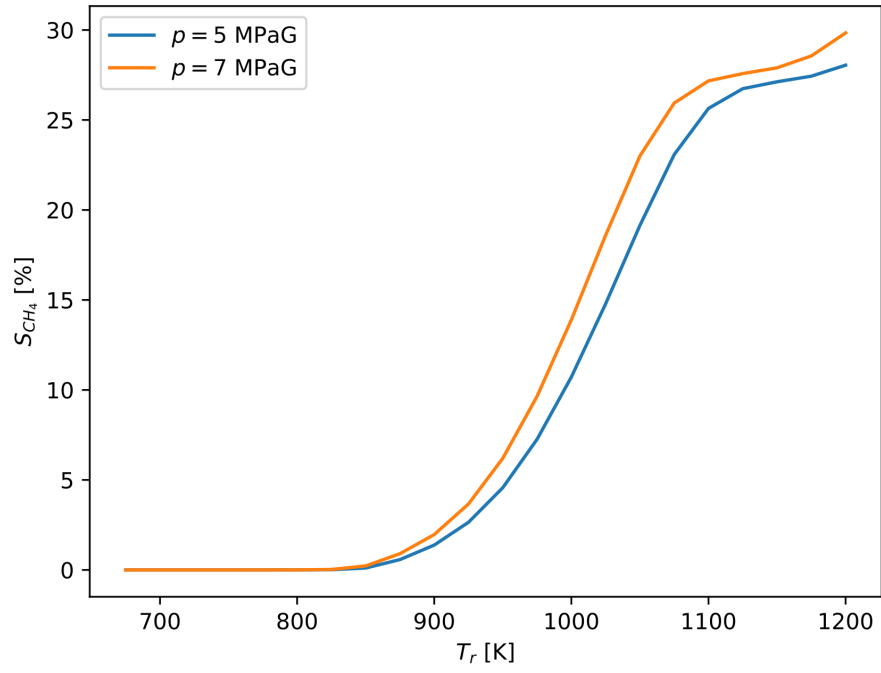


Figure D.4: Methane selectivity (real gas version)

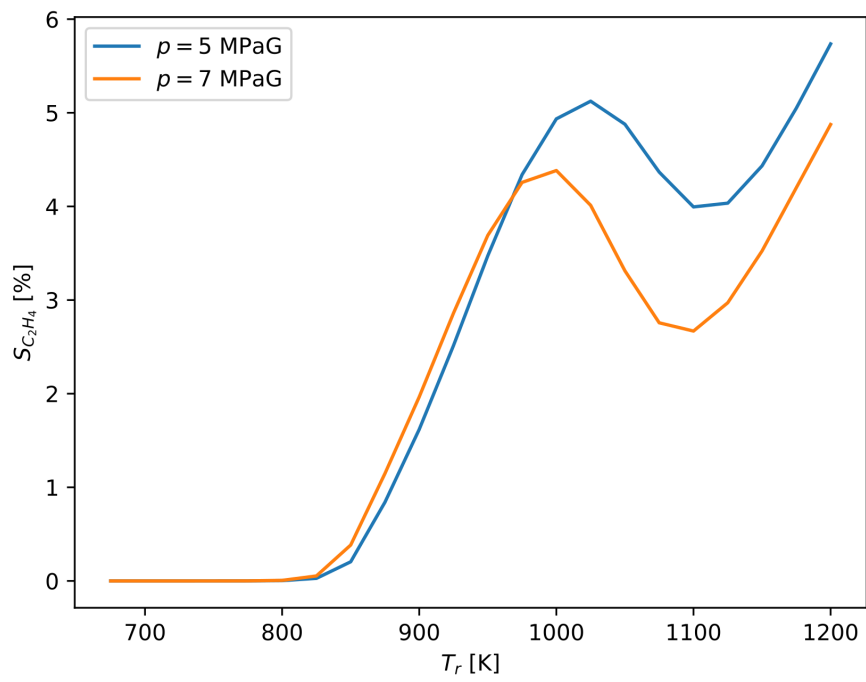


Figure D.5: Ethylene selectivity (real gas version)

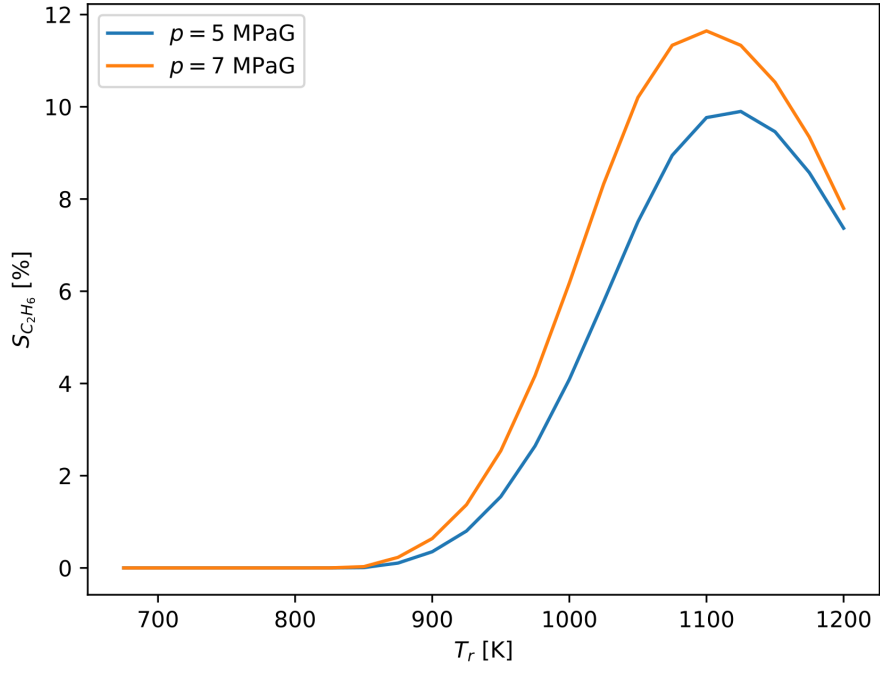


Figure D.6: Ethane selectivity (real gas version)

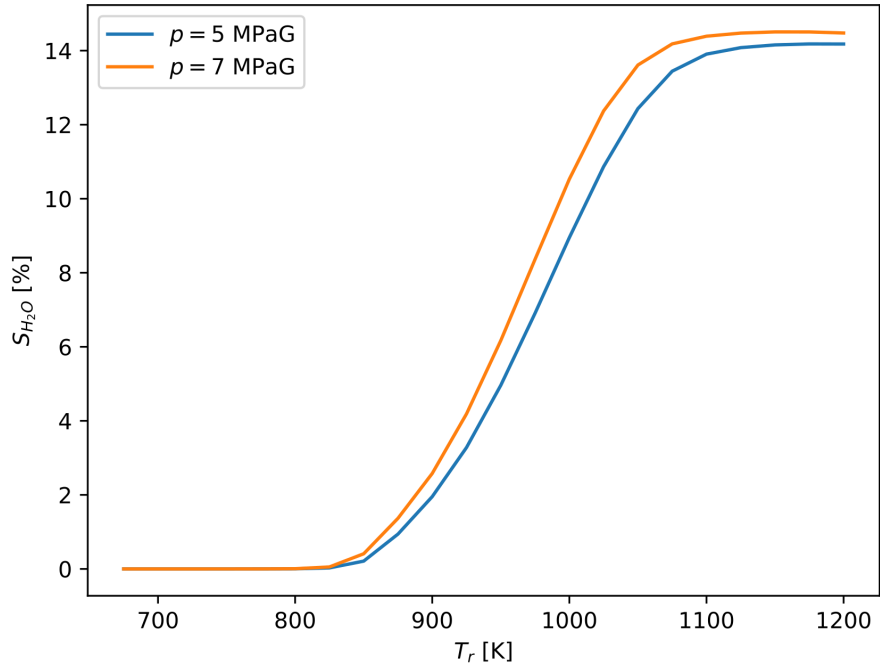


Figure D.7: Water selectivity (real gas version)

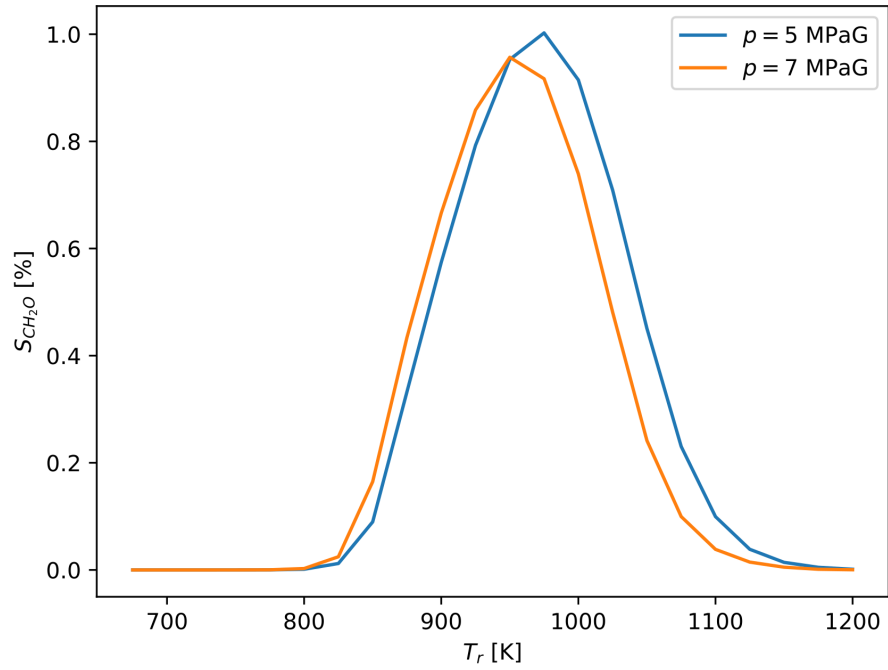


Figure D.8: Formaldehyde selectivity (real gas version)

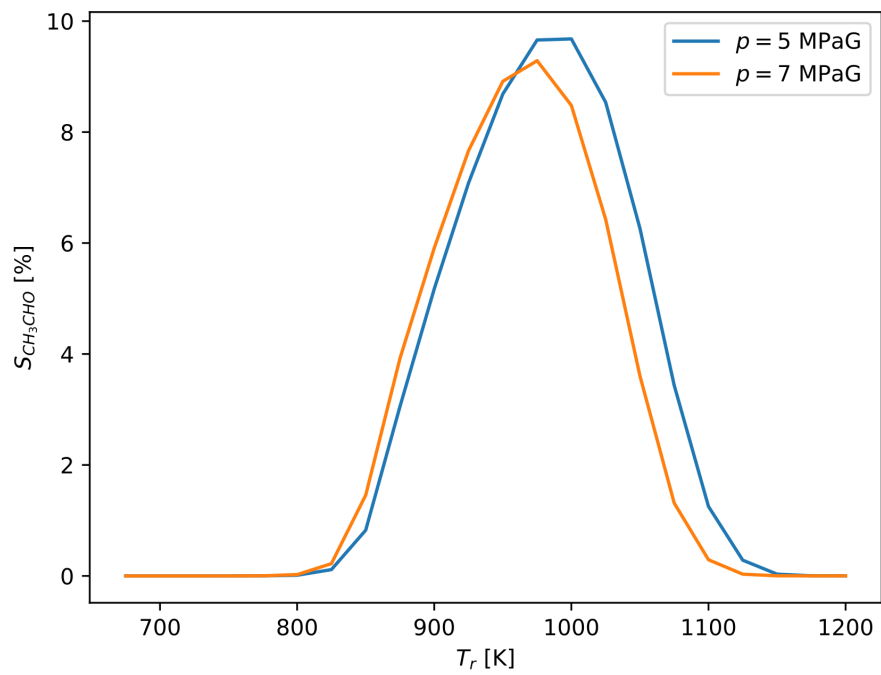


Figure D.9: Acetaldehyde selectivity (real gas version)

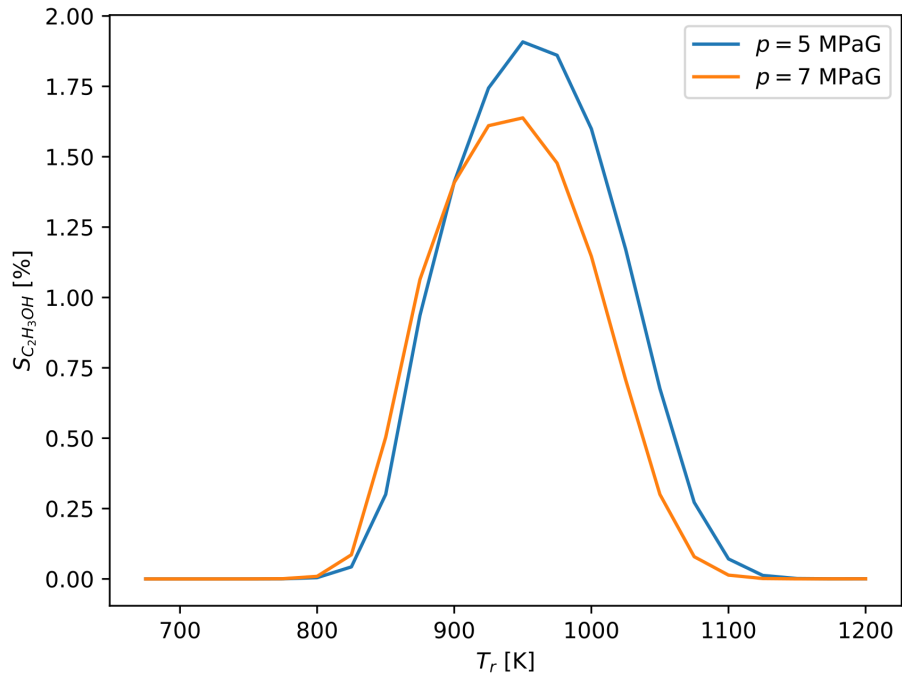


Figure D.10: Vinyl alcohol selectivity (real gas version)

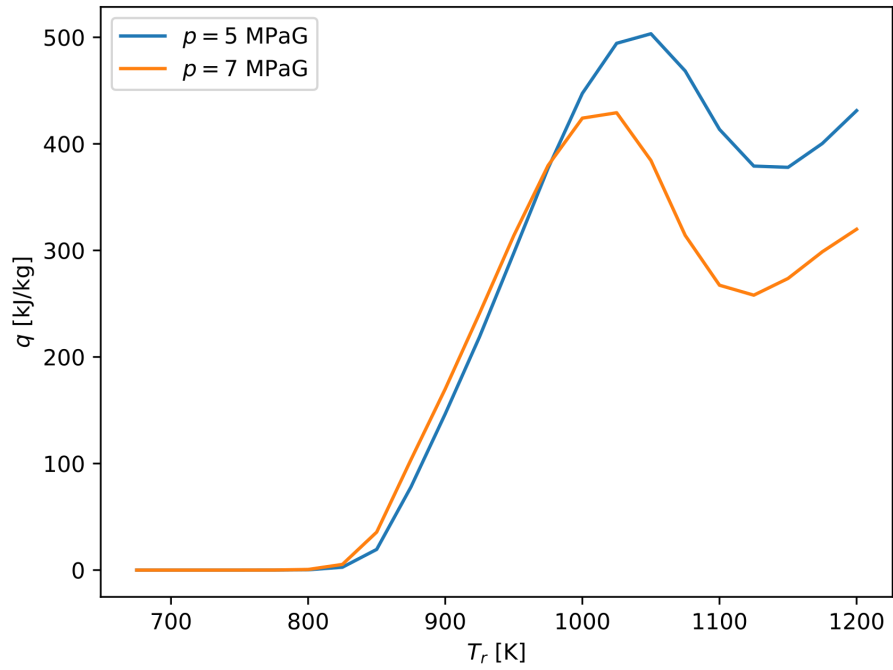


Figure D.11: Heat per unit mass absorbed by the reaction (real gas version)