

UNIVERSITY OF PRETORIA

DOCTORAL THESIS

Analysis of biodiesel by SFC×GC

5

by

Daniel MALAN

Submitted in partial fulfilment of the requirements for the
degree

10

Doctor of Philosophy

In the Faculty of Natural & Agricultural Sciences
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15 Declaration of Authorship

I, Daniel MALAN, declare that the thesis, which I hereby submit for the degree PhD (Chemistry) at the University of Pretoria, is my own work and has not previously been submitted by for a degree at this or any other tertiary institution.

SIGNATURE:

20

DATE:

“Learning is a peculiar compound of memory, imagination, scientific habit, accurate observation, all concentrated, through a prolonged period, on the analysis of the remains of literature.
25 *The result of this sustained mental endeavour is not a book, but a man.”*

Mark Pattison

UNIVERSITY OF PRETORIA

Abstract

Natural and Agricultural Sciences
Department of Chemistry

Doctor of Philosophy

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by Daniel MALAN

30

35 The Thesis Abstract is written here (and usually kept to just this page). The page is
kept centered vertically so can expand into the blank space above the title too...

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List of Abbreviations

EROEI	E nergy r eturned o n e nergy i nvested.
LCA	L ife C ycle A nalysis
LAH	L ist A bbreviations H ere
WSF	W hat (it) S tands F or
UNFCCC	U nited N ations F ramework C onvention on C limate C hange
IPCC	I ntergovernmental P anel on C limate C hange
CCGT	C ombined c ycle g as t urbine
HPLC	H igh p erformance l iquid c hromatography
GC	G as c hromatography
SFC	S upercritical f luid c hromatography
CCGT	C ombined c ycle g as t urbine
CCGT	C ombined c ycle g as t urbine

Physical Constants

Constant Name *Symbol* = *ConstantValue* with units

List of Symbols

a	distance	m
P	power	W (J s ⁻¹)
ω	angular frequency	rad

For/Dedicated to/To my...

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Introduction: Climate, fuel, and biodiesel

1.1 Energy, fuel and the atmosphere

Industrialized societies depend on reliable sources of energy. For the purpose of this discussion, the main types of energy can be counted as electricity and fuels, although they are interconvertible. Fuels for industrialized societies are predominantly found as underground mineral deposits, from where it is extracted by mining or drilling. They are found as solids, liquids and gases, which the energy industry refers to as *coal*, *crude oil*, and *natural gas*. Because these fuels are of biological origin, deposited during previous geological eras, and then metamorphosed and preserved by geological processes, these fuels are commonly referred to as 'fossil fuels'. Fossil fuel is also the feedstock of the chemical industry, but that falls outside of the scope of this discussion.

The large-scale exploitation of fossil fuels started in the middle of the 18th century, when the plentiful coal from the coalfields of Great Britain drove a development that is known to history as the Industrial Revolution. This development is closely associated with steam engines (Rosen 2012). The use of crude oil started in the middle of the 19th century, and is associated with the development of the automobile (Watts 2005, p. 42). The use of natural gas started in the middle of the 20th century and is associated with the introduction of gas-fired central heating in for homes in cold climates (Hanmer and Abram 2017). Fossil fuels also serve as feedstock to the chemical industry, but that topic lies outside the scope of this discussion.

There is no doubt that the use of fossil fuels as an energy source greatly improved the human lot. The mechanization of agriculture and the easy distribution of food by motorized transport have eliminated famine as a natural disaster (Angelis et al. 2007). The distribution of medical supplies by motorized transport and the rapid deployment of medical personnel have limited the impact and spread of epidemics (Ministere de la santé 2018). Heating and cooling of buildings have increased the habitable zone on earth. Artificial light have increased the hours available for mental activity, in particular extending the reach of entertainment, art and education.

However, in the context of chemistry, the uncontrolled use of fuels have at least two major problems.

The first problem with fossil fuel is that it is finite. There is only a certain amount of fossil fuel on earth. If all of it is extracted it will no longer be a reliable source

of energy, and the existence of industrialized societies and the complex civilizations that depend on them will be in jeopardy. It is tempting to think that civilizations would have the foresight to prepare for such an eventuality, but the historical record shows that societies can collapse when at the height of their powers (Diamond 2006).

The second problem with fuels is that they produce pollution wherever they are produced, processed, transported and used. Pollution is injurious to the health and well-being of individuals, societies and nature. If pollution is serious enough, it not only degrades society and the environment, but also negates the benefits brought by the application of energy: modern hospitals are energy-intensive, but if they are filled with victims of pollution there is no nett benefit.

The first approach to pollution from fuels has been to ignore it. Pictures from the early industrial revolution shows English towns coated with soot and choked with smoke (Flick 1980), and rivers became toxic sewers (Halliday 2001).

The development of public health, social responsibility (Szreter 2003) and an embryonic environmental movement (Williams 1965) lead to political pressure for the implementation of pollution controls, which governments gradually introduced and increased in strictness.

The first generation of pollution control offered essentially two options: concentrate or dilute.

I will illustrate these two options using a typical South African coal-fired power station. In such a power station coal is burned to produce heat, which converts liquid water into high-pressure steam. The steam is allowed to expand through a turbine, which converts the energy in the steam into rotary motion, which is used to turn an alternator that produces an electric current by rotating a set of electrical conductors in a magnetic field. The furnaces of such a power station produce a flow of waste. This waste is an *aerosol*: finely divided solids suspended in a mixture of gases.

The solid part is typically separated from the gas-phase part by filter bags and electrostatic precipitators: the collected material is known as *fly ash*. The gas-phase part might be sent through scrubbers to remove some of the gas-phase pollutants, capturing it in a solid form. The solid part of the power station's furnace waste has now been concentrated. It is transported to a storage site, where it is stored indefinitely. It goes without saying that concentrated pollutants should be encapsulated during storage in some way, otherwise it just becomes another source of pollution.

The gas-phase part of the pollutant is handled by diluting it. The outlet for the gas-phase stream of waste is through a tall stack, which ends high above ground level¹. At this altitude the wind is strong and steady, which rapidly carries the gases and remaining aerosols away and disperses it.

The dilution of pollutants might seem like an abdication of responsibility, but it is an reasonable response to pollution. At low enough concentrations pollutants that enter the biosphere are broken down by sunlight and microbes which render it harmless. This makes dilution a reasonable first attempt at controlling pollution.

The devil is, of course, in the details. For example, mercury that find its way into the environment is eventually converted by microbes to methyl mercury, which concentrates in aquatic animals. All rivers in the continental USA are now polluted by airborne mercury that originate from coal-fired power stations (Wentz et al. 2014).

¹The chimneys of those sooty Victorian towns were not there to disperse the smoke, but to create a 'draft', a flow of air created by the buoyancy of hot air. The better the draft, the more efficient the fire.

Some persistent organic pollutants, which also concentrate in the food chain, originate in fuel combustion. So while dilution was a reasonable first attempt at controlling pollution, it is certainly not the final answer.

The majority of fuels provide their energy as heat, which can be converted into useful work. This heat is obtained by combining the chemical compounds found in the fuel with atmospheric oxygen to form compounds with lower energy. The maximum amount of work that can be extracted from a given fuel can be estimated by examining the Gibbs free energy equation:

$$\Delta G = \Delta H + T\Delta S \quad (1.1)$$

For a given compound fuel compound, ΔH is determined by the difference in enthalpy of formation of the product waste compounds and the enthalpy of formation of the reactant fuel compounds. Since the reactant fuel compounds are given, ΔH is maximized by having product compounds with very low enthalpies of formations.

To maximize ΔS , the products should be as disordered as possible. This implies that *gas-phase* products composed of *small molecules* will yield more work.

The temperature T should also be as high as possible.

Because the industrial machinery in economically competitive, capital-intensive industries are highly efficient, the maximum amount of energy is extracted from their fuels for the lowest cost. Following Gibbs, the major compounds left over after extracting the energy from a fuel should have very low enthalpies of formation and be in the gas phase at the temperature of the process.

Because all fuels contain carbon as a major component, the extraction of energy yields compounds containing carbon. Most fuels also contain hydrogen. Reacting these fuels with the oxygen in air to extract maximal work will therefore yield water (H_2O) and carbon dioxide (CO_2).

(Of course I am not arguing that Victorian engineers designed steam engines using the Gibbs energy equation, but the variation-selection process (Vincenti 1990, Chapter 8) by which engineering improvements accrue would inevitably drive the development of heat engines fuelled by fossil fuels to emit large quantities of carbon dioxide gas.)

Water is of course not a pollutant at all, and carbon dioxide is only toxic at very high concentrations, and therefore, for most of the industrial era, carbon dioxide was easily dealt with by diluting it in the atmosphere, where it is also naturally present at low levels. To the extent that carbon dioxide was considered a pollutant it was assumed that it would be absorbed by the biosphere.

Photosynthesis, the process by which green plants capture the energy from sunlight to live and grow, does indeed remove carbon dioxide from the atmosphere, and an elementary model of the carbon cycle that assumes stability would seem to indicate that excess carbon dioxide in the atmosphere would be captured by photosynthesis and sequestered, leaving the carbon dioxide concentration in the atmosphere stable. Of course this model contains testable assumptions, which scientists could, and did, test.

The most famous of these tests is probably the “Keeling Curve” (Harris 2010). This is a continuous record of measurements of concentration of atmospheric carbon dioxide in the pristine air of the Pacific Ocean. This record starts in 1958 and shows that the carbon dioxide concentration of the atmosphere is increasing.

Paleoclimatologists have studied the hypothesis that the carbon dioxide concentration is stable over time. Not only have they found that the carbon dioxide concentration is *not* stable, they have also determined that the pre-industrial concentration

of atmospheric carbon dioxide was lower than it was in 1958 (Petit et al. 1999).

So it is clear that the carbon dioxide concentration in the atmosphere is rising because of the biosphere is not absorbing the carbon dioxide produced by the combustion of fossil fuels.

The projected concentration of carbon dioxide in the atmosphere is, however, still not at or even near toxic levels, which might make the continued dilution of carbon dioxide in the atmosphere seem like a viable disposal method.

Emitted gases, however, do not only have chemical properties and biological impacts, they also have physical properties. Of concern for the current discussion is carbon dioxide's absorbance of electromagnetic radiation, in particular the radiation arriving from the sun, and the radiation from the earth's surface out to space, both which must pass through the atmosphere. A molecule can absorb parts of this radiation by having its electrons excited, or by changing its vibration. Carbon dioxide is electronically very stable, and therefore absorbs only extreme ultraviolet radiation, just like the major gases in the atmosphere, molecular nitrogen and molecular oxygen. However it poorly absorbs near ultraviolet and visible light, in which is it also similar to the major gases. Because there is a dipole moment between the carbon atom and the oxygen atoms of carbon dioxide, it has vibrational modes which can absorb radiation in the infrared region of the electromagnetic spectrum. Oxygen and nitrogen do not have dipole moments, and therefore do not absorb infrared radiation strongly. This means that carbon dioxide will absorb infrared radiation in the atmosphere much more strongly than the major gases. The energy from the absorbed infrared radiation is of course turned into vibration, a form of kinetic energy, and this kinetic energy is randomly further distributed among the gases of in the atmosphere, appearing as an increase in temperature as the energy distribution moves towards equilibrium.

The most cursory understanding of the absorption of infrared radiation in the atmosphere by carbon dioxide therefore seems to say that an increase in the concentration of carbon dioxide in the atmosphere would lead to a higher average temperature in the atmosphere. This increase in temperature was first estimated by Svante Arrhenius in 1896 (Arrhenius 1897).

(The other major product of extracting energy from fuel is water. Its molecule also has a dipole moment, and it also absorbs infrared radiation strongly. However, its intermolecular properties sets an upper limit to its concentration: at high enough concentrations it will either condense into water or crystallize into ice and precipitate from the atmosphere to end up as surface water.)

Further research has only confirmed that industrial processes extracting energy from fuel is increasing the amount of carbon dioxide in the atmosphere by gigatons every year, and that this increase in concentration is leading to higher temperatures in the atmosphere. It had also become increasingly certain that this increase in temperature is inevitable and significant: it will change earth's climate². This projected increase in temperature and the accompanying change in global climate is bound to have impact on societies within the lifetime of people alive today, and a larger impact on future generations. Some of these projected changes are incompatible with the maintenance of the complex civilizations that are supported by industrialized societies (IPCC 2014).

Scientists do not inhabit ivory towers, and their research is funded by public money in the expectation that the resulting science will benefit their societies. As the

²The atmosphere is in contact with the hydrosphere, and the two exchange carbon dioxide. The carbon dioxide diluted in the atmosphere is therefore also diluted in the oceans. This leads to *ocean acidification*, a gigaton problem in it's own right, but one that falls outside the scope of this discussion.

385 understanding of carbon pollution grew, it became obvious to scientists that industrialized societies could not just continue diluting gigatons of carbon dioxide in the atmosphere, and they alerted policymakers. The iconic moment of this development was the testimony of Dr James E. Hansen, at the time director of NASA's Goddard Institute of Space Studies, before the Senate of the US Congress in 1988 (Shabecoff
390 1988). In the same year the scientists of the world came together and established the Intergovernmental Panel on Climate Change (IPCC) to create a coherent body of knowledge to inform decision-making. The IPCC has so far produced a series of five Assessment Reports, which assesses the science of climate change, its impacts, and ways to mitigate it (Allen et al. 2014).

395 (Carbon dioxide is not the only greenhouse gas and the IPCC reports consider each in detail, but because the other gases are not produced in significant quantities by fuels and the energy industry they fall outside the scope of this discussion.)

Industrialized societies currently depend on energy from fossil fuels. Huge investments have been made in infrastructure, large numbers of people find employment in this industry, and available alternative sources of energy are not nearly sufficient. The health and well-being of the greater part of the world's population depend on it. But the future health and well-being of those same societies also depend on ending that dependence. A logical conclusion would be that it would be in the best interest of industrialized societies to create plans to reduce the dependence on
405 energy from fossil fuels and exploit alternative energy sources.

But industrialized societies are also in economical competition with each other. This means that any society that spends resources on risky, expensive alternative sources of energy risks falling into a competitive disadvantage, and there is a surfeit of short-sighted politicians who will take advantage of this risk to create fear and so prevent planning for and investment in changes in energy production and use³.
410

Fortunately there are enough leaders who have vision, and based on the recommendations of the IPCC the governments of the world have come together to create the UNFCCC. The United Nations Framework Convention On Climate Change is an international agreement that structures the response of nations to limit their emissions of greenhouse gases. Two international treaties have been agreed to so far: the
415 Kyoto Protocol in 1997 (*Kyoto Protocol to the United Nations Framework Convention on Climate Change*. 1997) and the Paris Agreement in 2015 (*Paris Agreement* 2015).

These agreements attempt to reduce the amount of carbon dioxide released into the atmosphere by dividing the cost of reducing emissions fairly. While the Kyoto
420 Protocol invoked a complex carbon credit trading scheme, in the Paris Agreement nations pledge to reduce emissions of carbon dioxide into the atmosphere, and each is free to do so in a way that suits them best.

The Republic of South Africa is a signatory to the Paris Agreement, and therefore the country is legally bound to limit and reduce its emissions of carbon dioxide and other greenhouse gases. The country has so far promised to stop increasing
425 emissions between 2020 and 2025 (*South Africa's Intended Nationally Determined Contribution (INDC)* 2016).

1.2 Carbon footprints and carbon neutrality

Ending the emission of carbon dioxide by industrialized societies is an exercise in
430 balancing effort with consequences. Every reduction in carbon dioxide emissions

³The impact of political corruption is not negligible, but I will abstain from commenting on it.

must necessarily have an effect on the economy, and conversely, every change in economic activity will have an effect on carbon dioxide emissions.

A rational, discerning society in searching for ways to carbon dioxide emissions will therefore attempt to change their economy in such a way that the emission of carbon dioxide is limited or reduced. But in most societies there are many ways to
435 reduce carbon dioxide emissions, and decisions have to be made on which ones to implement. Such decisions must be based on sound information, and one way to generate that information is a discipline called *life cycle analysis* (LCA).

Life cycle analysis can yield rigorously-calculated data and comparisons, but it is
440 a very general method. For analyses that are very similar and differ only in context, it is possible to develop simplified, standardized life-cycle analysis tools.

One such tool is the *carbon footprint*. Every economic activity in an industrialized society generates emissions of greenhouse gases. These emissions might be far removed from the activity in space and time. A most obvious example of this is the
445 use of electricity: At the moment I'm using a computer to compose this paragraph and electric light illuminates the desk I'm working on here in my office in Pretoria. The electricity that powers the computer and the lamps are generated hundreds of kilometres from here, most of it on the Mpumalanga Highveld, in coal-fired power stations which emits carbon dioxide in the process. So my activity is far removed
450 from the associated emissions **in space**. But even before the coal was burned, the machines that mined it and transported it to the power station emitted carbon dioxide, so my activity is also removed from the emissions **in time**. The sum of all these emissions connected with my activity constitute the carbon footprint of my activity.

Although carbon footprinting is conceptually straightforward, it is analytically
455 rigorous and computationally complex. But there are standard protocols (World Resource Institute 2004) that can be followed, so that carbon footprints from different activities and different organizations are transparent and comparable.

Once an organization's activities have been footprinted, the organization can examine its operations and look at ways to change activities that will reduce that footprint.
460

If my university, for example, decides to install photovoltaic panels on the roof of my building, and use the electricity to illuminate my office, the activity will now most likely have a reduced carbon footprint, because photovoltaic electricity usually has a lower carbon footprint than coal-derived electricity.

To prevent a climate disaster, at some point industrialized societies will have to
465 change all their activities until they no longer emit any greenhouse gases. Such activities will have carbon footprints of zero, and will be known as 'carbon neutral activities'. There are also activities that are nett removers of carbon from the atmosphere, which would be 'carbon negative'.

In truth, in industrialized societies there are very few carbon neutral activities.
470 Even if I'm just sitting quietly in a pristine nature reserve, the food I am digesting and metabolizing have a positive carbon footprint: carbon was emitted to fix nitrogen from the air, which was used as fertilizer to help grow the food I ate, and is now in the proteins of my body. The very calcium and phosphorus in my bones were
475 sourced from mines that were powered by fossil fuels.

1.3 Internal combustion engines.

Carbon footprinting exercises quickly show that a major source for emissions is transport. Most transport in industrialized societies is powered by internal-combustion engines. They are called ‘internal-combustion’ engines because the chemical transformation that extracts the energy from the fuel is internal to the engine. This is in contrast to the power station steam turbines mentioned earlier, where the extraction of the chemical energy from the fuel happens outside of the engine. The engine is the device that produces the mechanical energy. These engines are usually powered by liquid fuels derived from crude oil, although some designs run on gas, and of course in South Africa Sasol and PetroSA supply us with liquid fuels derived from coal and natural gas.

In this discussion I will use the term *noxious pollution* to describe pollution that is directly harmful to humans and *carbon pollution* to describe pollution that leads to industrial climate disruption.

The simplest way to reduce an activity’s carbon footprint is to use the fuel that contributes to that activity’s footprint more efficiently. Fortunately market forces are aligned with this, because more efficient use of a fuel also reduces running costs. Discussing engine designs therefore almost always invokes *efficiency*. Efficiency of an engine is calculated by taking the ratio output power:input power. The greek letter η is used as a symbol for efficiency:

$$\eta = \frac{P_{out}}{P_{in}} \quad (1.2)$$

Conservation of energy dictates that the output power cannot be more than the input power, and therefore $\eta \leq 1$. The power is ‘lost’ to two factors: firstly entropy, as dictated by the Second Law of Thermodynamics, and secondly losses, such as friction.

1.3.1 Scaling and efficiency

The efficiency of engines scales disproportionately with its linear dimensions, by which I mean that the larger an engine is, the more efficient it is. There are three factors that improve efficiency in larger engines (Brown, Menon, and Hagen 2015):

1. Longer residence time: In larger engines, the reacting fuel spends more time in the engine. This gives reactions more time to reach equilibrium, and hence more energy can be extracted.
2. Smaller surface area to volume ratio: The volume of an engine increases with the cube of its linear dimension, but the surface area increases with the square of its linear dimensions. This means that larger engines have a smaller surface-to-volume ratio than smaller engines. Since losses take place at the surface, the loss per unit volume is therefore larger for smaller engines than it would be for larger engines of the same type. If the losses in larger engines are disproportionately smaller, we can expect larger engines to be more efficient than smaller ones.
3. Larger Reynolds number: The Reynolds number is a number that predicts the onset of turbulent flow, and is calculated from the viscosity, velocity and a characteristic linear dimension. The higher the Reynolds number, the higher the likelihood of turbulent flow. Turbulent flow promotes mixing, which leads

to improved combustion and hence higher efficiency. The larger the engine,
 520 the larger the characteristic linear dimension, and therefore the higher the likelihood of turbulent flow.

From the viewpoint of reducing carbon pollution, one should therefore aim to use a few large engines rather than a multitude of small engines.

1.3.2 Engine design and thermodynamic cycles.

525 The final design of a successful internal combustion engine is determined by the variation-selection process described by Vincenti (Vincenti 1990). Such a design sufficiently satisfies a wide range of requirements. These requirements might be explicitly expressed in documentation, or they may be implied, or they may be practical. These requirements would include, but are not limited to, capital cost, running cost,
 530 maintenance cost, sound, ease of maintenance, power output, emissions, surface finish, weight, mounting method, size, supply chain capability, shape, colour, fuel availability, operating temperature, altitude tolerance and torque.

From designers' attempts to fulfil these requirements arise the myriad of different engine designs, delivering anything from milliwatts to megawatts of power to
 535 anything from model aircraft to oil tankers. It is the good fortune of researchers who study the engine energy that there are only a few conceptual systems that explain how the internal combustion engines convert the chemical energy of the fuel into mechanical work.

The principles on which the different engines operate are named 'cycles', because
 540 the way they convert heat into work can be describe in terms of a series of events that are repeated in a endless cycle. The concept of a cycle is further entrenched because it is customary to explain the thermodynamic processes involved using at pV diagram, showing the changes of state of the working fluid during engine operation.

Theoretical thermodynamic cycles are useful because they can predict the performance of heat engines, and allows for comparison. In particular, it allows for
 545 comparison with theoretical maxima. The maximum efficiency of a heat engine is delivered by an engine running on the Carnot cycle. This is a hypothetical engine that uses only reversible processes to extract useful work from the temperature difference between two reservoirs of heat. It has been shown that the Carnot cycle
 550 offers the maximum possible heat extraction, and that the maximum efficiency is determined solely by the temperature difference between the hot and the cold reservoirs.

$$\eta_C = 1 - \frac{T_c}{T_h} \quad (1.3)$$

The Carnot cycle, however can only deliver an infinitesimal amount of work, because the heat transfer must be reversible, and therefore infinitesimal. A more
 555 realistic maximum efficiency is given by the Chambadal-Novikov efficiency (Hoffmann 2008):

$$\eta_{CN} = 1 - \sqrt{\frac{T_c}{T_h}} \quad (1.4)$$

This theoretical efficiency takes into account the irreversible processes that are inevitable in engines delivering real amounts of power.

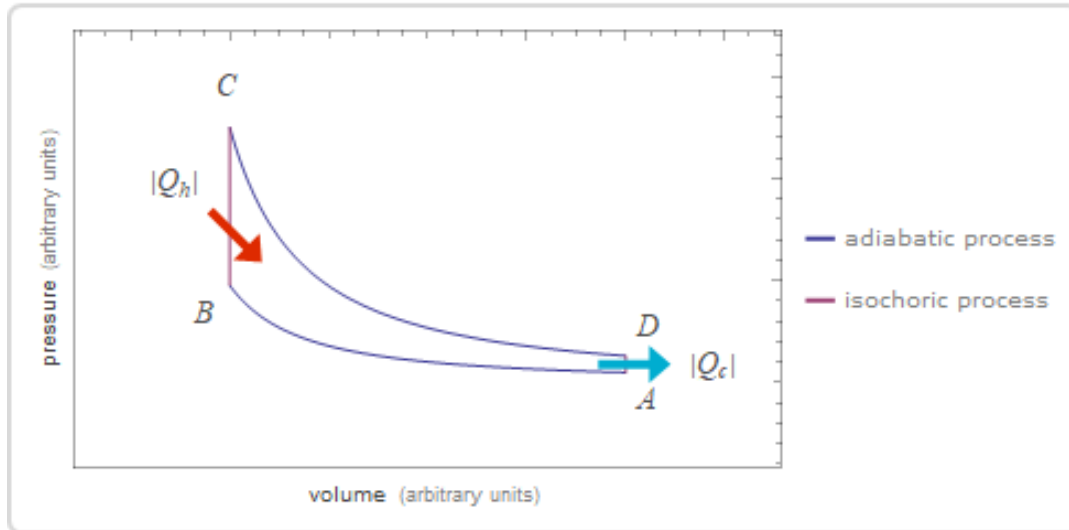


FIGURE 1.1: The pV diagram of the thermodynamic Otto cycle

Barring revolutionary new discoveries and inventions, there will be only three thermodynamic cycles and their corresponding engines on the market, as we enter the low-carbon era.

Otto engine and Otto cycle

The oldest of the internal combustion engines is the Otto engine. It is named after Nikolaus Otto, who developed the first working engine of this kind in 1876 (Cummins 1989, Chapter 9). In South Africa these engines are usually called ‘petrol engines’.

In the Otto engine, a homogeneous mixture of atmospheric air and vaporized fuel is compressed. This mixture is then ignited by an electric spark. The energy released by the chemical reaction between the oxygen in the air and the fuel vapour causes the temperature of the compressed air to rise, and consequently the pressure. If this, now hot, gas is allowed to expand in an expandable vessel, the motion of the vessel can be captured to perform useful work. Once the useful work is extracted, the vessel can be collapsed again to expel the exhausted air, and re-filled with a compressed air/fuel vapour mixture. This completes the cycle. The expandable vessel is usually in the form of a cylinder and piston, with the piston connected to a crank that drives a shaft that transfers the work from the engine to the machine being powered.

(These legs of the cycle are only loosely related to the ‘strokes’ of a four-stroke engine, and should not be confused for them.)

The theoretical efficiency of the Otto Cycle is given by

$$\eta = 1 - \left(\frac{1}{r^{\gamma-1}} \right) \quad (1.5)$$

where r is the *compression ratio*, $\frac{V_1}{V_2}$, and γ is the heat capacity ratio, which can be considered a constant for the purposes of this discussion.

This means that the efficiency of an Otto engine can be improved by increasing the degree of compression of the intake air before combustion.

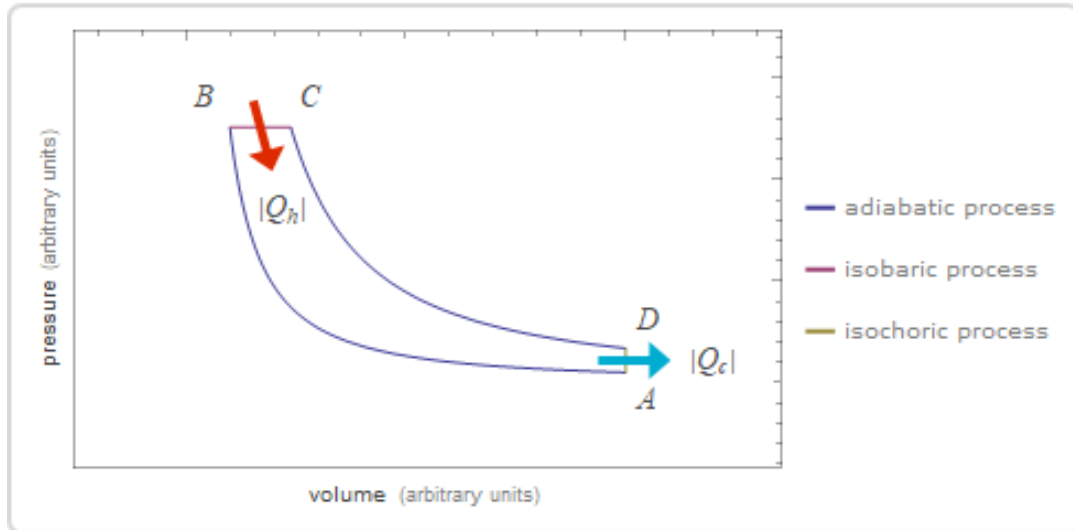


FIGURE 1.2: The pV diagram of the thermodynamic Diesel cycle

585 Diesel Cycle

In the Diesel engine, named after Rudolf Diesel who demonstrated the first engine of this type in 1897 (Cummins 1989, Chapter 14), air is compressed, and then a finely divided solid or liquid fuel is injected into the system. The fuel then reacts with the oxygen in the air. The energy released in the reaction appears as a higher temperature in the gas, and — following Gay-Lussac's Law — the pressure of the gas rises. If the gases expands in the confines of a collapsible vessel, useful work can be extracted from expansion of the vessel. Once the work has been extracted, the vessel can be collapse again to remove the now inert ('exhausted') gas and prepare for receiving the next charge of air, completing the cycle.

595 The theoretical cycle used to analyse the performance of the Diesel Engine is called the Diesel Cycle. (See figure 1.2)

The Diesel cycle differs from the Otto cycle in the heat addition step. In the Otto engine, the heat addition takes place when the homogeneous air/fuel mixture is combusts. This combustion takes place in a short space of time during which the engine parts move only a negligible distance. Hence the pressure rises rapidly. In the Diesel engine, the fuel is injected into a volume of compressed air, where it combusts. (There is no separate ignition source: the temperature of the adiabatically compressed air is higher than the fuel's ignition temperature, so that the fuel ignites upon injection. While this is another difference between the two engines, it is of second-order importance when discussing thermodynamic cycles.) Because the combustion takes place at the surface of fuel particles, the combustion rate is lower than the combustion rate of the homogeneous mixture in the Otto cycle. Hence the rising temperature is balanced by the motion of the engine, and the heat addition is essentially isobaric.

$$\eta = 1 - \frac{1}{r^{(\gamma-1)}} \left(\frac{\alpha^\gamma - 1}{\gamma(\alpha - 1)} \right) \quad (1.6)$$

610 where α is the *cut-off ratio*.

The term $\frac{\alpha^\gamma - 1}{\gamma(\alpha - 1)}$ is always larger than 1, and therefore, when we compare equation 1.6 with equation 1.5 it is clear that for a given compression ratio the Diesel cycle

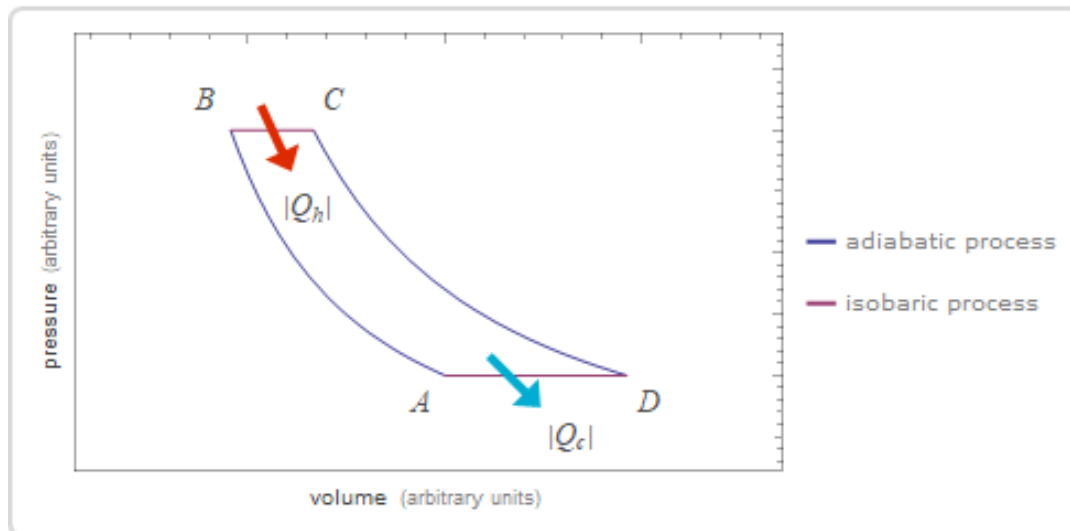


FIGURE 1.3: The pV diagram of the thermodynamic Brayton cycle

is always less thermally efficient than the Otto cycle.

However, at high compression ratios Otto engines start suffering from ‘knocking’, when the homogenous air/fuel mixture detonates, instead of burning smoothly. The shock waves from this detonation will damage the engine and lead to faster wear. (The *octane number* of a fuel indicates the compression ratio it can accommodate.) Because Diesel engines do not suffer from this problem, they are usually designed to for higher compression ratios than Otto engines and therefore are more efficient.

Gas turbines and the Brayton Cycle

The third internal-combustion engine important to industrialized society is the *gas turbine*. Gas turbines are used rarely in road transport, more often in marine and stationary applications, but thousands take to the sky every day, propelling aircraft (Morris 2017) carrying billions of airline passengers every year.

The first gas turbines were developed during wartime urgency to deliver pure jet thrust for military aircraft, but this proved to be an inefficient use of the available energy. Most modern turbine engines drive a shaft to extract rotational work. This shaft might drive a bypass fan (as used in airliner engines), a propeller (as used in smaller, low-speed aircraft), or a shaft which might drive a helicopter rotor or an electrical generator.

In operation, a gas turbine compresses air with one or more compressor stages. The compressed air passes through a combustion chamber, where fuel is added and combusted. As the now hot gases expands it passes through one or more turbine stages, which is connected to drive the compressor and the output shaft, which extracts work from the system. After the gas has passed through the turbine it returns to atmospheric pressure, optionally doing work on the engine in the form of thrust.

The theoretical thermodynamic cycle that is customarily used to analyse the gas turbine is called the Brayton cycle, named after George Brayton, who successfully manufactured a reciprocating engine based on this cycle. (See figure 1.3) Such engines are no longer manufactured (Cummins 1989, Chapter 10).

The efficiency of the Brayton cycle is given by equation 1.7

$$\eta = 1 - \frac{T_1}{T_2} = 1 - \left(\frac{P_1}{P_2}\right)^{\left(\frac{\gamma-1}{\gamma}\right)} \quad (1.7)$$

Because the fuel is continuously added to the compressed air and the combustion takes place in a heterogeneous mixture, gas turbines do not suffer from 'knocking' and therefore there is no upper limit to the compression ratio. The main figure determining the efficiency of the engine is the turbine inlet temperature, (*i.e.* the outlet temperature of the combustion chamber) which reaches 1600 °C in modern engines.

1.3.3 Noxious pollution from internal combustion engines.

Carbon pollution is not the only pollution emitted by internal combustion engines. There is also noxious pollution, which affects the societies in which they are used. There are ways to reduce or eliminate such pollution, but the implementation of such measures affect the efficiency of the engine.

Noxious pollution from internal-combustion engines come from different sources and have different effects.

Unburnt fuel

The combustion reactions in internal- combustion engines are very fast, but they are never at equilibrium. This means that at then end of a cycle, the exhaust gases are expelled from the engine contains, besides the carbon dioxide, also chemical intermediates and unreacted fuel molecules.

Unreacted fuel is a noxious pollutant, not only in its own right, but also, during the decomposition process in the environment, chemical reactions induced by sun-light produces ozone, a reactive oxygen species that leads to respiratory problems in victims of pollution (Davidson 1998).

Some of the fuel-like pollutants from internal-combustion engines are not present in the fuel. These compounds are formed in a process that might be called *pyro-synthesis*. They are themselves more stable than the compounds from which they originate, but not as stable as combustion end products, carbon dioxide and water. Because they are themselves quite stable, they require high temperatures to combust, which might not be achieved before they leave the engine as waste. Notable pollutants from this source are the polycyclic aromatic hydrocarbons (PAH) and dioxins.

One of the products of pyro-synthesis is particles of soot. These particles are agglomerations of nano-sized particles of pure, amorphous carbon. The agglomerations might include adsorbed PAHs and acids. Soot particles are very stable and only react at very high temperatures. Diesel engines in particular have a reputation for producing soot (Mohankumar and Senthilkumar 2017).

The final pollutant that can be classed as originating from partially combusted fuel is carbon monoxide. It forms readily when fuels are burned in oxygen-poor environments. Modern, well-maintained engines is a relatively rare cause of acute carbon monoxide poisoning (Reumuth et al. 2018), but chronic exposure to low levels of environmental carbon monoxide has harmful effects (Wright 2002).

Contaminants and additives.

Crude oil and coal contains not only carbon and hydrogen, but also other elements, most notably sulfur and nitrogen. Depending on the refining process, these elements might find their way into fuels. Organic nitrogen and sulfur will easily oxidize and

685 form stable oxides, yielding energy. Once outside the engine, however, the volatile oxides will dissolve in any water in the air, forming acids. (Duncan et al. 2016)

Fuel manufacturers add additives to fuels for various reasons, such as boosting octane rating or preventing corrosion. The prime example of additives as a source of noxious pollution was tetraethyllead, which was added to petrol as an octane booster. The emitted lead compounds were shown to be a pollutant that led to neurological impairment in its victims, and its use was phased out (Needleman 2000).

Side-reactions

Most internal combustion engines use atmospheric air as oxidant. This air is 21% oxygen, and 78% nitrogen. Although nitrogen is very stable and inert, at high temperatures it can react with oxygen. These reactions produce the oxides of nitrogen: 695 NO, NO₂, NO₃ and N₂O, and N₂O₅. They are collectively called NO_x.

These oxides can participate in the cycle that causes the photochemical smog. They will also dissolve in atmospheric water and form acids: this might happen far from the point of emission, resulting in *acid rain*.

700 1.3.4 Mitigating pollution from internal-combustion engines.

Pollution from internal combustion engines is a social ill, and most governments have regulations in place to limit and reduce this pollution. Engine and fuel manufacturers are working hard to reduce this pollution.

705 The noxious pollution from internal combustion engines can be reduced by various ways, but there are three complementary approaches: fuel formulation, cleanup and engine management.

Fuel formulation

Adding oxygenates improves the octane rating of fuel and reduces NO_x formation.

Exhaust gas cleanup

710 Exhaust gases from internal combustion engines can be “cleaned”, and there are basically two approaches. The first is catalytic conversion, in which the exhaust gases that contain the pollutants are passed over a catalyst bed. The catalyst (a proprietary formulation of platinum, palladium and/or rhodium), adsorbs the uncombusted volatile organic carbons and NO_x, and oxidizes and reduces them.

715 Secondly, filter systems can be used to remove particulate matter.

Engine management

As described above, the main source of noxious pollution from internal-combustion engines is uncompleted or undesired chemical reactions, and is not fundamental to the operation of the engine. By carefully managing the engine system, noxious 720 pollution can be reduced.

The oldest engine management technology is the oxygen or ‘lambda’ sensor, which measures the oxygen in the exhaust gases. Such a sensor, coupled to an engine-management computer, allows the metering of the exact amount of fuel needed for optimum combustion.

725 A newer technology is known as exhaust gas recirculation. This mixes the intake air of the engine with exhaust gases, effectively diluting the oxygen. This reduces peak temperatures, and thereby NO_x formation.

In *stratified charge* engines the distribution of fuel in the volume of intake air is controlled by selective fuel injection. By carefully having the fuel at the right place
730 at the right time can allow for higher compression ratios without inducing pinging. *Lean-burn* engines are Otto engines that use extremely high air:fuel ratios.

Electronic engine management systems result in much more efficient and less-polluting engines than non-managed 'mechanical' engines, but because engines for automotive applications endure such a wide range of operating conditions, they can
735 at best achieve a compromise between power, efficiency and emissions. It was this unsatisfactory compromise that led to the Volkswagen emissions scandal: manufacturers chose to cheat on emissions test rather than admit to the relatively poor performance of a managed engine optimized for low emissions (Mansouri 2016).

Efficiency implications

740 Attempts to mitigate noxious pollution from internal-combustion engines always have efficiency implications, and it's rarely an improvement. For example:

- Catalytic converters and filters absorb energy.
- The engines cannot approach their theoretical maximum efficiencies, because reducing NO_x emissions is handled by limiting maximum combustion temper-
745 atures.
- NO_x reduction catalysts require the presence of hydrocarbons, *i.e.* uncompleted reactions, which implies that not all energy is extracted from the fuel.
- Every treatment system added to the engine adds weight to the vehicle, which reduces payload and hence the total efficiency.

750 Before carbon pollution was a concern, it made sense to accept lower efficiencies as a necessary cost of reducing noxious pollution, but in a low-carbon future we cannot just keep on trading less noxious pollution for more carbon pollution.

1.3.5 Avoiding pollution from internal-combustion engines

The efficiency and cleanness of internal-combustion engines have dramatically in-
755 creased over the last century, and more improvements are being implemented. But these improvements have not been fundamental to the engines in any way, and have been driven mostly by government regulation, at the cost of increased complexity and a higher purchase price.

It would seem obvious that it would be a good idea to introduce alternative tech-
760 nologies.

Electrification

In principle, there is nothing special about internal-combustion engines: they are not an end in themselves. They merely deliver a source of torque, which can be coupled to machinery to do useful work. Before the industrial era such torque was available
765 from windmills and waterwheels, and today an alternative is the electric motor.

Electric motors are engines that use the interaction between electric current and magnetic fields to deliver useful torque to drive machines. Because they use electricity as a source of energy, they have no noxious emissions where they operate. Because they are not heat engines, their efficiencies are not subject to the Carnot limit, and efficiencies exceeding 95% are standard (Li and Curiac 2012).

Electricity, of course, is not necessarily carbon-neutral. Most electricity is generated in power plants that use fossil fuels as a primary source of energy. But because these plants are huge, and efficiency scales disproportionately with size, the energy output by the electric motor has a similar or lower carbon footprint than an equivalent internal-combustion engine (Doucette and McCulloch 2011).

Electricity grids are also increasingly being fed by solar and wind power, which are carbon-neutral at source. These renewable plants are also smaller and more flexible than their behemoth fossil-fuel counterparts, with lower capital costs and extremely low running costs.

Hence, in a low-carbon future, there is every reason to support or mandate the use of electrical motors for stationary applications wherever possible.

In automotive applications, *i.e.* in cases where the engine is used to move itself in addition to some form of payload, the application of electric motors is more demanding. In this case it is not easy to bring the electricity to the motor, although electric trains and buses fed by overhead conductors are splendid examples of the electrification of transport. So for electric vehicles to use the existing road network, they need to carry a source of electricity with them.

This source of electricity can be either a chemical battery, or a fuel cell. In a chemical battery power from the grid is stored in the form of reversible electrochemical reaction, and in a fuel cell the chemical energy from a fuel is directly converted into electricity. There are fuel cells that can use hydrogen as a fuel, and fuel cells that can use methanol as a fuel. (It goes without saying that the hydrogen and the methanol need to be sourced from low-carbon sources for fuel cells to count as low-carbon energy sources.)

The storage and transport of hydrogen remain hurdles to the large-scale adoption of hydrogen-fuelled automobiles, although a market seems to be developing for hydrogen-fuelled electric trains (Agence France-Presse 2018). Hydrogen fuel cells emit no carbon or noxious pollution at point of use.

Direct methanol fuel cells can react methanol with atmospheric oxygen in an electrochemical cell to yield electricity, with (carbon-neutral) carbon dioxide as a waste product. Little is known about possible noxious pollution.

At this time it seems that the electrification of road transport will be by chemical batteries. Lithium-ion batteries can now store enough energy and deliver enough power to make electric motor vehicles practical and attractive (Hayes et al. 2011), and some governments are considering plans to no longer allow the production of passenger vehicles propelled by internal combustion engines (Burke-Kennedy 2018) (Reuters 2018) (Gabbatiss 2018).

Carbon-neutral fuels

Another way to avoid the carbon pollution associated with internal-combustion engines is to change the fuel. Not all fuels are fossil fuels, and it is possible to use fuels that are carbon neutral, and in some cases carbon negative.

Apart from using hydrogen in a fuel cell, as described above, *hydrogen* can also be used as a fuel in Otto engines, because it will combust in air to yield heat. The

emissions are water and NO_x. Presently there are no hydrogen-fuelled Otto engines on the market.

Methanol is a common product of the fossil fuel industry, but work is underway to produce methanol by reducing carbon dioxide using solar energy. Such *solar methanol* might be used in direct conversion fuel cells, or in internal-combustion engines.

It is possible to harness the energy contained in the reduced carbon in biological materials and use it as fuel. Such fuels are known as *biofuels*.

1.4 Biofuels

Biological processes are an integral part of the carbon cycle, because photosynthesis in plants reduce carbon dioxide in the atmosphere to sugars, which is converted by plant physiology into structural cellulose and other metabolites.

The prototypical biofuel is of course wood, used in all societies for cooking and heating. This familiarity makes biofuels seem like an obvious and viable source of energy, but details matter, and switching from fossil fuels to biofuels to reduce carbon footprints of human activities is not a simple choice.

Firstly, the efficiency of photosynthesis is notoriously low: not above a few per cent, whereas the efficiency of a mass-produced silicon-based solar panel is in excess of 20%. In general it is much more efficient to capture solar energy in a PV panel and use an electric motor to provide the necessary mechanical power than to create a biofuel and use it to drive an internal-combustion engine.

Second, increased biofuel production has numerous impacts on the environment and society, which cannot be ignored.

Discussing all the factors that need to be studied to make such a decision is outside the scope of this work, but as an example a report prepared for stakeholders in the Netherlands (Smeets et al. 2006) uses the following criteria:

- GHG emissions – the use of biofuels should cause reductions of GHG emissions. The comparison should be done regarding the average use of fossil fuels, considering the life cycle of fossil and biofuels (i.e., well-to-wheel basis) and in case of biofuels reduction should be at least 30%
- Impacts over food supply – the production of biomass for energy must not endanger the food supply and other local biomass applications. The analysis should be developed considering possible changes of land use in the region of biomass production.
- Biodiversity – Biomass production must not affect protected or vulnerable biodiversity.
- The basic criteria are that violation of national laws and regulations are unacceptable.
- Local environmental effects – Principles include (a) soil and soil quality, that must be retained or even improved, (b) ground and surface water supply, that must not be polluted.
- Local economic effects – The production of biomass must contribute towards local prosperity.

- Social well-being – The production of biomass must not decrease the well-being of local societies.

Nevertheless, there are cases where using biofuels is a good option.

860 1.4.1 Bio-gas

Anaerobic bacteria can oxidize carbon compounds to methane. This methane is identical to the methane obtained from natural gas, and can be used for the same applications.

865 An excellent application for the use of bio-gas is waste remediation. Waste material from the agri-food industry can be highly polluting if not treated properly, emitting noxious chemicals into water and the potent greenhouse gas methane into the atmosphere. But when used as feedstock for bio-gas production, it reduces carbon pollution by capturing methane and displacing natural gas, and also prevents water pollution (I. Venter 2014).

870 Bio-gas can be used to fuel Otto engines or gas turbines.

1.4.2 Bio-ethanol

Yeast and other microbes can convert sugar or starch from plants into ethanol. This technology is as old as civilization. I'll leave it to the archaeologists to decide where beer was brewed first, but it is clear that between 3200 and 3000 BCE in ancient 875 Sumeria the brewing of beer was an activity regulated by the government (Damerow 2012). By 2000 BCE in ancient Egypt the technology of fermentation was harnessed well enough that bakeries and breweries were co-located (*Model Bakery and Brewery from the Tomb of Meketre* 1920).

Beer and wine can best be described chemically as aqueous solutions of sugars, 880 ethanol, flavourants and colourants, with or without suspended solids. It was not until the 8th century CE that Persian and Arab scientists mastered the art of distillation and purified ethanol (Modanlou 2008), and it was not until Pasteur that yeast was seen as a living organism, and ethanol a product of its metabolism (Barnett 2000).

885 I could not find a reference to the first use of ethanol as a fuel, but its flammability must have been noticed by the first distillers. By 1838 ethanol was common enough to be used in alcohol lamps as a source of heat in the chemical laboratory (Griffin 1838), and by the 1850s it was a major component of lamp oil used for illumination in the USA (Abebe 2008).

890 Ethanol as a fuel of internal combustion engines has a clear start date: in 1826 Samuel Morley was granted a patent for an engine designed to use ethanol as fuel (Cummins 1989, p. 79).

The industrial production of ethanol is a technologically advanced process. It is an active research field. A paper (Cardona and Sánchez 2007) reviewing the process 895 technology of producing bio-ethanol written in 2007 had garnered 644 citations by January 2019.

The industrial production of ethanol consists of three steps.

1. Fermentation
2. Distillation
- 900 3. Dehydration

The fermentation step is the biological process by which the yeast organism *Saccharomyces cerevisiae* convert the sugar and starch in the biological material to ethanol and carbon dioxide. This needs to be done in a sterile environment to prevent contamination by other micro-organism.

905 The distillation step is the physical process of separating the produced alcohol from the aqueous mixture in which it is produced. This generally produces an azeotropic mixture that contains 95.6 % ethanol (Kumar, Singh, and Prasad 2010).

While the processes of fermentation and distillation of ethanol for fuel is in principle the same as that of producing alcoholic beverages, the emphasis of the processes are very different. In the beverage industry the emphasis is on the development of complex flavours and a consistent, recognizable drinking experience. In 910 the fuel industry the emphasis is on efficiency and throughput. (Of course there are exceptions to this. I'm looking at you, heathen vodka!)

To produce fuel-grade ethanol from the distilled azeotrope, dehydration is a necessary third step. This step can be implemented by various distillation processes 915 that add a third compound, but in most modern plants the water is removed by adsorption onto molecular sieves (Kumar, Singh, and Prasad 2010).

Brazilian ethanol

Brazilian sugar-cane ethanol is an integral part of the country's energy network. 920 Most Otto-engine vehicles have 'flex-fuel' engines, which can be fuelled with any blend of ethanol and petrol. The industry is regarded as sustainable ((Smeets et al. 2006).

US maize

US maize ethanol is primarily blended with petrol to meet legislative requirements 925 of oxygenates in fuels. The production of maize is water-intensive and the fermentation process is carbon-intensive. The US ethanol from maize has a poorer energy balance and larger carbon footprint than Brazilian ethanol from sugar cane, but has a smaller water footprint (Mekonnen et al. 2018).

Ethanol can fuel Otto engines and gas turbines.

930 1.4.3 Fischer-Tropsch fuel from biomass

It is possible to heat woody biomass with steam and in a low-oxygen environment to produce synthesis gas, which can be passed over a catalyst to produce a mix of fuel products. Such a fuel could be called a bio-fuel, but (with apologies to my 935 colleagues at Sasol) I think this scheme is so lacking in imagination as to not deserve further comment.

1.4.4 Refined vegetable oil: "Green diesel"

The petroleum industry has developed a collection of chemical processes, such as hydrogenation, oxygenation and cracking. This collection of processes can be applied to vegetable oils to produce a fuel for diesel engines and gas turbines. This 940 path is being followed by the aviation industry (Chiaramonti et al. 2014).

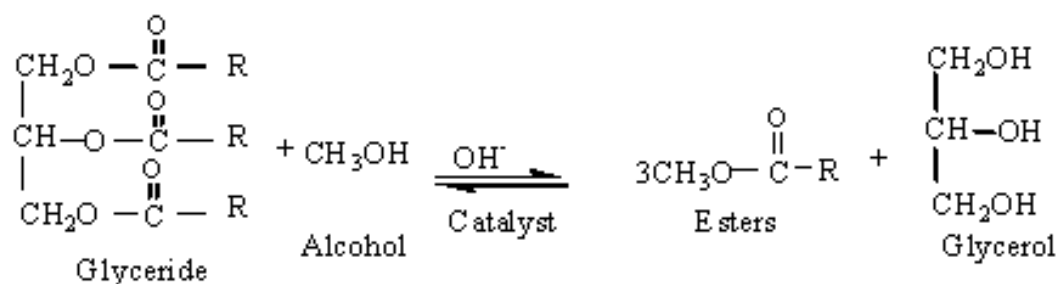


FIGURE 1.4: Transesterification

1.4.5 Biodiesel

Oils and fats have been used as fuels since antiquity, most obviously as a fuel for lamps: olive oil has been identified as the fuel used in lamps dating from around 600 CE (Kimpe, Jacobs, and Waelkens 2001), and at the Paris World Fair in 1900

945 Rudolf Diesel demonstrated an engine that ran on peanut oil (Knothe 2010).

During the energy crisis of the 1970s, the South African government looked at alternative sources of fuel. Experiments were done with sunflower oil in tractors, but there was a problem with the formation of carbon deposits around the injector nozzles. Seeing that the clogging of the injectors might be caused by the high viscosity of the sunflower oil as a fuel, the transesterification of the oil was implemented,

950 replacing the glycerol in the sunflower oil with methanol. This created an oily liquid with a lower viscosity, which proved to be a trouble-free replacement (Van Niekerk 1980).

Such a transformed oil is termed *biodiesel*. It consists primarily of a mixture of fatty acid methyl esters, often abbreviated into the acronym FAMES.

955 Compared to ethanol, biodiesel production is relatively simple, the main method sharing much with the ancient technology of making soap. This simplicity makes the production of biodiesel attractive to small and decentralized manufacturing, and consequently governments consider biodiesel production an attractive proposition:

960 it can create job opportunities in rural population and it can create a stable market for farmers who produce vegetable oil crops.

Biodiesel is not yet carbon neutral: the methanol used to create the methyl esters is a product of the petroleum industry, and therefore biodiesel emissions contribute to global warming. But replacing fossil diesel fuel with biodiesel results in a nett

965 reduction of carbon emissions, with the future possibility of replacing fossil-derived methanol with carbon-neutral bio-methanol (Shamsul et al. 2014).

1.5 The significance of biodiesel and its quality control.

In a complex technical, economic and social environment it is likely that there will always be a need that can be best met by internal combustion engines. The decision on

970 the type of engine and the decision on the fuel for that engine are not independent, as Cummins reminds us (Cummins 1989):

Our generation faces a similar challenge in a real liquid fuel energy shortage that will come within the lifetime now living. As we plunge into

the seeking of solutions to our dilemma, we must never forget that *an engine and the fuel it consumes are inseparable partners*; the one cannot progress without the full cooperation from the other. This precept is vital to the planning of future powerplants, since an engine's design determines its fuel and binds us to our future resource requirements .

While the variation-selection process by which real engineering progress is 'blind', *i.e.* the combination of factors that make a design successful is not known at the start of a development (Vincenti 1990), scientific knowledge provide guidance in the form of insight into processes and theoretically achievable targets for performance. Using the scientific knowledge we have today, we can risk a forecast: if society is determined that its carbon footprint should be reduced with minimal noxious pollution the application of internal combustion engines would tend towards the following:

1. Larger: Because larger engines are more efficient than smaller engines, larger engines will be preferred. (See section 1.3.1)
2. Low-carbon: The preferred engine would be fuelled by carbon-neutral fuels. (Section 1.3.5)
3. Constant speed: Engines are most efficient when they can work at constant load. (Section 1.3.4)
4. Efficient: Engines with high efficiency should be preferred, which implies engines with high compression or pressure ratios. (Section 1.3.2)
5. Cleanup: The exhaust should be amenable to cleanup, *i.e.* the exhaust gases of the fuel-engine system should not contain compounds that are incompatible with available converter or filter technologies. (Section 1.3.4)

From this it should be clear that the optimal engine of the future will not be an Otto engine, because it will always have a limited compression ratio and its catalytic exhaust cleanup will always require stoichiometric air:fuel ratios, which puts bounds to efficiency increases.

Because it is the most efficient engine, the gas turbine will play an important role. However, its exhaust temperature is very high, which begs for energy recovery to increase the efficiency of the system. Such systems are already seen in the *combined cycle gas turbine* (CCGT). But energy recovery systems are not light and small, so their best application outside aerospace (where the excess heat is utilized as thrust) appears to be stationary electricity generation.

For automotive applications the engine that will best contribute to reduce the carbon footprint of the activity that uses it will be a large Diesel engine with exhaust cleanup to remove NO_x and soot, fuelled with a carbon-neutral fuel.

In choosing between refined vegetable oil and biodiesel as a fuel, is most likely that biodiesel will have a lower carbon footprint. Refinery operations are energy intensive, which might add to the carbon footprint of the fuel, and refineries are not usually near the point of use, so that transport will also add to its carbon footprint. The carbon emissions of biodiesel production are comparatively low. (At this point it is important to note that these observations are not definitive: carbon footprints are not predicted, they must be calculated.)

Buying large, highly efficient diesel engines with sophisticated management systems and exhaust cleanup require high capital investment. In an economically competitive environment they therefore need to bring reliable returns, which implies

1020 high availability, as measured by frequency of breakdown and length of time between maintenance stops. Such high reliability can only be achieved if the manufacturer understands the fuel-engine system well and it behaves predictably.

1025 In a low-carbon future, therefore, well-characterized biodiesel might be expected to play a central role in non-electric ground transport and industrial application where electrification is not possible.

1.6 Conclusion: the role of chromatography.

The development of the fuel-engine systems depends heavily on the chemical characterization of fuels and engine emissions, and chromatography has always played a central role: some of the earliest researchers developing gas chromatography were
1030 employees of a petrochemical company (Keulemans, Kwantes, and Zaal 1955).

This thesis explores the possibility of applying comprehensive two-dimensional (supercritical fluid \times gas) chromatography to the chemical analysis of biodiesel for the purpose of characterization and quality control.

$PV \neq nRT$

The ideal gas law does not
apply to supercritical fluids.

2

Introduction: Carbon dioxide and chromatography

2.1 The chemical industry

Industrialized societies depend on chemicals. (In this discussion I define chemicals as pure substances that are produced by industry for industry.) Chemicals might be used in the processing of products, or blended with other chemicals in formulations that might be sold to users as products. In a familiar example, sugar is a chemical produced by the sugar industry from sugar cane or sugar beet. It is a pure substance (sucrose) that is mostly used in the industry as an ingredient for processed food. Other uses of sugar include coatings for medication, and feedstock for engineered micro-organisms that produce pharmaceuticals. (Sugar is a rare example of a chemical that is also sold to consumers.)

The chemical industry produces a huge variety of products, from compounds as simple as hydrochloric acid to compounds as sophisticated as cyanocobalamin (Figure 2.1). All of these chemicals help produce the products indispensable to industrialized societies. Nevertheless, the chemical industry is not held in high regard by people outside the industry. A part of this negative perception comes from the chemical industry's reputation for fatal accidents and pollution (Gumm 2015).

The list of incidents is long and examples easily spring to mind: In 1984 a leak at a chemical plant in Bhopal, India, caused the death of thousands of people and the injury of thousands more (R. Varma and D. R. Varma 2005). Stratospheric ozone is struggling to recover from depletion caused by the reckless emissions of chlorofluorocarbons (Ball et al. 2018). Plastics microparticles are now found everywhere in the oceans (Woodall et al. 2014), and the pesticide DDT is found in the breast milk of Inuit mothers (Gibson et al. 2016).

The chemical industry is also a prodigious producer of greenhouse gases. Apart from the carbon dioxide emitted by the production of the energy that power chemical processes, some chemical processes emit carbon dioxide as a waste product. Most notable of these is the reduction of atmospheric nitrogen as the first step in the production of nitrogen fertilizers. Of all the greenhouse gases monitored by the IPCC, only carbon dioxide, methane and nitrous oxide are found in nature: the others are exclusively products of the chemical industry (IPCC 2014).

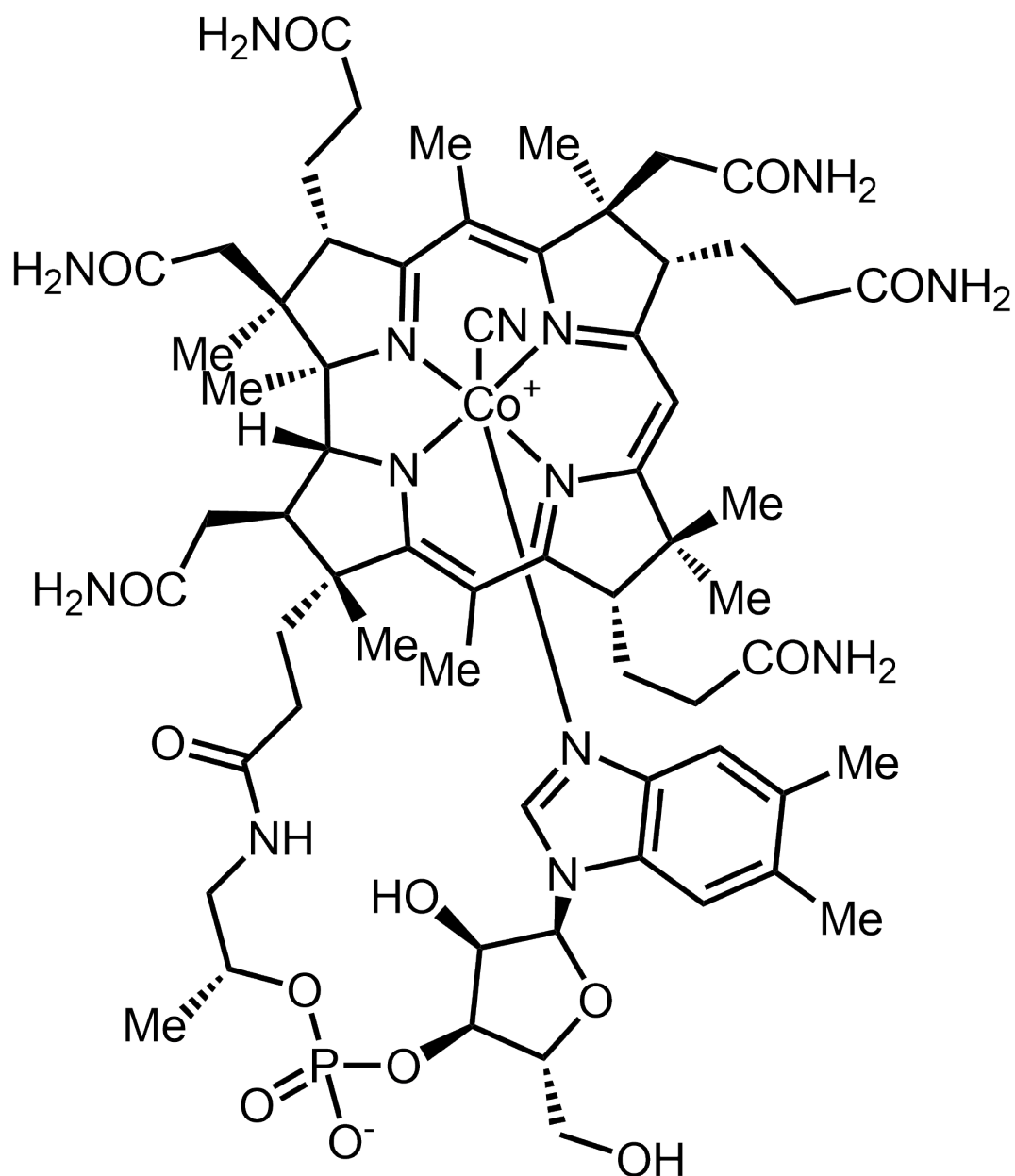


FIGURE 2.1: The chemical structure of cyanocobalamin, a form of vitamin B12. This compound is produced on the tonne scale by the chemical industry.

No chemical has ever jumped out of a lab, multiplied uncontrollably, and spread into the environment to poison or pollute: they have all been introduced into the environment by human ignorance, negligence, or recklessness. All chemicals be-
1070 have well when used in properly controlled environments, but human actions can let them escape and damage and pollute. But while we try to solve the intractable problem of human behaviour, we as chemists cannot just lay blame: we must pay attention to the intrinsic safety of chemicals and chemical processes.

2.1.1 “Green chemistry”

1075 The date of the birth environmental movement is conventionally set to 1962, when the biologist Rachel Carson published the book *Silent Spring*, which pointed out the destruction of nature by the unrestricted use of pesticides, and the dangers of overuse (Carson 2003). This was a direct imputation of the chemical industry, because the pesticide products contained many chemicals.

1080 Chemists are human, and the realization uncontrolled that chemicals can have detrimental effects lead at least some chemists to reflect on their own work. This has given rise to the concept of *green chemistry*. Although the term has no rigorous definition or quantitative measure (Linthorst 2010), a set of 12 principles or guidelines are proposed:

- 1085 1. It is better to prevent waste than to treat or clean up waste after it is formed.
2. Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. Wherever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the
1090 environment.
4. Chemical products should be designed to preserve efficacy of function while reducing toxicity.
5. The use of auxiliary substances (*e.g.* solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.
- 1095 6. Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.
7. A raw material or feedstock should be renewable rather than depleting wherever technically and economically practicable.
- 1100 8. Unnecessary derivatization (blocking group, protection/deprotection, temporary modification of physical/chemical processes) should be avoided whenever possible.
9. Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10. Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation
1105 products.
11. Analytical methodologies need to be further developed to allow for real-time, in process monitoring and control prior to the formation of hazardous substances.

- 1110 12. Substances and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires.

While these guidelines are clearly written with synthetic chemistry in mind, it does not mean that they do not apply to analytical chemistry. For example, Principle 7 suggests that, when possible, one should use hydrogen rather than helium as mobile phase in capillary gas chromatography: hydrogen is renewable, whereas helium is a finite resource and from time-to-time there are reports of shortages (Kornblut 2019).

One large area of the greening of chemistry is changing the use of solvents. Principle 5 recommends that solvents use be avoided, if possible — most solvents used in chemistry are ultimately derived from petroleum and are toxic to some degree. But solvents play a large role in many kinds of chemistry, and eliminating their use in the near future seems unlikely. Searching for and characterizing bio-derived, non-toxic, non-persistent solvents is an active field of research (Clarke et al. 2018).

1125 But there are a few solvents in already current use that are inherently “green”, such as water or ethanol.

One such naturally green solvent is carbon dioxide.

2.1.2 Carbon dioxide as a green chemical

Carbon dioxide as a chemical is used in industry in a few key areas.

- 1130 • Carbon dioxide is often used in firefighting, in the form of portable fire extinguishers or room flooding systems. In this last use it is displacing the ozone-depleting halomethane (Halon).
- When liquid water is supersaturated with carbon dioxide, the gas desolvates slowly in the form of streams of tiny bubbles. This phenomenon makes beverages prepared from water supersaturated with carbon dioxide (or *carbonated water*) interesting to drink, and a large, international beverage industry is based on carbonated water.
- 1135 • Carbon dioxide has a freezing point of -77°C , and the solid can be conveniently obtained by evaporating liquid carbon dioxide at atmospheric pressure. The evaporating liquid rapidly cools the stream of carbon dioxide, lowering the temperature of the stream to below the freezing point, and the gas crystallizes into the solid. The resulting ‘snow’ can be compressed into blocks, which only slowly sublimates into gaseous carbon dioxide, keeping the temperature at the freezing point. Packing frozen food products together with this ‘dry ice’ allows for it to be transported cold.
- 1140 • Pellets of dry ice can be entrained in a jet of air, and used to abrade surfaces for cleaning (Spur, Uhlmann, and Elbing 1999). This use of carbon dioxide can displace toxic solvents or abate the noxious dust produced by blasting operations.
- 1145 • Carbon dioxide is a ‘natural refrigerant’ (Pearson 2005), and can be used to displace hydrofluorocarbon refrigerants, which are potent, long-lived greenhouse gases.
- 1150

- Carbon dioxide can be used as a preservative and anti-oxidant in packaged food. If air in a packaged food is removed by purging the headspace with carbon dioxide, the growth of microbes can be discouraged, extending the shelf life of the product (Jacobsen and Bertelsen 2002).
- Carbon dioxide can be used to extract compounds from natural products.

Of these uses, extractions are economically the most important.

2.2 Extractions using carbon dioxide

2.2.1 Commercial extractions

There are several commercial processes that use carbon dioxide to extract valuable products from plant material.

Plant oils

Vegetable oils are obtained from various crops, and can be extracted from the plant material by pressing, heating or extraction. High-pressure carbon dioxide has been used to extract vegetable oils from various plants, although it seems that this process has only found niche applications so far (Eisenmenger et al. 2006; Grażyna and Anna 2018).

Hops

Hops is an essential component in the brewing of beer. It imparts a desired bitter flavour, stabilizes the beer during storage, and assists with foam formation (Schönberger and Kostelecky 2011). Hops is a seasonal crop with a limited growing range, but the demand for beer is not limited to certain areas or seasons. The creation of hops extract makes it possible for brewers to benefit from hops without owning a hops plantation or storing and transporting dried hops over long distances. All hops extracts produced today are extracted by carbon dioxide (Hunt et al. 2010).

Coffee

Coffee is an international industry, with coffee drunk in many cultures and in many forms. One of the attractions of coffee is the effects of the psychoactive substance found in the coffee bean, *caffeine*. Caffeine is a mild stimulant and promotes wakefulness. A small proportion of coffee drinkers enjoy drinking coffee, but prefer to avoid the stimulant effect, which might induce insomnia or irritability. For these coffee drinkers the market supplies *decaffeinated coffee*.

Given the large amount of coffee traded (an estimated 167.47 million bags of coffee in the 2018-2019 coffee year (Coffee Market Report December 2018 2018))¹, if only a small percentage of coffee needs to be decaffeinated, it will be a large amount of coffee to process, and industrial processes will be necessary to supply the demand.

Decaffeination of coffee is achieved by selectively extracting the caffeine from green (*i.e.* unroasted) coffee beans using carbon dioxide. This is the largest use of carbon dioxide for extraction (Ramalakshmi and Raghavan 1999). The extracted caffeine is sold for use in medication and ‘energy’ drinks.

¹The factoid that “coffee is the second-most traded commodity after oil” has been proven to be untrue (Greenberg 2017).

2.2.2 Analytical Extractions

Extraction is not only an industrial process, but is part and parcel of analytical chemistry. The first extractions using carbon dioxide was not aimed at developing an industrial operation, but to develop methods for analytical chemistry. This method is usually called SFE, for supercritical fluid extraction.

2.2.3 Why carbon dioxide?

But what makes carbon dioxide a suitable solvent for extraction?

There are two aspect to this question. The first is about the *greenness* of carbon dioxide. It is non-toxic, non-persistent, non-flammable, non-corrosive, inexpensive, commercially available, and a waste product. (It goes without saying that this carbon dioxide is sourced from a carbon-neutral source, perhaps the brewing industry.)

The second aspect of the desirability of carbon dioxide lies in its physical properties and the conditions under which we use it.

Chemists will intuitively understand that gaseous carbon dioxide has no solvating properties, and that liquid carbon dioxide should not behave much differently than any other solvent. Both these statements are true under 'normal' circumstances.

But consider the case of an isobaric cooling of a volume of gas. The gas-liquid transition takes place because energy is removed from the system. At some point the kinetic energy of some of the molecules becomes less than the energy of the intermolecular forces, and the molecules prefer to clump together, *i.e.* it condenses. The remaining gas molecules receive the excess energy, and therefore stay in the gas state, until more energy is removed, leading to more of the gas condensing. During this process the temperature remains constant, and this temperature is known as the boiling point.

Now consider a solute (solid or liquid) in the same volume of gas being cooled. In this case, as the gas cools, the gas-solute intermolecular forces can become stronger than the gas-gas intermolecular forces at a temperature which is higher than the boiling point. In such a case the gas molecules will clump around solute molecules, while the kinetic energy of the gas molecules are still too high to allow condensation. Now the gas has obtained solvating properties and the solute will become truly dissolved in the gas.

The same effect can be imagined to happen during the isothermal compression of a gas.

If there are more than one solute in the volume of gas, some might dissolve in the gas, while others one might not. This means that the solvating gas can be *selective*. It can also be seen that the solvating power of the gas will depend on the temperature and the pressure of the gas. This means that the solvent becomes *tunable*.

While the dense gas has solvating properties, it still has the physical properties of a gas:

Diffusivity The solvating gas maintains its low diffusion coefficients, which means that it can easily diffuse into porous material, and that solutes will rapidly diffuse through it.

Surface tension The solvating gas has a low surface tension, which means that it will readily 'wet' surfaces and penetrate porous material.

Viscosity The solvating gas has a low viscosity, which means that it takes little energy to pump it.

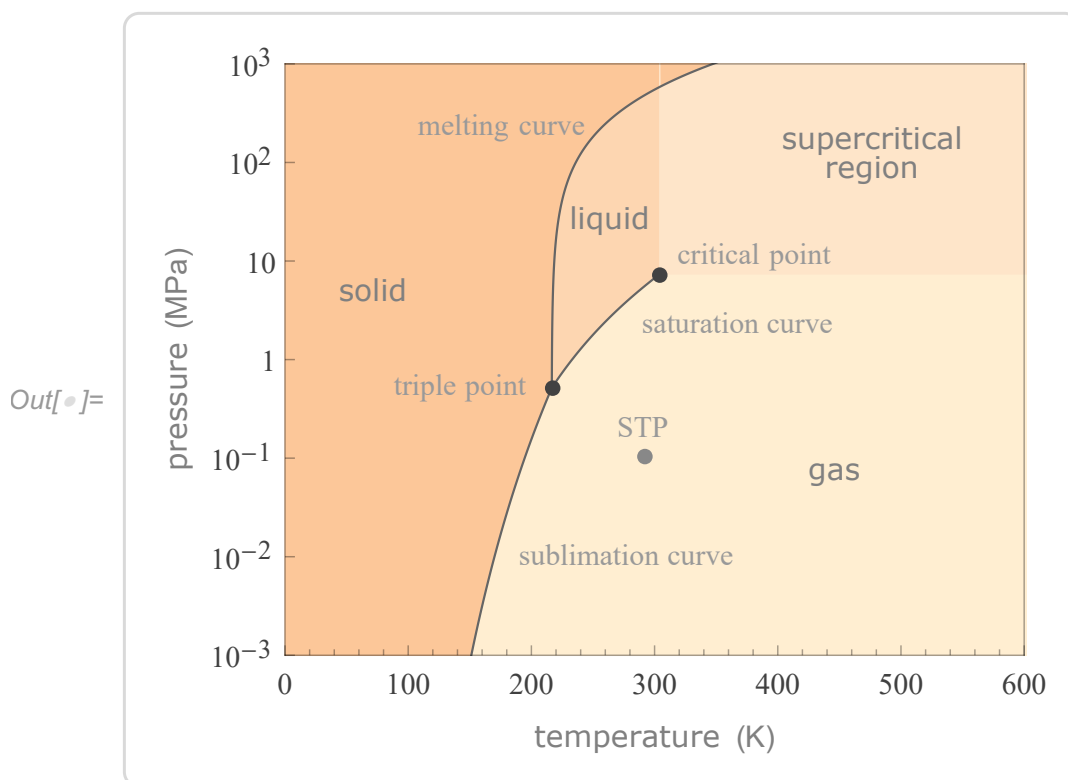


FIGURE 2.2: The phase diagram of carbon dioxide

For historical reasons such solvating gases are known as a 'supercritical fluids', because they were first obtained by heating a liquid at high pressure (Berche, Henkel, and Kenna 2009), so that the temperature and pressure of the substance is higher than its *critical point*. The critical pressure of a substance is the pressure above which it is impossible to create a gas-liquid phase transition by isobaric cooling, and the critical temperature is the temperature above which it is impossible to create a gas-liquid phase transition by isothermal compression. When the gas is at its critical temperature and critical pressure, it is at its critical point. The critical point is very different from the *triple point*: there is no equilibrium involved (See figure 2.2). The terms 'supercritical fluid' and 'dense gas' are synonyms (Randall 1982) — the adjective 'dense' in 'dense gas' of course implies that the gas behaviour is far from that of an ideal gas.

There are no discontinuities in binary diffusivity when temperature is changed from above to below the critical temperature (Lauer, McManigill, and Board 1983). Hence extractions are often done under conditions which are not technically 'supercritical' but still yields its benefits.

The critical pressure of carbon dioxide is 304.12 K (31.10 °C) , and the critical pressure is 7.39 MPa (72.9 atm). This temperature and pressure are easy to achieve in the laboratory with standard chromatographic instrumentation, or in an industrial plant with standard process engineering technologies.

Carbon dioxide is gaseous at ambient conditions. This means that once it has been used in its role as extractant, and it is exposed to the atmosphere, it will rapidly evaporate, without needing added heat, and leaving no residues.

Any pure compound will have a supercritical point. Compounds with technologically feasible supercritical points and useful chemical properties include ammonia, methanol, CFCs/Freon, hydrocarbons (propane, butane), water and sulfur hexafluoride. All of these lack green attributes: hydrocarbons pollute, the CFCs deplete ozone, sulfur hexafluoride is a potent greenhouse gas, and methanol and water are liquid at ambient conditions.

For these reasons the term supercritical fluid extraction is practically synonymous with extraction using high-pressure carbon dioxide.

It is also possible to use supercritical fluids as reactants. This topic falls outside the scope of this discussion.

Modifiers

The carbon dioxide molecule has zero dipole moment and the bulk fluid a low dielectric constant, so supercritical carbon dioxide is expected to be a non-polar solvent. (Although in practice the solvent behaviour is more complex, partly explained by the high quadrupole moment of the carbon dioxide molecule (Raveendran, Ikushima, and Wallen 2005).)

While the solvating power of a supercritical fluid is certainly 'tuneable' by adjusting its pressure and/or temperature, the range in solubility might be quite limited in practice. Just as with other solvents, it is possible to add a co-solvent or *modifier* to the supercritical carbon dioxide. This makes it possible to increase the solubility of polar compounds in the supercritical fluid. Methanol, ethanol, formic acid, and water are examples of suitable green modifiers for carbon dioxide (Herrero et al. 2010).

When modifiers are used the carbon-dioxide, modifier and solute forms a system with four degrees of freedom (modifier percentage, solute concentration, pressure, and temperature), which can become difficult to model. While this is a challenge for process engineers who need to design efficient industrial systems, analytical chemists can afford to be pragmatic and use heuristics to find suitable conditions (Wells, Zhou, and Parcher 2003).

Practical extractions

Figure 2.3 shows a schematic diagram of a system set up for supercritical fluid extractions.

Carbon dioxide (a) is readily available from suppliers of industrial gases, and high-purity grades are available. Chromatography-grade solvents are usually used as modifiers (d). High-pressure pumps (HPLC type) are used to compress the carbon dioxide (b) and the modifier (c), which are mixed together at the appropriate ratio. The mixture gets pumped into the (optionally heated (f)) extraction cell (e), which contains the material that needs to be extracted. Having extracted the extract from the material, the supercritical fluid passes through a pressure-control mechanism (g). This allows the pressure of the supercritical fluid to drop to ambient, turning it into a low-density non-solvating gas. The extract becomes desolvated, and precipitates in the collection vessel (h). The operation of the system might be either static or dynamic: in static operation the supercritical fluid is pumped into the system, the flow is stopped, and the matrix/fluid mixture is given time to approach equilibrium. Then the fluid is expelled and the extract collected. In dynamic operation the supercritical fluid is pumped through the extraction cell and the extract collected continuously.

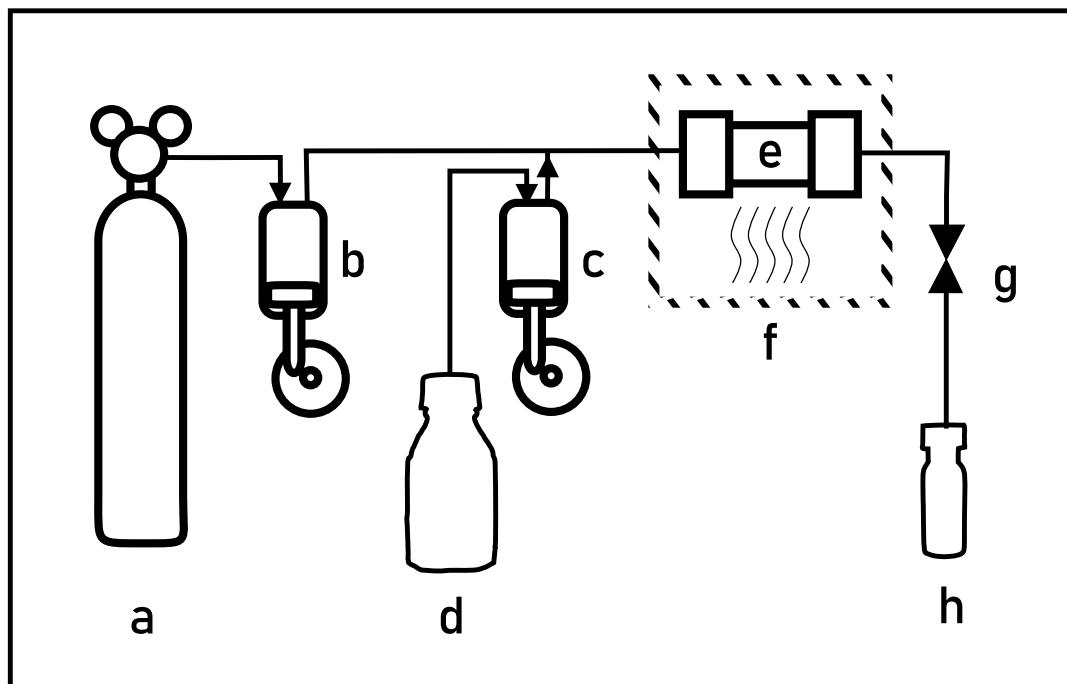


FIGURE 2.3: A diagram of an SFE system. (a) CO₂ supply (b) High-pressure SF pump (c) High-pressure modifier pump (d) Modifier reservoir (e) Extraction cell (f) Pressure control (g) Collection vessel

2.3 Supercritical Fluid Chromatography

An analyte will extract out of a matrix into a given solvent with a certain efficiency and at a certain rate. While this is important while finding an optimum extraction method, otherwise its relevance is limited.

However, *different* analytes will extract out of a matrix with *different* efficiencies and at *different* rates. In a 1906 paper the Russian botanist Tsvet applied this observation to the dynamic extraction of a bed of calcium carbonate that had mixture of plant pigments applied at the inlet end, using petrochemical solvents. The different extraction efficiencies and rates of adsorption and desorption on the calcium carbonate surface lead to the *separation* of the compounds in the mixture. Tsvet called this method of separation *chromatography* (Ettre and Sakodyskii 1993a; Ettre and Sakodyskii 1993b). With time this method became generalized, and today chromatography is a major, established scientific field with many ramifications and a myriad of applications.

Because of the different technologies used in its applications, chromatography is conventionally classed by the state of its mobile phase as either *gas chromatography* (GC) or *liquid chromatography* (LC). However, as we have seen, solvating gases can also extract analytes from solid stationary phases, and hence the term *supercritical fluid chromatography* (SFC) was created for these kinds of separations.

Supercritical fluid chromatography as practised today bears a great resemblance to *high performance liquid chromatography* (HPLC). The main reason for this is that there is a large overlap between the technology used for HPLC and the technology needed for SFC. In particular, both use high-pressure pumps and columns packed

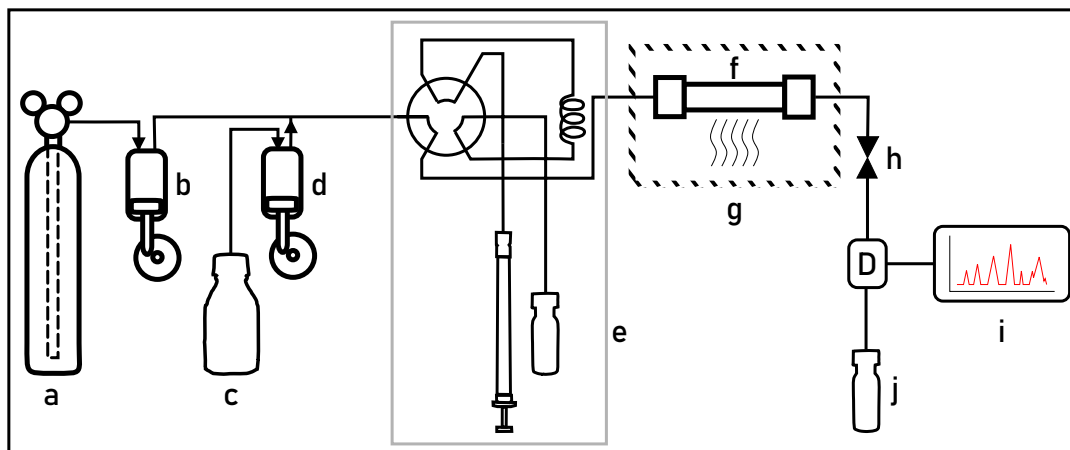


FIGURE 2.4: A diagram of an SFC system. (a) CO₂ supply (b) High-pressure SF pump (c) Modifier reservoir (d) High-pressure modifier pump (e) Injection system (f) Column (g) Optional heating (h) Back-pressure control (D) Detector (i) Data system (j) Optional fraction collection.

with particles of very small diameter, and use optical detectors. The same instrument manufacturers who supply HPLC instrumentation also supply SFC instrumentation.

2.3.1 SFC and FID

1335 But SFC was not always a technique based on HPLC technology. In the 1980s SFC was practised using open tubular columns and flame detectors, so the instrument designs looked more like GC instruments than HPLC instruments, and SFC was sold as a replacement for GC (Poole 2003).

1340 During this era the detectors used for SFC was the flame-based detectors used for CG, in particular the flame ionization detector (FID).

1345 The *flame ionization detector* was invented near-simultaneously in South Africa and New Zealand (Ettre 2008). The core of the system is a flame of hydrogen gas burning in pure air. The measured signal is the conductivity of the flame plasma, which is measured by applying a -100 V potential difference between electrodes at the tip and the base of the flame. There are very few free ions in the hydrogen flame, so the conductivity is normally low. But organic compounds introduced into the flame creates a number of free ions, which increases the conductivity of the flame gases. The change in conductivity is measured by measuring the current between the two electrodes, using an electrometer.

1350 As a first approximation the signal produced by the FID is proportional to the number of carbon atoms in the analyte. This is rather surprising, until the mechanism of its working is elucidated. At high temperature in the hydrogen-rich core of the flame, all hydrocarbon atoms are reduced to methane (Holm and Madsen 1996). Once it gets into contact with the hot oxygen in the outer layers of the flame there is a chemi-ionization reaction. The electric field acting on the ions creates a flow of ions, which can be measured as an electric current.

The FID's shining strength as a detector is its tremendous linear dynamic range of 10^7 . Combining the linear dynamic range with its carbon sensitivity makes it an excellent detector for quantifying organic compounds.

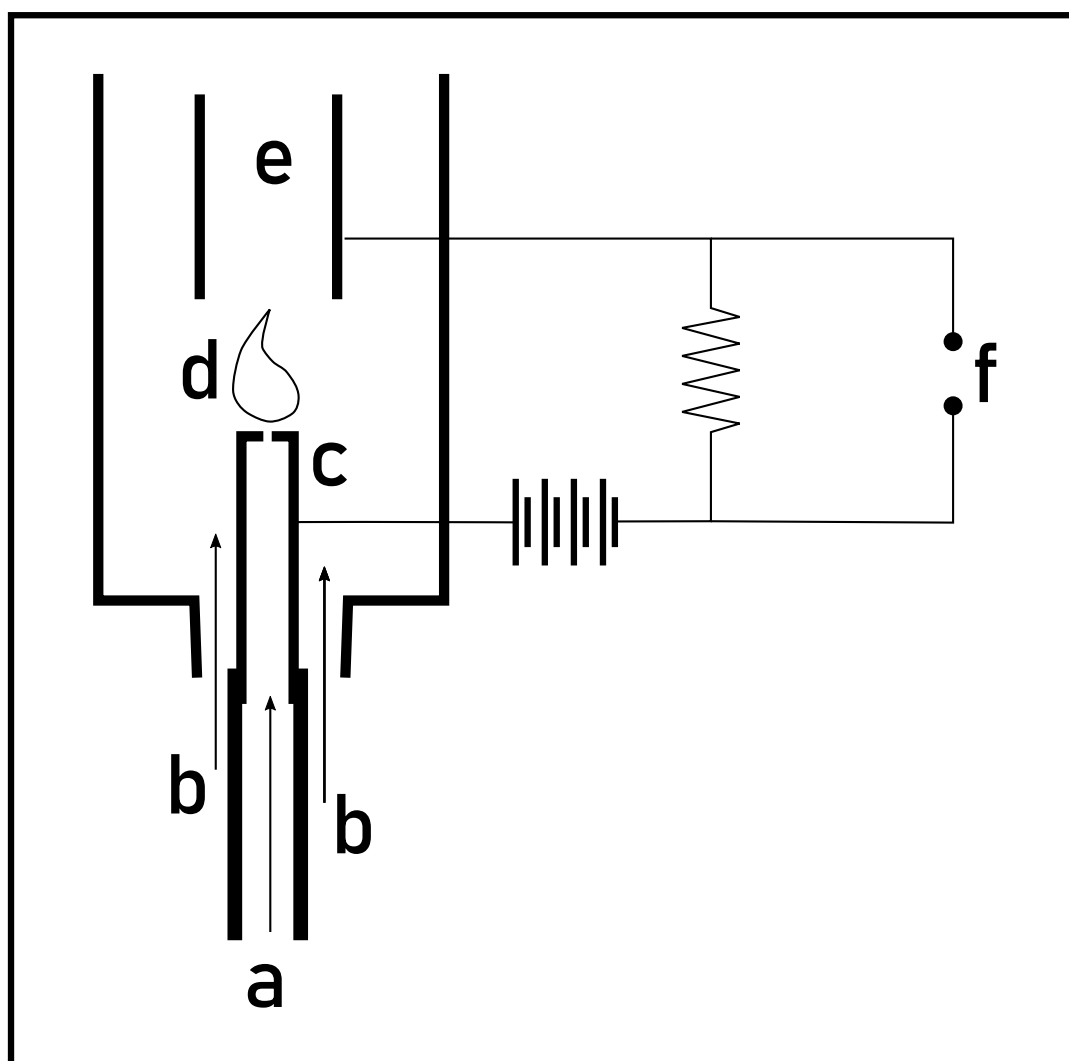


FIGURE 2.5: A schematic diagram of the flame ionization detector. (a) Mixture of column eluate and hydrogen gas (b) Clean air (c) Metallic flame tip electrode (d) Collector electrode (e) Conductivity signal

1360 During perdioid of history that SFC was seen as a variant of GC, the FID was the detector of choice. But when SFC started looking like HPLC, and the selectivity of the chromatography started being manipulated by adding modifiers (see Section 2.2.3), the FID lost its utility. The quantity of modifier added to the carbon dioxide mobile phase swamps the FID detector, making it useless as a detector. In contrast, 1365 if the chosen modifiers are transparent at the relevant wavelengths, optical detectors are more useful in SFC using modified carbon dioxide as a mobile phase.

2.3.2 SFC×GC

In chromatography, the analyte in the eluate can be detected to yield information about the sample, or fractions of eluate can be collected for further purification or 1370 characterization, or both. If fractions are collected, there is nothing that prevents the chromatographer from subjecting a collected fraction to another chromatographic separation.

For example, a synthetic chemist might use column chromatography to separate their target compound from side-reaction compounds, collecting fractions of the elu- 1375 ant. If the compounds are colourless, the chemist might use *thin-layer chromatography* (TLC) to examine the fractions for presence and purity of the relevant compounds.

If the product and the side-product were co-eluting it would not help to use the same chromatographic system (*i.e.* combination of stationary phase and mobile phase) for the TLC examination, because the co-elution would not become apparent. 1380 If, however, the chemist changed the mobile phase, or switched to a different stationary phase for the TLC examination, then it is quite likely that the two compounds would be separated.

For example, if a synthesis involving sugars were being attempted, two sugar enantiomers would likely co-elute on a silica clean-up column. Investigating the 1385 sugar fraction using a TLC plate with a chiral stationary phase would reveal the presence of stereoisomers.

The second, chiral separation (on TLC) is said to be *orthogonal* to the first (packed column) separation.

Such a separation is an example of a two-dimensional (2D) separation. In ana- 1390 lytical chromatography, 2D separations are powerful tools.

The simplest 2D chromatography is called *heart-cutting*. In such a case a frac- tion of interest is collected from the first dimension (¹D) separation, and subjected to a second dimension (²D) separation. For example, a fraction collected from an HPLC separation could be injected into a gas chromatograph. The separation on the 1395 GC dimension would obviously be very different from the separation on the HPLC dimension, and therefore we can say that the orthogonality is high.

Heart-cutting is a useful way to get detailed information from a sample, but it is technically demanding and labour-intensive. It is usually employed for challeng- ing separations in well-understood samples, because peaks of interest in the first 1400 dimension must be captured for injection on the second dimension.

If, however, one collects the eluate in equal fractions and do identical separa- tions on each of the fractions, then one enters the domain of *comprehensive multi- dimensional chromatography*. The comprehensive coupling of orthogonal chromatogra- phies does not demand a previous understanding of the sample, and doing exactly 1405 the same separation for each fraction allows the process to be automated.

A 2D separation can be called comprehensive if the following three criteria are met (Giddings 1987):

1. Every part of the sample is separated by two distinct chromatographic processes.
- 1410 2. Equal percentages of all sample fractions are separated by the second process.
3. Compounds resolved by the first dimension separation remains resolved.

To effectively distinguish between heart-cut and comprehensive 2D couplings, a terse nomenclature was developed. Simple coupling between systems is designated by a hyphen (" - "), for example HPLC-GC. This corresponds to the usual notation of a coupled detector coupled to a chromatograph, for example GC-FID or GC-MS. Com-
1415 prehensive coupling is denoted by a multiplex sign (" × "), for example GC × GC. If it is not clear from the context, the detector can be specified using a hyphen, as in GC × GC-MS.

Of the comprehensive coupled chromatography techniques, GC × GC is the most
1420 mature, with a selection of powerful instruments on the market.

This thesis further explores the implementation of SFC × GC, as first developed by Venter and Rohwer (A. Venter and Rohwer 2004; A. Venter, Makgwane, and Rohwer 2006).

In this implementation of SFC × GC, fractions of the eluate of the SFC is trans-
1425 ferred to the GC. The mobile phase is changed from carbon dioxide to hydrogen in the modulating interface, and the GC dimension is a conventional open-tubular capillary separation with FID detection.

Any volatile modifiers or additives added to the SFC mobile phase will be separated from the analytes by the GC dimension. This makes it possible to use the
1430 FID as a detector in an SFC × GC chromatograph where the SFC is based on HPCL technology.

The 2D separations are *fast* chromatographic separations, *i.e.* separations optimized for speed, sacrificing resolution. This is achieved using fast temperature programming of the GC separation.

1435 The high orthogonality of the SFC and the GC separations enables novel comprehensive 2D chromatography, which we applied to the chemical analysis of biodiesel.

In a book that I took from a shelf

...

Ancient proverb

3

Literature survey

3.1 SANS 1935

1440 3.1.1 Subsection 1

3.1.2 Subsection 2

3.2 SFC

3.3 Fast Gas Chromatography

$$pV \neq nRT$$

The universal gas law does not
apply to supercritical fluids

4

Instrumentation: Supercritical Fluid Chromtography

This thesis discusses the development of a comprehensively coupled (supercritical fluid \times gas) chromatograph and its application to the analysis of biodiesel. The discussion on the experimental work divides naturally into two parts: this chapter discusses the supercritical fluid chromatography (SFC) and the next chapter discusses the gas chromatography (GC).

4.1 SFC

As discussed in Chapter 2, an SFC chromatograph consists of a supply of mobile phase, a pump, a pressure control system, a modifier control system, a column, a pressure relief system and a detector

4.1.1 Mobile phase

As mobile phase we used carbon dioxide. The benefits of carbon dioxide as a solvent and mobile phase is discussed in Chapter 2.

We used 99.995 % pure carbon dioxide supplied by Air Products. Our colleagues in industry also uses food grade or technical grade carbon dioxide and they have not reported any significant impurities.

As modifier we used LiChrosolv®methanol from Merck. This is an 'HPLC-grade' solvent, of which the purification is optimized for the removal of UV-absorbing impurities. Using this grade of solvents is important when using optical absorbance or fluorescence detectors, because lowering levels of impurities improve limits of detection. It is quite likely that less a expensive grade of modifier would be suitable for our SFC, because we do not use an optical detector.

4.1.2 Pump

As pump we used a Varian 8500 HPLC pump. This pump had its control electronics removed, and it was controlled from a personal computer by software written for the purpose.

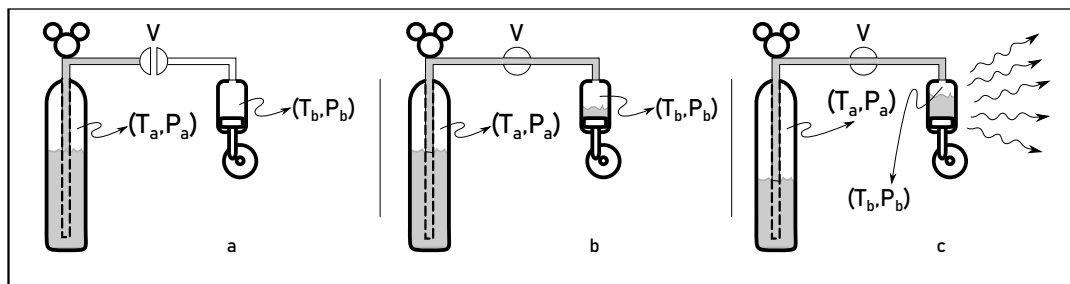


FIGURE 4.1: Diagram to help explain the filling of the carbon dioxide pump. (a) The pressure in the reservoir P_a is much higher than the pressure in the receptacle P_b . The valve is closed, so there is no flow. (b) The valve is open and some carbon dioxide has flowed from the reservoir to the receptacle. But $P_b = P_a$, so there is no flow. (c) When the temperature in the receptacle $T_b < T_a$, then $P_b < P_a$, following Gay-Lussac's law. Flow will continue until all the vapour in the receptacle has condensed.

The Varian 8500 pump is driven by a stepper motor. This kind of motor turns in discrete steps, instead of at a constant rate. It is driven by pulses of electric current, rather than a continuous current, and therefore the speed of the motor can be controlled by varying the rate of the pulses. This makes it relatively simple to control the speed of the motor from a computer.

The Varian 8500 pump has a built-in pressure transducer that provided an electronic signal proportional to the pressure at the pump outlet.

The Varian 8500 pump is a piston pump with a 250 ml capacity that needs to be refilled between strokes. Refilling means that one has to stop chromatography, which makes it important to fill the pump to full capacity, so that chromatographic runs are not interrupted. This means that the pump needs to be filled with carbon dioxide in the liquid phase rather than the vapour phase. Compressing either would create the appropriate phase for doing chromatography, but compressing a vapour would leave one with a much smaller volume of high-pressure carbon dioxide than compressing a liquid.

Filling a pump with liquid carbon dioxide is more difficult than one might imagine.

Imagine a reservoir of liquid carbon dioxide, equipped with a dip tube, connected to an empty receptacle via a valve (V). (See Figure 4.1) One can assume that the receptacle is empty and contains only carbon dioxide vapour at atmospheric pressure, say 1 atm. The vapour pressure of the vapour above the liquid in the reservoir is about 55.3 atm (5.6 MPa). When the valve (V) is opened the high-pressure vapour in the reservoir will expel the liquid carbon dioxide through the dip tube and through the valve, into the receptacle. In the low-pressure environment of the receptacle the carbon dioxide will boil. Soon there will be some liquid carbon dioxide in the receptacle, with the rest of the receptacle volume filled with gaseous carbon dioxide. When the system comes to equilibrium the pressure in the receptacle (P_b) will equal the pressure in the reservoir (P_a), and there will be no flow of liquid carbon dioxide. One can attempt to now increase the flow by increasing the volume of the receptacle (for example by withdrawing a pump piston), and hence decreasing the vapour pressure there. But any flow from the reservoir will lead to expansion of the headspace of the reservoir. This will lead to cooling of the vapour, and therefore

lower pressure and therefore lower flow. The final result of this process is that the receptacle is never filled to capacity with liquid.

The only way to restore the flow from the reservoir to the receptacle is to create a pressure difference $P_a - P_b$. While it is possible to create an overpressure in the reservoir by adding a headspace gas, it is technically challenging and expensive. It is simpler to use the Guy-Lussac gas law. According to this law the ratio of the pressure to the temperature of a gas is constant so that $\frac{P_b}{T_b} = k$. This means that a decrease in temperature will lead to a decrease in pressure. The way to fill the reservoir to capacity is to ensure that the temperature of headspace vapour T_a is higher than the temperature of the headspace vapour T_b . Because safety regulations prohibit the heating of a cylinder of pressurized gas, the way to ensure $T_a < T_b$ is to cool the receptacle. This cools the headspace vapour, and following the Gay-Lussac law the pressure P_b decreases, the difference $P_a - P_b$ increases and the liquid flows until the receptacle is filled to capacity.

In the case of the Varian 8500 pump the cooling of the pump was achieved by wrapping a coil of copper tubing around the cylinder, and pumping a chilled heat-exchange fluid through it. A chiller with a mechanically cooled tank with a 20 l capacity was filled with a solution of 5.0 l of diethyl glycerol in about 10 l of water. This mixture has a freezing point of -15 °C, which can be cooled by the chiller without freezing. (If the coolant freezes a layer of ice forms on the cooling plate of the chiller, which isolates the remaining liquid from the cooling plate and limits the minimum temperature of the coolant.) An inexpensive submersible water pump (designed for decorative water fountains) was used to pump the coolant through the circuit. This pump can deliver 800 l of water per hour at a head of 1.2 m.

For some experiments we also used a SFT-10 pump from Supercritical Fluid Technologies (Newark, Delaware). This is a purpose-built two-piston pump with a sapphire valve seats and a Peltier-cooled head. This is a much better technology than the HPLC pumps. It takes up less space and does not need refilling, since it feeds directly from the cylinder. This pump had its own microprocessor controllers on board, and flow and pressure could simply be commanded from the PC through a USB cable.

4.1.3 Pressure control system

In chromatography the figure of merit by which the performance of a system is measured is the distance by two compounds are separated. This is known as the *resolution*. But the days of separating coloured compounds in glass packed columns are long past and the direct measurement of distances are now relegated to thin-layer chromatography. Instead, we have to make do with proxies for distance such as *retention volumes* or *retention times*.

Retention times are particularly convenient today, because it can easily be measured by computer systems.

Retention times, however, depend on a known flow rate of the mobile phase through the column. The flow rate need not be constant, although for the sake of simplicity a constant flow rate is preferred. Ideally, the flow rate should also be adjustable.

The need for an adjustable, constant flow rate can be met by using a control system. Control systems are well understood by engineers, among whom it is a major field of study (Koenig 2009).

Figure 4.2 shows a diagram of a simple process control system. Some aspect of the process under control is measured, which yields the *process variable* (PV). The

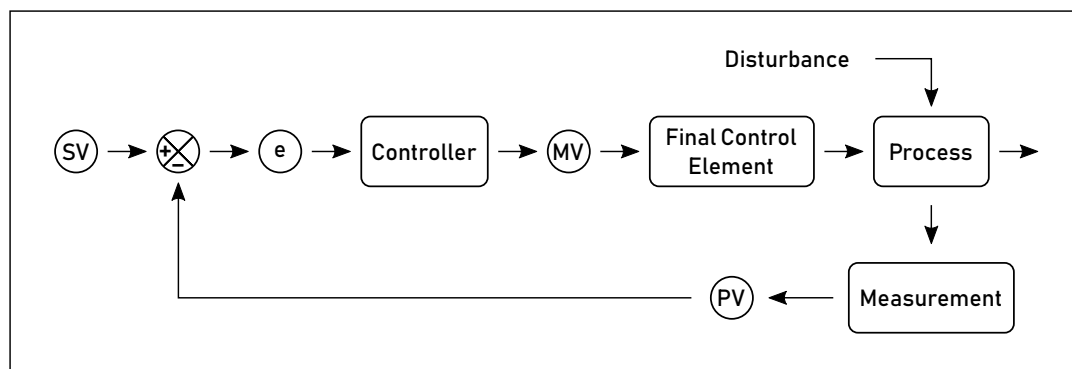


FIGURE 4.2: Schematic diagram of a closed-loop control system. (SV) Set Value, (PV) Process Variable, (e) Error, (MV) Manipulated Variable

PV is compared to the *set value* (SV), and the *error* (e) is obtained by finding the difference. The error is provided to the controller, which calculates the *manipulated variable* (MV). The MV is used to drive the final control element, which adjusts the process with the aim of producing a smaller error.

Chromatographic systems conventionally works under pressure control or flow control regimes. Either is suitable: constant pressure systems usually yield constant flow if other parameters are held constant. Because flow measurement is more complex than pressure measurement, pressure control is the older, simpler and less expensive control method. We therefore selected pressure control as our control regime.

In our system the pressure measured by the on-pump sensor was the process variable (PV). This was compared to the set value (SV) set on the computer console. The controller was a software algorithm, implemented as a virtual instrument in the programming environment LabVIEW. The controller computed an output value for the manipulated variable (MV), which was the rate at which pulses were sent to the pump, in hertz. The digital input/output (DIO) interface of a National Instruments PCI-6014 multifunction data acquisition board created those pulses and sent them to the pump's electronic interface.

The software used a PID (Proportional-Integral-Derivative) controller module, with the Integral and Derivative contributions disabled. While enabling the Integral and Derivative contributions would add to the accuracy of the controller, we could not find a suitable, simple tuning procedure. Tuning the controller from adequate performance to optimum performance would consume resources while not improving the chromatography.

4.1.4 Modifier Control

The modifier needs to be present in the mobile phase at a known and controlled concentration.

There are various SFC-modifier mobile phase supply units on the market. They tend to be a expensive and complex, because they require the use of two controlled, high-pressure pumps. Given that our needs were rather modest, we elected to use a simpler system.

Instead of accurately pumping the supercritical fluid and the modifier, we only pump and control the supercritical carbon dioxide and add measured volumes of modifier.

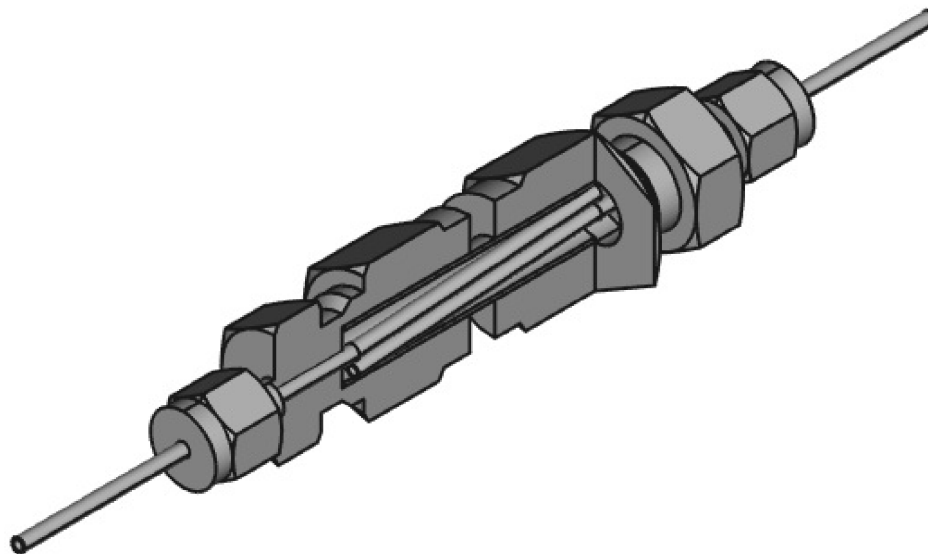


FIGURE 4.3: A cutaway diagram of the mixing chamber design. The chamber is designed for the mixing of the modifier and the supercritical carbon dioxide.

The modifier control unit consisted of a six-port valve, a fixed-volume measuring loop, and a mixing chamber.

The unit operates by filling the measuring loop with modifier, and then switching the measuring loop into the flowing mobile phase. The modifier is washed into the mixing chamber, where it is intimately mixed with and dissolved in the supercritical carbon dioxide. The concentration of modifier in the mobile phase is determined by the switching rate of the sampling valve. Given that about 3 volumes of supercritical carbon dioxide is needed to wash the modifier out of the loop, the highest concentration of modifier that can be added in this manner is about 25 %.

Figure 4.3 shows the chosen design of the mixing chamber. The inlet and outlet pipes of the mixing chamber extend far into the chamber, to break up plug flow and encourage rapid mixing.

The modifier injection valve position was commanded from the controlling PC by electronic voltage pulses.

4.1.5 Sample injection

The sample inlet was a two-position rotary valve with an internal sampling volume (Figure 4.4). In one position the sampling volume was filled with a syringe, and when the valve was commanded to inject the sampling volume was switched into the carrier mobile stream.

The reader might be more familiar with the six-port valve as an injection system. The benefit of the internal groove injection valve is that it allows a much smaller volume to be injected. Using this small volume makes it possible to inject samples without dilution, which simplifies sample preparation. A drawback of this design is that it is not possible to vary the volume of sample injected.

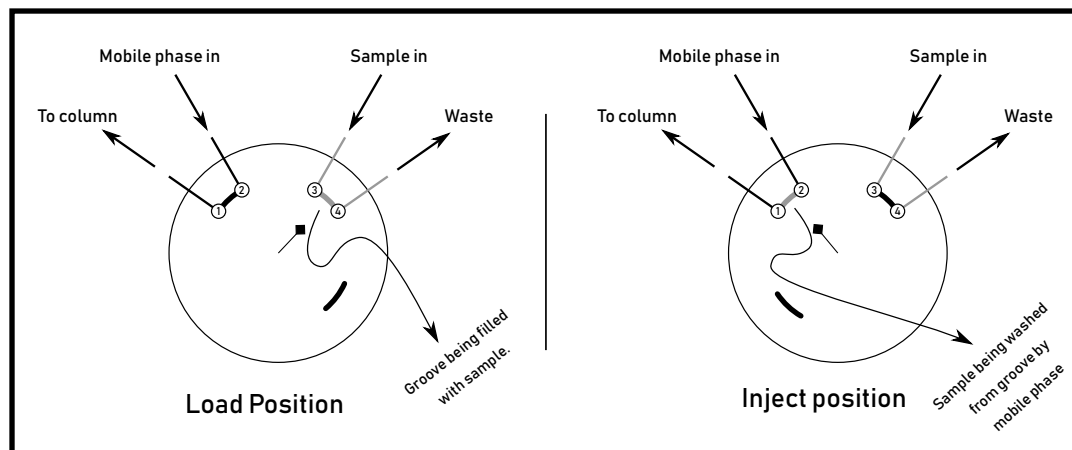


FIGURE 4.4: A schematic diagram of the sampling valve.

The sample volume was 5 μl

The injection valve position was commanded from the controlling PC by electronic voltage pulses.

4.1.6 Column

1615 The separation power of a chromatographic system can be modelled by the equation

$$R_s = \left(\frac{\sqrt{N}}{4} \right) \left(\frac{\alpha - 1}{\alpha} \right) \left(\frac{\bar{k}}{1 + \bar{k}} \right) \quad (4.1)$$

where, R_s is the *peak resolution*, N is the *number of plates*, α is the *separation factor*, and \bar{k} is the *retention factor*.

The number of plates N can be increased simply by making the column longer, at the cost of increasing the time of the run.

1620 The maximum length of the column is determined by the pressure drop available that will still yield adequate flow. In capillary gas chromatography the openness of the column and the low viscosity of the gas-phase mobile phase routinely allows columns 100 metres long at inlet pressures of a few atmospheres. In HPLC the high viscosity of the mobile phase and the narrow, tortuous pathways between the small particles of the packing material means that the columns are typically 100 - 200 mm long, requiring hundreds of atmospheres of inlet pressure for adequate flow.

1625 The low viscosity of an SFC mobile phase makes it possible to use packed columns, such as those developed for HPLC use, but make them much longer. This allows a higher number of plates in the chromatographic system at the cost of nothing more than a longer column.

1630 The SFC column we used in the SFC \times GC system was a set of five HPLC columns (150 mm \times 4.6 mm, 3 μm particles) (Restek, Pinnacle DB Silica) connected in series.

1635 The stationary phase in this column is 'bare silica', which is usually considered 'polar'. That means that the packing of the column consists of porous silica particles with no organic phase covering its surface, and hence one that will interact strongly with polar molecules. In contrast, the ubiquitous 'C18' stationary phase used in reverse-phase HPLC is 'non-polar'. The particles of such a stationary phase are coated with octadecyl chains bonded to its surface, and hence will tend to interact strongly with non-polar molecules. The base material of the particles is usually

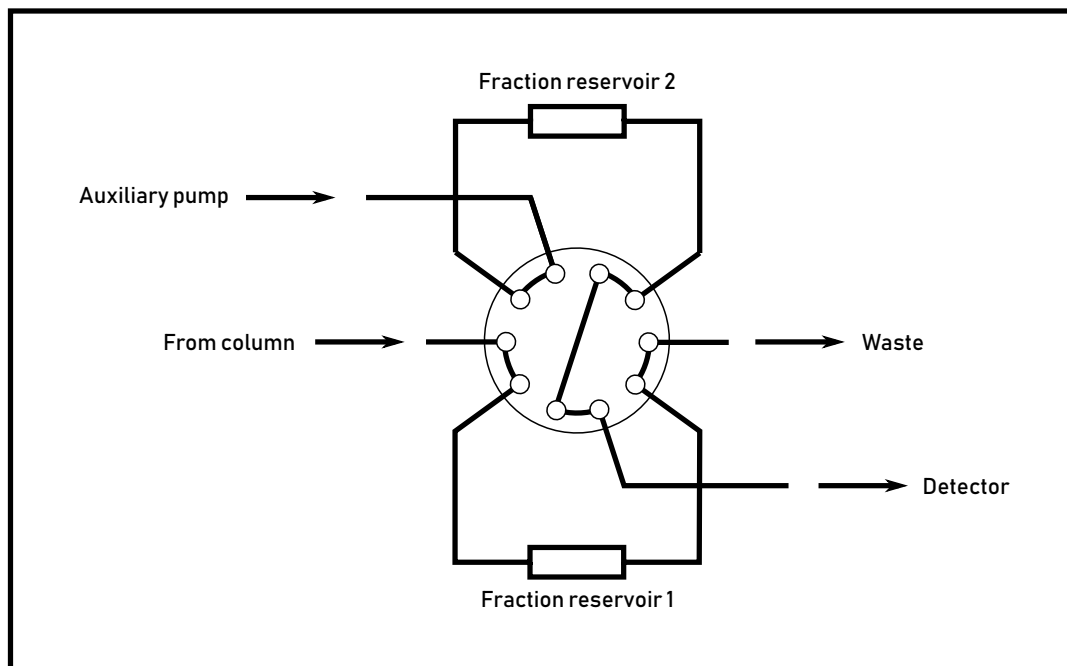


FIGURE 4.5: A schematic diagram of a valve configured to allow continuous-flow fraction collection.

1640 silica, but that is because creating uniform particles of a given size from silica is a mature technology and not because silica is important to the separation mechanism. (In fact, some care has to be taken to deactivate the silica so that it does not contribute to the retention. Such a mixed retention mechanism can lead to peak tailing.)

Stopped-flow

1645 Among analytical chemists it is the convention that chromatographic runs are done without interruptions. Synthetic chemists doing purification by chromatography, by contrast, are quite happy to close the stopcock and wait for a convenient time to finish the purification. This difference in behaviour is explained by differences in understanding. The chromatographer is acutely aware that any excess diffusion
1650 can broaden peaks, which leads lower resolution. The analytical chemist knows from experience that diffusion in the liquid phase is slow enough to not make much difference to resolution.

In our SFC×GC chromatograph we collect fractions of SFC eluate and separate them by GC. It is possible to collect, store and inject fractions of SFC eluate while maintaining continuous flow, for example using a dual storage loop system like the
1655 one depicted in Figure 4.5. But such systems require careful selection of volumes, fraction collection reservoirs with matching volumes, and an auxiliary pump.

Instead of such a system, we opted for a stop-flow system. In this system a fraction of the SFC eluate is collected, and then the flow through the column is stopped.

1660 While the flow is stopped the collected fraction is subjected to separation by GC.

In packed columns, "eddy diffusion is always the main cause for peak broadening at any temperature and at high velocities" (Gritti and Guiochon 2006). During the period that the flow is stopped only longitudinal diffusion contributes to peak broadening, which is small compared to eddy diffusion. Using the simple stop-flow

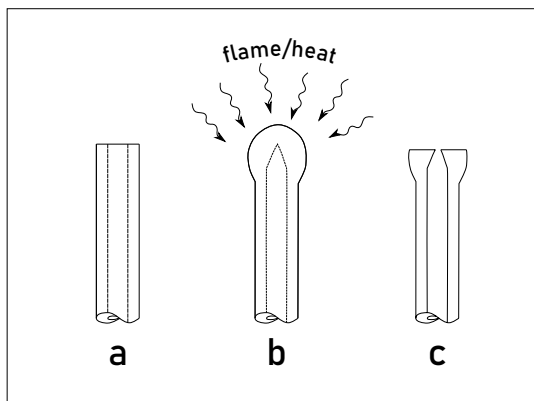


FIGURE 4.6: The steps of making a Guthrie restrictor. (a) Cut length of quartz capillary (b) Heat with flame to soften glass and create internal cone (c) Grind down end to expose orifice of the appropriate size.

1665 technique of sample collection will therefore not have a major effect on the resolution of the ^1D chromatography.

The flow in the SFC was stopped by a six-port rotary valve using three of the ports, directing flow either to a blocked-off port or to the depressurizer, in effect making it an on-off controller.

1670 4.1.7 Pressure Relief

No matter the kind of SFC system one uses, at some point the eluate needs to be depressurized. This can be before or after the detector. If depressurization happens after the detector, then the details of the mechanism doesn't matter much, because the information has been obtained and the eluate can be discarded. If, as in our case, 1675 the depressurized eluate needs to still pass the detector, it is important to not lose the resolution achieved by the column. This means that the design of the depressurizer requires some care.

The main concern in depressurizer design is premature desolvation of analytes. This causes *discrimination*, which is the differential treatment of substances where 1680 identical treatments are expected. In particular, compounds of higher molecular weight tend to desolve first from the supercritical fluid, and might precipitate in the wrong place if the depressurizer is not designed to prevent it.

Depressurization can be done either statically or dynamically. In a dynamic system there is an active element that controls the flow of the eluate in such a way as to 1685 maintain the pressure upstream of the active element of the controller. Such a device is often called a *back pressure regulator*, and is usually an electro-mechanical device with digital control. They tend to be complex and expensive.

In static depressurization there is no active pressure control. A simple *restrictor* is used to limit the flow between the high pressure of the SFC and the low-pressure 1690 outlet.

Textbooks often discuss different restrictor designs. (The book by Luque de Castro, Valcárcel, and Tena 1994, provides an example.). Our preferred depressurizer was the 'integral' or Guthrie design (Guthrie and Schwartz 1986). Figure 4.6 shows the steps in manufacturing the Guthrie restrictor.

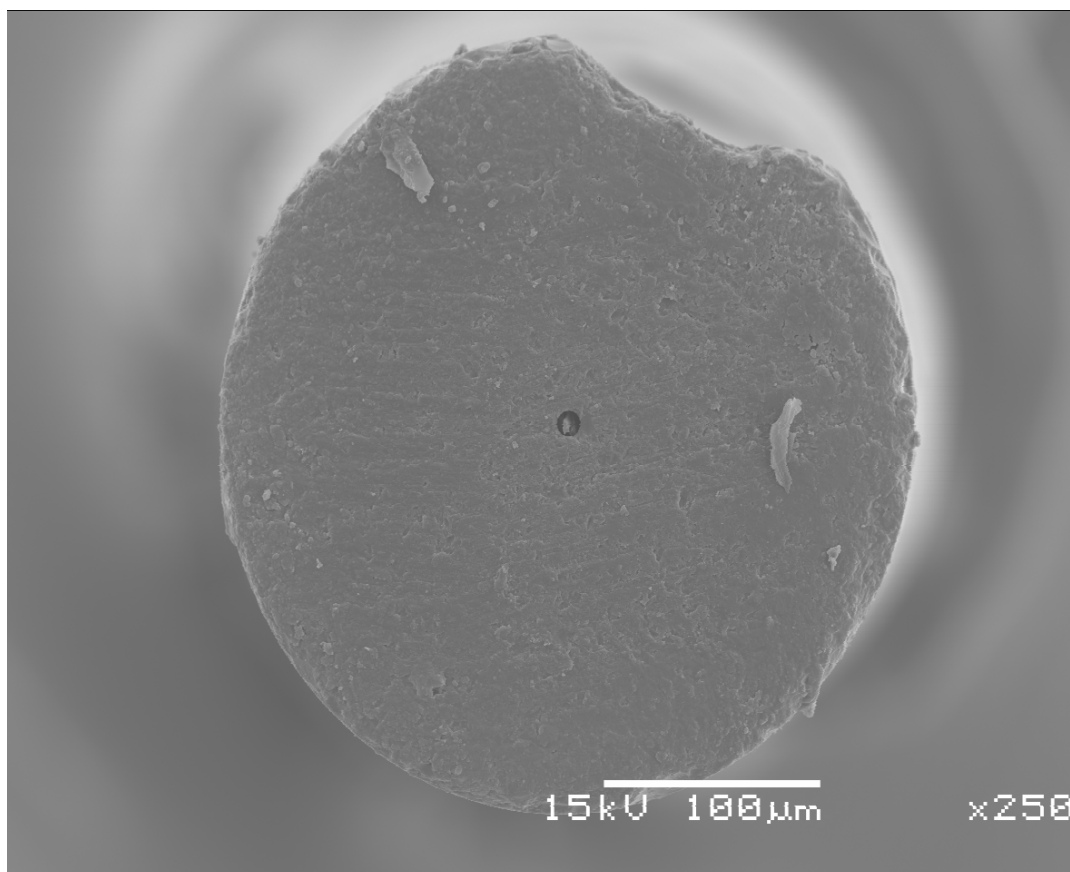


FIGURE 4.7: An electron microscope photograph of a restrictor tip, showing the size of the orifice.

1695 We found this restrictor robust and fairly simple to manufacture. It was possible to adjust the flow to a given flow rate. This design of restrictor should eliminate discrimination, because the decompression takes place in a very short space.

1700 However, the Guthrie design proved prone to blockage. These blockages could not be eliminated by incorporating a 0.5 μm filter before the restrictor, which prompted an investigation into the cause of blockages.

To rule out the possibility that it was particles that caused the Guthrie restrictor to become blocked, we first had to determine the diameter of the orifice. This proved to be harder than expected: optical microscopy was not able to give a simple, unambiguous measure of the orifice diameter.

1705 Scanning electron microscopy (SEM) showed that the orifice diameter of a Guthrie restrictor is about 10 μm, as shown in Figure 4.7 This makes it very unlikely that particles with an origin in the SFC system blocked the restrictor: even the 3 μm particles from the column packing material should not block this restrictor.

1710 Experience had taught us that the restrictor did not block if the flow was continuous. It was only when the pressure in the restrictor cycled that blockages occurred. To eliminate the possibility that it was material from the stop valve (see Section 4.1.6) that caused the blockages, we cycled the pressure by switching the pump on and off, allowing the pressure to bleed off through the restrictor. This way of cycling the pressure did not prevent blockages.

1715 Examination of blocked restrictors with electron microscopy revealed that the restrictors became blocked by a soft material. Backscatter SEM mode allows the

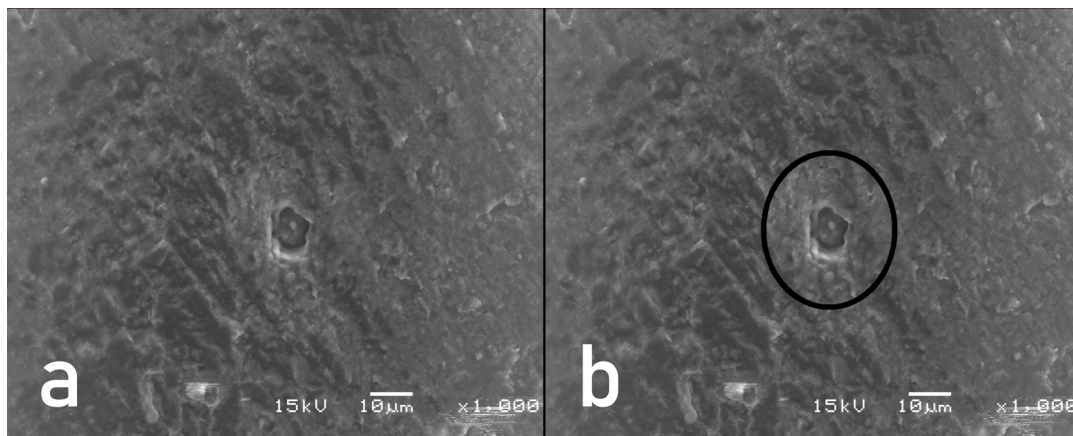


FIGURE 4.8: An electron microscope photograph of a blocked restrictor orifice. (a) Original image (b) Image with black circle showing estimated original orifice location

energy of X-rays to be measured by energy-dispersive spectrometry, which yields information about elemental composition. While much care must be taken before this information can be used for quantitation, it revealed that the deposited material contains significant quantities of carbon and oxygen, and possibly some chlorine. This points to the probability that the material blocking the column is organic in nature, and possibly polymeric. See Figure 4.8.

We could not determine the origin of the material, but it seems likely to be the column, because without a column there was no blockage. We eliminated the possibility of blockage by sample material by using a brand new column. We suspect that it might be remnants of surfactants used in the synthesis of the silica gel stationary phase that are leached out of the column packing, and then precipitates in the restrictor when the pressure drops and the compounds desolvate.

The smallness of the orifice contributes to the plugging problem. With a diameter of 50 μm , a solid sphere that fits in this capillary will have a volume of .065 nL, or 65 pL. This means that nanogram quantities of material can easily block the restrictor.

Being satisfied that an unfortunate combination of restrictor design and column packing was the likely cause of the blockages, we decided to choose a different restrictor design. The choice was a simple linear restrictor and we trusted that heating the end of the restrictor would prevent discrimination.

The linear restrictor was 800 mm long and had an internal diameter of 0.050 mm.

4.1.8 Detector

In this supercritical fluid chromatograph there was no dedicated detector: the role of the detector was taken by a gas chromatograph. This gas chromatograph collected fractions from the SFC, and separated them in fast chromatographic runs with an FID detector, yielding comprehensive 2D chromatograms. This chromatograph-as-a-detector is described in Chapter 5.

*I feel the need ... the need ... for
speed...*

Top Gun

5

Instrumentation: Fast temperature programmed gas chromatography

1745

A gas chromatograph consists

5.1 Main Section 1

5.1.1 Subsection 1

5.1.2 Subsection 2

1750

5.2 Main Section 2

In a book that I took from a shelf

...

Ancient proverb

6

Instrumentation Performance

6.1 Main Section 1

6.1.1 Subsection 1

1755 6.1.2 Subsection 2

6.2 Main Section 2

In a book that I took from a shelf

...

Ancient proverb

7

Application: Analysis of biodiesel

7.1 Main Section 1

1760 7.1.1 Subsection 1

7.1.2 Subsection 2

7.2 Main Section 2

In a book that I took from a shelf

...

Ancient proverb

8

Conclusion

1765 8.1 Main Section 1

8.1.1 Subsection 1

8.1.2 Subsection 2

8.2 Main Section 2

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