“Design of microdistillation device”

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2016 / 2017
ABSTRACT

During the last decades, scientists had been widely attracted for microchemical processing technology, due to its efficient mass and energy transfer as well as the increased safety they provide. Microstructured devices offer the possibility of intensifying distillation operations by providing high ratios of contact areas to volume, high driving force gradients and considerably short transport distances. However, the development of such separation micro devices has proven to be a very challenging task. Indeed, the high surface-to-volume ratio prevailing at microscale results in an unstable boiling and thus in a drop of the distillation efficiency. It is therefore essential to ensure good thermal control in a lab-on-a-chip device in order to precisely achieve a certain desired temperature profile. So far, the existing micro-distillation concepts presented in literature are based on conventional heating and cooling methods, involving external heat transfer systems. The latter are characterized by high energy consumption and the difficulty to establish the required local temperature profile along the microdevice, leading therefore to the reduction of the driving force for mass transfer in the microdistillation process.

In order to overcome these issues, we aim to point towards a novel heating system intended to operate alongside a microdistillation system. Therefore, several novel microheating sources are presented and compared, allowing to shape up a study of the different characteristics and a proposal of the integration of an innovative heating source in a microdistillation system is done. Integration of localized temperature controlled heat transfer systems within the microdistillation device constitutes a promising route to providing rapid and efficient heating / cooling along with a reliable control of local temperatures, with important potential to improve distillation efficiency while reducing the energy requirement of the whole system as compared to existing microdistillation systems.
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0. OBJECTIVES

The aim of this work is the development of a design approach of a microdistillation device with control of local temperature profile by means of an integrated localized heating / cooling system. For this purpose, the following tasks will be carried out:

1. Establishment of the state-of-the-art based on literature review of the existing concepts of microdistillation and heat transfer microsystems.

2. Determination of the potentials and limitations of the microdistillation and microheating methods for localized heat transfer systems integrated in a micro-fluidic device.

3. Elaboration of the design for a novel microdistillation device based on the evidence found in objective 2, entailing a microdistillation concept along with an integrated localized heat transfer system.

4. Design approach of the experimental set-up intended to operate the proposed microdistillation device.
1. Theoretical framework

The term distillation refers to a general class of methods used to separate components from a mixture based on a difference in their volatilities. Large investigation has been done concerning the optimization of distillation units as well as investigation on a wide range of novel methods to carry out distillation on innovative ways. In general, a distillation process involves heating the fed mixture in one end, so called the hot end, and cooling in the opposite side of the distillation device, at the cold end. By heating the mixture to its boiling temperature, it experience a phase change, and starts switching from liquid to vapor. The vapor flows through the channel towards the cold end, where it condenses. By doing so, the fraction of the liquid that is not withdrawn of the system, which will depend on the settled reflux ratio, flows back towards the hot end. In the meanwhile, since liquid and vapor phases are away from equilibrium, a driving force appears between both phases, which enable mass exchange between them. Thus, as the vapor phase moves toward the cold end, it becomes enriched in the more volatile component. Correspondingly, as the liquid phase moves toward the hot end, it becomes enriched in the less volatile component. Light and heavy products are withdrawn of the column at the extremes when it is incorporated in a complete distillation system.

By miniaturizing the separation process, improvement on the mass transfer performance through the production of large gradients and high surface-to-volume ratios is achieved. At micron scales, the significance of gravitation is reduced in lieu of surface forces. The possibility to operate without needs of gravity will allow, for example, carrying out a distillation at the outer space during interspatial missions as a recycling method, taking into account that the resources are extremely limited in such operations. Besides, the size of the systems is significantly reduced. This size reduction is not only an advantage in interspatial missions, but also in operations at industrial scale. The costs of the ground are continuously growing, and the feasibility of the distillation processes are strongly dependant on that costs. Reducing distillation to a ‘micro’ operation will provide a huge improvement for the companies investing in processes which entail distillation steps. Offshore production of methanol and oil from impregnable and unfeasible natural resources reservoirs is also a possible application of microscale distillation. In contrast to areas where traditional chemical plants are
constructed, offshore production plant’s space is extremely limited and valuable. The process intensification possible in microchannel architecture allows smaller, lighter devices to produce quantities of chemicals comparable to larger reactors. That means that commercially significant quantities of methanol and oil can be produced on a ship’s deck, which is far smaller than the footprint of a terrestrial plant. The energy needs of such devices are also reduced, given the inherently small size and the high surface-to-volume ratios. Therefore, also the overall operating costs are reduced, contributing to a less costly operation.

This significant reduction of the characteristic scale also entails limitations, which need to be taken into account and overcome. One of the major challenges of distillation at microscale is the increased heat-losses encountered due to the high surface-to-volume ratio of the channel as well as the temperature control inside the channel. In order to ensure a steady and efficient operation of microdistillation systems, it is of vital importance to have a precise control of the temperature profile described along the channel. Conventional heating/cooling methods offer a poor performance when operating at microscale, and therefore studying the feasibility of a novel integrated localized heat exchange method is of major importance. Given the small size of the microdistillation devices, the throughput that they can offer is also reduced. Hence, another important challenge is the numbering up of the throughput to an industrial interest. That means that the quantity of obtained products should be increased in order to become an economically feasible operation.

**Figure 1.** Comparative relation between the dimension of a conventional distillation column and the first proposed microscale distillation column [1]. They satisfactorily performed the distillation of a methanol-water mixture, which was traditionally carried out by a 4.8 meters long column, with a 0.54 meters long column, showing a size scale of 9 to 1.
Within the next sections, a deep review of the most studied and promising microdistillation and microheating technologies previously brought up in literature will be carried out. It is of vital importance to glance at the state-of-the-art in order to understand the technology and eventually propose an improved device to carry out an optimized microdistillation operation.

1.1 Microdistillation units with different principles

The improvement of distillation columns has been a current subject of research, based essentially on three main key directions: energy integration, improved design of apparatus and novel ways of carrying out the operation. Energy integration offer important improvements but bring more difficult operation and control problems of the overall systems. Optimized design also carries an energy reduction within, but the already done research on the field of distillation is so laboured that obtaining major improvements is a challenging matter. Nevertheless, during the last decades scientists have brought up several promising alternatives posing as alternatives to conventional distillation. The concept of microdistillation has been deeply studied and promising results had been obtained, accomplishing purities up to almost pure components as products. Several operation principles have been reported in literature. Even though, physic and thermodynamic properties involved and governing the performance at such scale are not equal to those at conventional scale. This matter leads to one of the major challenges that operating at microscale faces, which is the numbering up of the throughput in order to make the process feasible to use a microdistillation device for industrial purposes.

The following section is a study of the several systems that have been brought up by researchers during the last decades in order to improve the performance and diversify the applications of the microdistillation operation. The basic principles governing the systems, the promising characteristics and future applications and the challenging aspects presented will be studied and presented below.
1.1.1 Microdistillation using segmented flow

A microdistillation can be operated within a micro structured system with the help of carried (sweeping) gas, which is usually nitrogen or similar noble gases acting as the phase contactor along the microchannel, thus obtaining a dispersed-phase micro-contact, and a membrane micro-separator. The process takes place below the boiling points of the individual mixture components and is based on the difference between the partial vapor pressures of the relevant components in the liquid mixture. Hartman et al. (2009) [2] developed a novel device taking advantage of this principle. Figure 2 is a representation of the developed device.

![Figure 2](image_url)

**Figure 2.** Proof of the concept device designed by Hartman et al. (2009) [2] used to achieve a single stage distillation, based on a segmented flow and a later separation by capillary action.

The liquid mixture and the carried gas are introduced into the microchannel forming slug flow. The liquid components evaporate, in a way that a non-equilibrium condition occur between liquid and gas phase. Such condition, leads to a continuous mass exchange between the vapor slugs along the channel, driven by the carrier gas. A rather long channel is required in order to approach the liquid–vapor equilibrium state. Afterwards, a membrane micro-separator is used to separate enriched vapor from liquid...
based on capillary forces and eventually the vapour-carrier gas phase, which does not flow through the separator membrane, passes across the membrane surface to an outlet. The liquid phase which wets the porous membrane flows through the pores of the membrane to another outlet by means of capillary action. The vapour–carrier gas phase does not flow through the membrane because the minimum pressure needed to overcome the capillary pressure difference has not been achieved. With this separation step, the whole microdistillation process is completed, and two different steams enriched with the two components of the initial mixture respectively are obtained. Due to the structure of this system, no reflux is possible, and hence just a single-stage microdistillation can be realized.

1.1.2 Vacuum on hydrophobic membrane distillation

Within this approach, the design of the microdistillation chip is based on fabricating microfluidic channels precisely endorsed in a set of layers through which the liquids and vapor currents will flow given a specific function. Figure 3 shows explicitly the design of each layer in the chip presented by Zhang et al. (2010)[3] along with its given functions, and by having these multiple levels and channels, a distillation process can be done. The device is divided in two zones as occurs in a normal scale distillation column: stripping and rectifying sections separated by the feed entry channel. A PTFE hydrophobic membrane is placed between liquid and vapor channels. Two different temperature gradients are needed, supplied by a hot plate at bottom of the device and a layer containing a cooling water flow.

After feed is introduced continuously into the distillation channel as a liquid it is heated at the hot stripping section under action of a hot plate placed beneath. Once the liquid starts to vaporize, due to the hydrophobic nature of the PTFE membrane, only vapor can penetrate inside dried membrane pores to the vapor channel. A vacuum pump is connected to the vapor outlet and thus the permeated vapor moves left and partially condenses at the L–V interface of the cold rectifying section where pressure $P_1$ is larger than the total vapour pressure of liquid $P_2$. 
Figure 3. Proof of concept device designed by Zhang et al. (2010)[3]. The scheme depicts the overlapping micro-layers and describes its function within the chip.

Figure 4 shows the temperature gradients and the vacuum driving force. As well as a refluxed flow, the condensed liquid fills the liquid channel of the rectifying section and moves toward the liquid outlet. A mass exchange between both phases occurs through the membrane which acts as the interface. The vapor flowing left in the vapor channel contacts the liquid moving right in the liquid channel at the upper surface of the membrane to establish a repeated condensation and evaporation. By doing so, mass transfer takes place from one phase to the other because of the fundamental tendency of the mixture to approach equilibrium compositions. As the process proceeds, separation is achieved in which the more volatile component is extracted out from the cold vapor outlet and the “heavier” liquid is forced out from the hot liquid outlet, conditioned by the certain established outlet flow rates.
1.1.3 Zero gravity distillation utilizing the heat pipe principle

Through this approach, distillation operation takes advantage of the so called heat pipe principle in order to carry out the separation of a mixture within a microscale environment. The basic structure of heat pipes is usually based on a tubular metal structure closed at both ends, as represented in Figure 5. The device is divided in three essential parts: an evaporation zone, where the fluid is heated to a certain temperature and partially changes its phase, as happens in a conventional reboiler, an adiabatic transportation zone, where the generated vapor is conducted by pressure difference away of the heat source, and a condensation zone, where the vapor is cooled and thus condensed. Afterwards, the fluid flows back to the hot end. However, this fluid return does not rely on gravity, but on the capillary action granted by a porous material rolled on the pipe walls, such as a wick or a mesh.
The wick structure is saturated with the liquid obtained from the condensation zone, and is transported due to the capillary pressure caused by difference in curvature of the liquid menisci. By doing so, a reiterative system is established within the pipe.

This principle was first regarded as a possibility to work as a distillation column by Seok and Hwang (1985)[1]. They proved the feasibility of such apparatus to separate mixtures of ethanol-water and methanol-water with satisfactory results. The mixture is fed at some point of the channel, and the temperature is fixed at the heating end to properly evaporate the fed mixture. The performance is equal to that observed in a heat pipe, but with the novel feature that given that liquid flows through the porous medium from the cold to the hot end in countercurrent flow to the vapor and, because at the wet porous medium interface the liquid and vapor phases are away from equilibrium, mass exchange between phases occurs all along the channel. As the vapor phase moves toward the cold end, it becomes enriched in the more volatile component. Correspondingly, as the liquid phase moves toward the hot end, it becomes enriched in the less volatile component. Light and heavy products are withdrawn of the column at the extremes when it is incorporated in a complete distillation system and hence obtaining separated outflow steams with a determined purity. 

**Figure 6** depicts the principle of operation of such system.
The device encompasses the elements encountered in a traditional distillation column. A feed inlet, bottom and distillate outlets intended to withdraw the products and a temperature gradient in order to carry out the evaporating of the mixture. The difference lies on the use of a capillary wick or mesh in order to drive the condensed refluxed liquid from the cold end back to the hot end, in lieu of the gravitational force. Wide research has been made regarding this principle, and after Seok and Hwang proved its feasibility, during the following decades, novel devices and approaches have been brought up, running towards a better distillation performance, in terms of separation efficiency, energy consumption and control parameters.

1.1.4 Centrifugal force distillation

As aforementioned, gravity loses its impact the more reduced is the size of a distillation device in gain of other types of forces, such as surface forces, due to the high volume-to-surface ratio. However, some research has been done pointing out the possibility of design of a microdistillation device based on centrifugal forces. Instead of capillary forces, MacInnes et. al. (2010)[4] demonstrated the operating principle of a microdistillation device which drove the liquid phase by means of centrifugal forces. A prototype device using a rotating spiral microchannel to produce multistage distillation was designed and used to separate 2,2-dimethylbutane from an initial 50:50 mixture.
with 2-methyl-2-butene. The device achieved 6.6 stages (HETP was 0.53 cm) for the separation of 50 mol% 2,2-dimethylbutane/2-methyl-2-butene mixture, operating at 5000 rpm.

The rotating spiral approach uses centrifugal force to maintain segregation of the phases into parallel-flowing liquid and vapour layers. When centrifugal force is opposed by pressure gradient along the channel, these layers can flow counter currently. In the spiral channel, the vapour and liquid phase flow counter-currently. In place of gravity, the component of centrifugal acceleration along the channel drives the liquid outward along the spiral and the vapour can flow inward, with appropriate adjustment of the pressure gradient. Figure 7 depicts the principle of operation of the rotational spiral device.

![Figure 7. Operating principle of the distillation device design by MacInnes et al. (2010) [4]. The direction of the forces is pointed out, as well as the temperature gradient generated along the channel and the inlet and outlet flows.](image)

In order to control the phase contacting between both phases, it is possible to adjust the rotation angle and pressure gradient along the channel. By doing so, adjustment of the phase flow rates and the contacting layer thicknesses is allowed. Thus, it is possible to take full advantage of the rapid mass transfer that is potentially available for small microchannel dimensions. A large number of separation stages to be reached, given that his efficient contact can be maintained over long channel distances. Furthermore, the generated Coriolis force causes a secondary movement of both phases, thus leading
to an enhanced mass transfer. As the vapor phase moves toward the cold end due to the pressure gradient, it becomes enriched in the more volatile component. Correspondingly, as the liquid phase moves toward the hot end, it becomes enriched in the less volatile component. Light and heavy products are withdrawn at the extremes when it is incorporated in a complete distillation system.

1.2 Phase contacting

One of the key factors in order to achieve an efficient and proper separation of the fed mixture is the control of the hydrodynamics within the microchannel, such as the fluid flow. It is hence essential to establish an interface between both liquid and vapor channels so that a controlled contact between them is achieved, and thus let mass exchange happen. Given that in a microfluidic environment, surface forces are the main driving force for liquid flow instead of the dominance of gravity presented in conventional scale, novel strategies to establish the liquid-vapor interface are required. Many research has been done regarding to different contacting principles and contactor designs in order to obtain an improved overall performance. There are several approaches that have been investigated, which are classified into two major groups: continuous-phase and dispersed-phase microcontactors.

1.2.1 Continuous-phase microcontactors

In continuous phase micro-devices the goal is to keep both phases continuous and use a certain contactor to create an interface between them as a medium to enable mass exchange to occur. In these devices the channel is divided into two sections, one for the gas and another for the liquid, separated by the contactor. Such contactor is a key issue to obtain a stabilized gas-liquid interface. Both streams are also ideally withdrawn separately at the respective outlet. In the case of a falling film microcontactor, as exemplified in Figure 8, liquid flow is driven by gravity as represented in micro-structured plates with a typical thickness of ~100 μm are incorporated to stabilize the liquid film. As aforementioned, the smaller the size of the device, the less influence of gravity is experienced. For that reason, non-gravity based methods were investigated. A
porous mesh or a membrane microcontactor is used in overlapping microchannels, through which vapour and liquid steams flow without phase dispersion in two different microchannels. In order to promote mass exchange, a counter-current flow shall be settled. The non-equilibrium condition between the two phases will act as the driven force. The functioning of such principle is shown in Figure 9.

Back and McCready (1998) [5] studied interfacial mass exchange for concurrent gas-liquid flow. It was shown that mass-transfer coefficients were strongly dependant on the flow regime and its fluctuations. As turbulence in the bulk flow increases, mass-transfer capability grows. Accordingly, a laminar bulk flow provides less velocity fluctuation and, consequently, a smaller mass-transfer capability. Given the significantly low flow regimes that are inherently implied in microfluidic environments, the turbulence of the flow is minimal. Therefore, the high degree of film mixing obtained in previous studies needs to come from another features. It can be assumed then that the porous medium is responsible for such high mixing, due to its countless inner channels that provide random depths for the fluid flow. From this statement can be obtained that the design features of the microcontactor, such as the wetting angle, wick thickness, porosity and pore diameter, are of crucial importance on achieving a high degree of mixing.
1.2.2 Dispersed-phase microcontactors

In dispersed-phase microcontactors a gas-liquid dispersion is created by an inlet which induces mixing of the gas and liquid streams. It contains a dual feed arrangement that mixes phases in ordered slugs or lamellae in the feeding section, where dispersion is formed. After they pass through the inlet section, both phases are delivered to a single channel. By heating this channel, the fed mixture evaporates partially and enters the gas slug with a certain composition, thus creating a non-equilibrium condition between both phases, and creating a driving force for mass exchange to occur. In this configuration, radial mass transfer is improved to the detriment of axial mass transfer, resulting in plug flow behaviour and improved heat/mass transfer. Figure 10 represents the operation principle of such configuration.

![Figure 10. Dispersed phase operating principle within a microchannel](image)

The hydrodynamics obtained depend on various parameters, but one of the most critical is the ratio of the gas-to-liquid flow rates. By increasing the ratio, the flow regimes changes and this affects the mass transfer between the phases, because of the different velocity profiles and interfacial area.

It must be noted that, although in dispersed-phase reactors transport limitations between the two phases are significantly reduced, there is generally a degree of uncertainty concerning the actual fluid geometries and available interfacial areas. The flow patterns are also affected by the channel size, phase superficial velocities, surface tension, wettability and inlet condition. Furthermore, a latter separation of the two
phases at the end of the process is needed. Such problematic is often solved by means of the addition of a porous medium, which by means of capillary action entrains the liquid phase and given that the minimum pressure needed to overcome the capillary pressure difference has not been achieved, the vapour–nitrogen phase does not flow through the membrane and flows towards an outlet.

1.3 Localized heat transfer micro-systems

Miniaturization of components has been the defining trend in the world of electronics during the past 50 years. Temperature control has become extremely important in ensuring the precise control of thermally sensitive devices and operations. This field of study encompasses an extremely wide range of applications and lines of investigations, in a wide variety of disciplines, namely electronics[6] and biotechnology [7]. Distillation is an extremely temperature dependant operation, and therefore it is no exception of being a focus of interests for many researchers. That is why during the last decade the approaches to accurate localized temperature control within microfluidic systems have been of great interest, and researchers have brought up a wide bundle of approaches to fulfill the demanded operation conditions. The development of lab-on-a-chip requires the integration of multiple functions within a compact platform, which is readily transportable and can deliver rapid data output. One such functionality is the control of temperature, either in terms of profile (homogeneous or gradient) or in terms of the accessible temperature range, in both cases with the greatest accuracy possible.

Indeed, the regulation of temperature is a critical parameter in managing many physical, chemical and biological applications. Nevertheless, the difficulty encountered with many procedures for on-chip heating is a dilemma between accuracy and complexity, as well as the temperature range demanded to achieve a certain operation’s efficiency or desired purity of the products. A variety of different approaches has been investigated, from external heating sources to Joule heating, microwaves or the use of lasers to cite just a few examples. The scope of the technical solutions developed to date is impressive and encompasses for instance temperature ramp rates ranging from 0.1 to 2,000 °C/s
leading to homogeneous temperatures from −3 °C to 120 °C, and constant gradients from 6 to 40 °C/mm with a fair degree of accuracy.

The following section aims to highlight the potential of previously developed micro heating and micro cooling systems reported in literature. One of the systems at which scientists have paid more attention is the so called Polymerase Chain Reaction (PCR). This system requires an extreme temperature control to become a successful operation, and therefore a wide variety of systems addressed to control and optimize this operation is available and currently under a deep research. For that reason it will be a promising investigation line to follow, and to study its feasibility of being incorporated on-chip in a microdistillation device aiming to work as a precisely controlled and localized heat source for a microdistillation operation.

### 1.3.1 Joule heating effect

Joule heating, also referred to as resistive or ohmic heating, describes the process where the energy of an electric current is converted into heat as it flows through a resistance. In particular, when the electric current flows through a solid or liquid with finite conductivity, electric energy is converted to heat through resistive losses in the material. The heat is generated on the microscale when the conduction electrons transfer energy to the conductor's atoms by way of collisions. From an equation based view, Joule effect can be described by the following laws. The fundamental formula for Joule heating is the general electrical power equation:

\[
P = (V_A - V_B) \cdot I
\]

Where \( P \) is the power, standing for the dissipated energy per unit time, which the converted from electrical to thermal energy, \( (V_A - V_B) \) represents the voltage drop across the resistive element, and \( I \) represents the current traveling across it.
By applying Ohm’s law, a relationship between the dissipated power and the resistance of the certain resistor is obtained:

\[ P = I^2 \cdot R \]

In some cases, such dissipated heat is a matter of problems for engineers to design a certain device, since the generated heat may lead to overheating or other unwanted effects. However, such generated heat can be of great interest for operations were a heat source is needed such as distillation. Furthermore, given the aforementioned laws that rule this effect, heat shedding can be accurately controlled by means of variance of the applied voltage, the current or the resistance. A proper control of these parameters allows a precise knowledge and regulation of the dissipated heat, given that the relationship between them is linear. Therefore, Joule effect can be turned into a certainly promising possibility of using such dissipated heat as the heat source of a certain device. The advantage of working at microscale is the low level of heat required, and thus the voltage to apply is extremely low. That leads to a reduction of energy consumption, and the overall operation costs.

Many research has been done towards the implementation of a Joule effect heater into a microfluidic device. Results had been varied, and a wide range of designs and operation features have been brought up. Most of the reported results in the literature involve either whole system heating or a heating zone of size much larger than the interest zone, as showed by Jiao et al. (2008)[8]. However, approaches to accurate temperature control within microfluidic systems have been also proposed by De Mello et al. (2004)[9]. The authors demonstrated controlled Joule effect heating of ionic liquids in a co-running channel that was external to the main fluidic system, and presented a microfluidic device incorporating working fluid channels with a serpentine-like geometry and parallel channels in which ionic liquids are Joule heated with an AC current. Consequently, the internal temperature can be easily and directly controlled. Temperature measurements were performed using three thermocouples. The configuration of the proposed device as an example of Joule heating is depicted in Figure 11.
However, precise control of Joule heating for large variations of temperatures remains difficult regarding the conductivity of ionic liquid proposed. Selva et al. (2010)\cite{10} demonstrated the possibility of uniform heating of a cavity with great accuracy. In order to achieve this goal, they proposed a tool intended to optimize a resistor pattern capable of generating constant temperature along the cavity. They focused on shape optimization for the heating resistance, which allows leaving space on the substrate for other potential surface functionalities, and a decrease in resistor surface area resulting in lowering the required heating power. By means of an integrated resistor built with the same dimensions as the cavity, a high level of integration was achieved. For application purposes, a compact resistor allows increasing the number of cavities in which temperature can be independently controlled.

Dinca et al. (2009)\cite{11} introduced a novel concept of integration of the localised micro heater into the microdevice. The main purpose of the study was to present a micro polymerase chain reaction (PCR) device. Such device requires a precise control of temperature to achieve a satisfactory result, and for that reason they developed an appropriate microheater based on the Joule effect presented for a bundle of thin film metal resistors. The device encompassed a miniature thermal cycler incorporating

\textbf{Figure 11.} Schematic of microfluidic device incorporating co-running heating channels proposed by De Mello et al. (2004)\cite{9}. The working fluid channel is shown in black and the co-running heating channel in grey. Both channels are 150 mm wide and 50 mm deep. Crosses mark position of thermocouples for temperature measurements.
Platinum (Pt) thin layers used as heating source based on Joule effect, acting as well as the temperature sensors, screen-printed on a ceramic plate. A representative example of the basic operating principle of a thin film heating structure elaborated with COMSOL Multiphysics is showed in Figure 12.

![Figure 12. Representation of a thin film resistor ruled by Joule effect. A certain voltage is applied at one end of the metal resistor and, due to the resistance offered by the material, a dissipated voltage-dependant heat appears. In the scheme, the brightest the colour, the higher the quantity of generated heat.](image)

**1.3.2 Chemical reaction heat exchange**

Many chemical reactions require a certain heat exchange in order to take place. On one side, there is a type of reactions which release energy in form of heat when they occur. These are the so called exothermic reactions. They may occur spontaneously, and since the heat generated is lost to the surroundings they are denoted by a negative heat flow. On the other side, there is a type of chemical reactions which require a certain amount of energy supply in order to proceed, these are endothermic reactions. These can't occur spontaneously and a heat source must be involved. The control of such heat exchange can be achieved by knowing the thermodynamic properties of the chemical agents, the reaction kinetics and operating parameters under which reaction takes place. By settling the proper flow of a certain mixture and taking into account all the aforementioned characteristics, when contact between the working fluid channel and the heating/cooling channel will lead to a system where a chemical reaction may be working either as a heating source or as a heat sink.
The use of endothermic and exothermic processes to locally regulate temperature in a microchannel was first studied by Guijt et al. (2003) [12]. The authors proposed an approach for on-chip-based temperature control, based on the use of endothermic or exothermic processes in microchannels to respectively cool or heat solutions in an adjacent microchannel. The operating principle is depicted in Figure 13.

The temperature control channels are directly integrated in the chip and localization of the cooling or heating effect is controlled by positioning the endothermic or exothermic processes at the reactant flow interface. In demonstration experiments, the evaporation of acetone was used as an endothermic process to cool a microchannel. Additionally, heating of a microchannel was achieved by dissolution of concentrated sulphuric acid in water as an exothermic process. Furthermore, multiple cooling and heating systems could be integrated along a single reaction channel, allowing multiple temperature control units on a microdevice where multiple endothermic and exothermic processes occur in parallel. Within this approach, temperatures ranging from −3 °C up to 76 °C with ramps about 1 °C/s can be achieved.

Figure 13. Schematic of the principle of operation of the device designed by Guijt et al. (2003)[12]. The Y-junction allows the mixing of the two agents intended to react, and let the heat exchange begin. The nature of the solvents and the angle (θ) of the junction are parameters of significant importance.

Maltezos et al. (2006)[13] carried out an optimization of the approach previously proposed by Guijt in 2003. In their work, they presented a novel solution to the so
common problem of heat control when the size of the apparatus is reduced to microscale, with a localized cooling through evaporation of volatile materials within microfluidic channels. It is well known that refrigeration can be achieved through the endothermic mixing of compressed gas with an evaporating liquid. Within this work, they intended to show that this phenomenon also applies in microfluidic environments. Thus, small channels were fabricated to carry out the refrigeration, and connected to form simple Y junctions with two input channels in the same way that in Figure 13. Within this method, one of the channels is for the refrigerant and the other for the gas. Once they are mixed, evaporation occurs throughout the cooling channel, using the working fluid heat as the heat source and a heat flow from the hot working fluid to the cooling channel is established. By varying gas inlet pressures, refrigerants, and angles of the microfluidic junctions, optimal cooling conditions were found. Refrigeration rates in excess of 40 °C/s were measured, and long lasting subzero cooling in the junction could be observed. This method stands for a cheap and completely integrated solution for microfluidic heating, and especially for cooling. However, it was also found that it may be difficult to accurately control the heat exchange between both channels.

1.3.3 Microwave heating

Within the past sections, the temperature control has been performed by on-chip integrated microheating devices. In those cases, heat diffuses from the heat source towards the channel containing the working fluid. Thus, the totality of the generated heat does not reach the target fluid and some heat becomes lost through the diffusion process. For that reason, during the past few years, using microwave energy to heat and drive chemical reactions has become increasingly popular in the chemistry community. The singularity that differentiates heating by microwave from the aforementioned techniques is basically that microwaves are based on heating the liquid in the bulk. That means there is no use of a heating source that transfers heat by diffusion to the liquid. Within this approach, the energy is directly generated in the fluid under the action of the microwave’s energy. While conventionally the heat comes from the outside and goes into the reaction mixture by convection currents (resulting in a very hot vessel wall), microwaves go through the almost microwave-transparent vessel wall and directly heat the reaction mixture. The operating principle of this technology is depicted
One of the many advantages of using rapid ‘microwave flash heating’ for chemical synthesis is the dramatic reduction in heating ramp/rate and times.

**Figure 14.** Schematic illustration of the two dielectric heating mechanisms: dipolar polarization (dipoles align in the microwave field) and ionic conduction (ions move in the microwave field).

This non-classical heating method has matured to an established technique that is heavily used in academia and industry. Active safety features for chemical synthesis in order to allow safe processing, even under extreme temperature and pressure conditions have been developed. Superheating of solvents in sealed vessels is the key advantage in microwaves synthesis, since due to the Arrhenius law the reaction times can be considerably shortened. The schematic difference between conventional heating and microwave heating is showed in **Figure 15**, extracted from [14].

**Figure 15.** Graphic illustration of heat introduction and temperature distribution into a reaction mixture for (a) conventional heating and (b) microwave heating.
Therefore, microwave synthesis in sealed vessels gives access to a much wider range, applying temperatures far above the boiling point of the used solvents. Dedicated microwave reactors allow the reaction vessels to remain completely sealed throughout the whole experiment process and therefore act as highly convenient autoclaves. Today, the ability to selectively and precisely control the temperature of fluid volumes ranging from a few microliters to sub-nanoliters in microfluidic networks added to the aforementioned features, has lead to a big number of industries to invest huge amounts of economical resources to the development of microwave heating techniques. One of the industries which has made the biggest effort on investigating this technology is the pharma-chemical industry. Many reaction parameters, such as reaction temperature and time, variations in solvents, additives and catalysts, or the molar ratios of the substrates, can be evaluated in a few hours to optimize the desired chemistry, thus significantly reducing operation costs.

1.3.4 Infrared laser heating

Infrared (IR) radiation is a type of electromagnetic radiation. Its light is the part of the EM spectrum that people encounter most in everyday life, although much of it goes unnoticed. It is invisible to human eyes, but it can be noticed as heat. It is one of the three ways heat is transferred from one place to another, the other two being convection and conduction. Infrared’s heating operation is illustrated in Figure 16 and Figure 17, extracted from [15]. With the increasingly fast development of microelectronics, the infrared laser diode became a cheap and reliable technology with a wide variety of applications. The laser is now an easy and simple way to thermally interact with a material and it is thus a rational approach in order to heat precisely fluid volumes.

In order to do so, the laser is used to heat the surface of its target by infrared radiation. The absorbed power depends on the wavelength (λ), and the underlying characteristics of the heated species or material. The most relevant processing parameters are the laser power and the beam/material interaction time. More recently, the laser has been used as a tool for the direct heating by using the beam as a localized and highly controllable heat source.
Infrared heaters are usually classified by the wavelength they emit, and there exist several types of radiation generation, such as heat lamps, metal wires and ceramic infrared heaters. The spatial precision is easily around a micrometer and the volumes employed in microfluidics allow low power consumption. Even if it is not an integrated method (for the moment, the laser remains out of the chip), it offers a cheap and spatially reconfigurable heat source that can be precisely addressed. However, the scope of the research regarding this heating method is not well extended, and hence there is a significant lack of literature of microfluidic environments heated by an infrared laser. Besides, the problematic of achieving spatial homogeneity along the heated chamber is still a challenge for this technology. Many of the efforts are pointed towards solving problems with temperature non-uniformity, i.e. by varying the lens configuration intended to defocus the laser beam to achieve a more uniform temperature distribution. The experimental results obtained thus far are not appealing to be enough to fulfil a microdistillation needs.
2. Materials and methods

A deep review of the most studied systems during the last decades, either regarding microdistillation methods or microheating devices for several purposes, has been done within the past sections. In this section, the aim is to illustrate the differences between the presented systems and methods and to point out the strengths and weaknesses offered by each of them. Such balancing will be carried out by extracting the information of each reported performance and, afterwards, an accurate comparison between the crucial characteristics that define either microdistillation and microheating systems will be elaborated. The possibility of incorporating some of the presented features to a novel microdistillation device will be studied.

2.1 Microdistillation systems balancing

2.1.1 General overview

The following is a general data sheet of the systems showing the basic characteristics of the most relevant microdistillation approaches reported in literature. Figure 18 contains information about capillary driven systems.

<table>
<thead>
<tr>
<th>Author</th>
<th>Driving Force</th>
<th>Contactor</th>
<th>System considered</th>
<th>Separation efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seok and Hwang (1985) [1]</td>
<td>Capillarity</td>
<td>Fiberglass wick</td>
<td>Methanol/Water Ethanol/Water</td>
<td>5cm HETP</td>
</tr>
<tr>
<td>Hibara et al. (2008) [16]</td>
<td>Capillarity</td>
<td>Micropillar structures</td>
<td>Ethanol/Water</td>
<td>Distillate: 19%wt ethanol; Bottom: 8,6%wtethanol</td>
</tr>
<tr>
<td>Tonkovich et al. (2007) [17]</td>
<td>Capillarity</td>
<td>Woven stainless steel mesh</td>
<td>Hexane/ Cyclohexane</td>
<td>0,83cm HETP</td>
</tr>
<tr>
<td>Lam et al. (2011) [18]</td>
<td>Capillarity</td>
<td>20μm micropillars</td>
<td>Acetone/ Ethanol</td>
<td>5,4 TP</td>
</tr>
<tr>
<td>Sundberg et al. (2009) [19]</td>
<td>Capillarity</td>
<td>Metal foam</td>
<td>Methyl formate/ Methanol</td>
<td>5cm HETP</td>
</tr>
</tbody>
</table>

Figure 18. Summary of the basic characteristics of the most significant capillary-driven microdistillation systems.
The bundle of systems proposed within the principle of operation of a capillary driven force has been proliferous within the last decades. Back in 1985, Seok and Hwang [1] first demonstrated the principle of operation and feasibility of this concept using lined glass fiber material to induce liquid flow in a horizontal mini-size distillation tube (see Figure 6). The separation results were satisfactory, but the heat control and thus the temperature profile were not properly controlled. Heat losses were an important challenge to overcome. Furthermore, they found several difficulties of construction and measurement due to the technology of the moment. Thus, they had to assume several operating parameters in order to obtain the most accurate possible results. This work was modeled by Ramirez-Gonzalez et al. (1992)[20] characterizing the working principles of the device.

Hibara et al. (2008)[16] designed a different microdistillation device consisting of a micropillar based structure for the separation of a 9.0 wt% ethanol/water mixture. The nanostructures were included to facilitate vapor condensation. The device did not conduct any liquid reflux back to the heating zone, and the separation performance was therefore limited. The reported bottom stream consisted of 8.6 wt% ethanol, whilst the distillate contained 19 wt% ethanol.

Tonkovich et al.(2007)[17] investigated the possibility of exploiting remote, offshore gas reserves. Natural gas in many offshore regions is plentiful, but lacks access to the market because of the obvious logistical challenges and costs. Conventional process technologies are not well suited for operation on floating vessels that are highly space and weight constrained and may challenge vessel stability during inclement weather. Within this work, the authors proposed an attractive variant of the traditional natural gas extraction methods, converting the gas into a liquid product on a floating production, storage, and offloading vessel by means of microchannel process technology units. Microfluidic devices had been typically applied to single unit operations, and within this work the authors aimed to design an entire on-board microchemical plant. The microdistillation device was part-forming of an entire micro chemical plant based on using natural gas and air to produce a liquid methanol product. Natural gas was converted to synthesis gas using steam reforming. The methanol distillation unit used six microchannel assemblies. The size of the distillation unit is lower than conventional
scale, but far from representing a microfluidic device. The authors gave out no experimental result data, and thereby a critical analysis of the weaknesses and strengths of the floating plant performance is not possible. An experimental test should be carried out in order to do so.

Lam et al. (2011) [18] further decreased the device’s dimensions. Furthermore, instead of using foreign wick materials, the capillary action for liquid movement was induced by arrays of fabricated micropillars along the walls of the microchannel. Both liquid feed and liquid reflux flowed along the micropillar regions, whilst the vapour from evaporation of the liquid flowed in the center of the microchannel counter-currently. The distillation chip was used for separation of acetone/water and methanol/toluene mixtures achieving 4 equilibrium stages for the former and for the latter estimated at total reflux conditions. Separation depended strongly on the operating conditions, and a certain decrease or increase in the heating and cooling resulted in poorer separation. The separation performance was clearly affected by the heating and cooling temperatures, parameters that were the most challenging aspect of the study given that the heating methods used were not extremely accurate.

Sundberg et al. (2009) [19] built a similar flat microdistillation device using metal foams as the convective wick for the separation of an n-hexane/cyclohexane mixture. They intended to improve the difficulties encountered by other authors, principally the heat losses. Even though, in their work they also found difficulties during the experiments due to lack of degasification and heat losses. Degasification was not carried out properly and this caused a lack of repeatability. They encountered problems on controlling the heat supply and withdraw, and ended up with the statement that the solution was not yet optimal. However, the major improvement was the large reduction in the hold-up volume, without significant difficulties in achieving stable operation.

**Figure 19** summarizes the work brought up by researchers taking advantage of other driving force principles.
Wootton and deMello (2004) [9] separated 50 mol% acetonitrile-dimethylformamide and 50 mol% dimethylformamide-toluene mixtures using a microdistillation chip with the aid of helium as a carrier gas. The inert helium was added to drive the vapour flow through the chip. The chip consisted of three regions: evaporation, condensation and carrier gas–liquid separation. The separation efficiency of the chip was found to be equivalent to 0.72 equilibrium stages.

Another single-stage integrated microdistillation system consisting of a segmented flow unit and a membrane gas/liquid separator was demonstrated by Hartman et al. (2009) [2] (see Figure 2). The distillation chip allowed ample time for mass exchange between the two phases. The vapour and liquid flows were co-current and were driven by nitrogen gas, which was subsequently separated by a gas–liquid membrane separator based on capillary action. The chip was operated isothermally. A 50 mol% methanol/toluene mixture was separated into 22 and 79 mol% methanol in the bottom
and distillate streams, respectively, and the separation was equivalent to a single equilibrium stage.

Even though the promising features of carrier gas microdistillation, the major limitation is that no reflux can be circulated back to the microchannel because of the unidirectional flow of the carrier gas, which means that the best achievable separation is limited to a single stage. Furthermore, an additional gas–liquid separator is required after the distillation process to remove the carrier gas, which increases the complexity and thus the difficulty to control the overall operation.

In the work of Zhang et al. (2010) [3] a multilayered microchip used for vacuum distillation was designed, fabricated and tested by rectification of a water–methanol mixture (see Figure 3). The polymer chip employed a cooling channel to generate a temperature gradient along a distillation channel below, which was separated into a channel for liquid phase and a channel for vapour phase by an incorporated microporous PTFE membrane. The temperature gradient was controlled by adjusting hotplate temperature and flow rate of cooling water to make the temperatures in the stripping section higher than the increasing boiling points of the water-enriched liquids and the temperatures in the rectifying section lower than the decreasing dew points of the methanol-enriched vapours. The proposed microdistillation was promising due to the minimized concentration polarization, less reagent consumption and cost. However, such technology is only applied in Zhang's work, and hence the separation efficiency could be further improved by optimizing the device and the parameters, namely the width of the channels, the temperature-gradient and the membrane pores size.

MacInnes et al. (2010) [4] proposed a rotating spiral microchannel distillation device, in which the liquid and vapour layers were segregated into two parallel counter-flows along the channel under the combined effects of centrifugal forces and the pressure gradient (see Figure 7). The spiral channel network was formed on an optical glass substrate with a thickness of 2.3mm by an isotropic wet etching process. Access holes were drilled in a second optical glass plate (with a thickness of 1 mm), and the drilled plate was then bonded to the patterned substrate via a thermal fusion process to form the completed chip.
Ziogas et al. (2011)[21] designed a plate-type microdistillation device resembling a conventional distillation column. The stainless steel structure consisted of 35 mm × 5 mm channels separated by a rectangular square mesh (size 0.31 mm and wire diameter of 0.2 mm) which was the equivalent of a distillation tray. A reflux condenser, a distillate drum, and a bottom reboiler were also incorporated in the device. The mesh retained the liquid by capillary forces but allowed vigorous contact between the liquid and the vapour phases.

When reducing the size of the microdistillation device, an inherently increase of the dominance of the surface forces in lieu of the gravitational forces appears. For that reason, when a distillation system is reduced to microscale, there is no possible way to carry out the operation by means of gravitational or centrifugal forces. Such systems can be reduced, but not at a micrometric scale. Hence, the requirement of counter-current vapour/liquid flow for multistage distillation has led researchers to prefer the use of non-gravitational forces to rule microdistillation operation.

Within a quick glance to the tables, it can be noticed that the major effort by scientists to investigate a feasible system to distillate at microscale environment has been done under the scope of the capillary driven systems. When studying a system, it is of vital importance that the background of previous studies is rich enough to provide a sustainable quantity of information in order to evaluate and improve in a certain field. Researchers had taken capillarity as the most promising driving force for microdistillation, and thus the bundle of literature is remarkable.

2.1.2 Size balancing

Although these devices showed the feasibility of multi-stage distillation using mini-scale features, the sizes of the majority of them did not actually fall within the true definition of microscale systems (at least one dimension of the channel in sub-millimeter scale). The developed devices are usually on the millimetric scale. The following is a set of figures ponderating the significant size of the reported devices.
Figure 20 contains the sizing of the microdistillation devices ruled by the heat pipe principle, and thus capillary force. As can be seen, the differences between them are remarkable. The length of the devices is in almost all studies below half a meter. Besides, in many of them the microchannel is configured as a serpentine, so the length is not taken as a straight line. The greatest differences are found in the channel's width and
depth. In capillary driven systems, significantly small values of 0.6 mm in width and 0.3 mm in depth are found in Lam’s work. The contactor thickness is dependent on the channel’s size. Mesh contactors are typically bigger, with values between 1 and 5 mm. As aforementioned, it is difficult to implement foreign wick materials in extremely reduced devices, and thus in such cases other microcontactors are used, namely arrays of micropillars, as in the work of Tonkovich (0.178 mm) and Lam (0.2 mm).

**Figure 21.** Sizing of the previously reported microdistillation systems driven by sweep gas. The graphs depict the size of the channel in three dimensions (length, width, depth) represented in millimetres.
Many of the represented channel sizes do not reach the ‘micro’ condition that they are supposed to accomplish. The channel's width and depth should be under that size barrier. The work of Tonkovich et al.(2007)[17] shows a remarkable size reduction, as well as the work of MacInnes et al. (2010)[4] and Zhang (2010)[3]. However, it was in the study of Lam et al. (2011) [18] who did put a great effort regarding the reduction of the size of the microdistillation device they proposed, whilst maintaining a satisfactory result. The dimensions of the actual microchannel were extremely reduced as no other author did before, thus reaching the micrometric scale in both width and depth of the microchannel, maintaining a comparable length to the other systems.

Figure 22. Diagram representation of the sizes of the devices proposed by MacInnes et al.(2010) [4] (a) driven by centrifugal force, the device proposed by Zhang et al.(2010) [3] (b) driven by Vacuum through a hydrophobic membrane and the proposal of Ziogas et al.(2011)[21] (c) taking advantage of both centrifugal force and capillarity.
2.1.3 Efficiency balancing

The knowledge of efficiencies has fundamental importance in the design and performance evaluation of distillation columns. Several alternatives are available to compose the efficiency model and methods to predict the overall efficiency of distillation columns, depending on the underlying features of the current column. Within this section, the efficiencies found within the performance of the aforementioned devices will be exposed and discussed. It must be taken into account, that the efficiency performed is dependent on the operating conditions and the inherently different characteristics of each study. However, in order to elaborate a balancing between them one of the most generalized ways to quantify the efficiency of the column will be used; the calculation of the Number of Theoretical Plates (NTP). Commonly known as column efficiency, the number of theoretical plates is a mathematical concept and there exist several methods through which its values can be calculated. Columns with high plate numbers are considered to be more efficient, that is, have higher column efficiency, than columns with a lower plate count. Another measure of the overall theoretical efficiency of a distillation column is the Height Equivalent to a Theoretical Plate, denoted as HETP. It is inversely proportional to the NTP of the system. It can be obtained by dividing the length of the column over the number of theoretical plates, and is usually reported in centimetres. The shorter each theoretical plate, the more plates are "contained" in any length of column. This, of course, translates to more plates per meter and higher column efficiency.

![Figure 23. Efficiency values represented in terms of Number of Theoretical Plates (NTP).](image-url)
The graphs presented above give an idea of the efficiency performed in every system. Glancing at the big picture, it can be seen that the systems driven by capillary force, on the left side of the diagrams, all show a high number of NTP and a low HETP, features which are typical of high efficiency distillation columns. Concerning the sweep gas systems, only a single stage, or even less, operation is achievable because of its underlying working performance. The vacuum system presented by Zhang shows a performance comparable to that offered by zero gravity capillary driven devices. From this data is extracted therefore, that the capillary driven systems have inherently higher operation efficiency than the rest of the presented methods.

**Figure 24.** Efficiency values represented in terms of Height Equivalent to a Theoretical Plate (HETP).

**Figure 23** depicts the NTP values performed by the apparatus hereby compared and **Figure 24** shows the performed HETP of the systems studied in literature.
2.1.4 Product’s purity balancing

One of the key factors when taking distillation under consideration, is the level of purity of the products, both distillate and bottom. The level of purity of the outlet products depends on the capacity of the distillation column to reach a certain composition of the withdrawn steams. It is strongly dependant on other factors, such as the feed composition and temperature, heating cooling duties, flow rates of the currents and the column’s reflux, as well as the column design. Therefore, at a certain column’s operation parameters, the goal is to achieve the maximum purity of the products maintaining a high level of efficiency. A study of the purity achieved in the previously proposed systems will provide another point of comparison between them, and will enable a further balancing in order to make a final statement for the most appropriate system proposal. In Figure 25 a representation of the purities obtained in previously developed systems is presented. In many of these works, several parametric studies were carried out in order to optimize the actual system. To construct the graph, the highest purity data obtained by the respective authors is used. The molar fraction in ‘y’ axe refers to the fraction of the more volatile component of each stream, named first in ‘x’ axe.

![Mole fraction (mvc)](image)

**Figure 25.** Plot of the level of the purities achieved by the previously studied microdistillation devices.
The graph explains the differences in the purity results obtained for a distillation performance. Seok and Hwang performed an almost complete separation of a Methanol:Water mixture. Tonkovich and Sundberg tested their systems by distilling Hexane:Cyclohexane, obtaining satisfactory results. Lam performed an Acetone:Ethanol distillation, obtaining an almost pure stream of Ethanol in the bottom of the device and a decent distillate purity. The works of Hartmann, Zhang and MacInnes performed a rather improvable degree of purity in the respective outlet streams, for mixtures of Methanol:Toluene, Methanol:Water and 2,2-dimethylbutane and 2-methyl-2-butene respectively.

2.2 Microheating systems balancing

2.2.1 Overall review

The use of microfluidic devices in chemical and biological synthesis is an area of highly increasing interest due to the characteristics offered by such systems. The research within this field has been wide during the last decades, and the literature regarding this theme is wide. However, as aforementioned in this work, a continuously challenging issue within this field is the ability to control and monitor temperature within the microchannel. An also interesting matter raised by the authors is the level of accuracy while stating that the temperature is homogeneous on a whole cavity. Most of the applications of these devices are strongly related to an accurate temperature control, and the difficulty encountered with many procedures for on-chip heating is a dilemma between accuracy and complexity. The level of integration of the heating system within the whole microdistillation apparatus is also a key issue to take into account and has been also a major challenging milestone for researchers. The key characteristics of a heating method, such as range of temperatures, ramp rate and accuracy, and the power needs are explained for each system and eventually categorized in the remarks section. Approaches to accurate temperature control within microfluidic systems have been varied, as well as the applications towards which the systems are intended to be used. Within this section, the aim is to point out the potentials of the most promising systems, even though initially they were designed for other purposes, of being incorporated in a microdistillation chip.
De Mello et al. (2004)[9] developed a microfluidic device incorporating working channels with a serpentine-like geometry and parallel channels in which ionic liquids are Joule heated with an ac current. Consequently, the internal temperature can be easily and directly controlled. Devices can be heated rapidly or slowly, depending on the applied voltage. The serpentine-like geometry was also studied by Lao et al. (2000)[22] with integrated platinum heaters and sensors. Based on the same heater geometry, Mavraki et al. (2011)[23] developed a simple microfluidic chip made of Pyralux™. Temperature control can be also performed using platinum thin layers as heaters as Dinca et al. (2009)[11] presented within a micro PCR reactor device using this type of heater. Figure 26 and Figure 27 are tables with the most significant microheating systems and their basic information.

<table>
<thead>
<tr>
<th>Author</th>
<th>Heating method</th>
<th>Heating element</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wu et al. (2009) [24]</td>
<td>Joule effect</td>
<td>Conductive silver microwire</td>
<td>PCR</td>
</tr>
</tbody>
</table>

Figure 26. Most significant heat exchange systems presented in literature ruled by the Joule heating effect.

Generally, it seems that there is currently no consensus on any given technique that would satisfy all the requirements specified by the complete range of applications; however each of the techniques described here has successfully demonstrated the integration of temperature control for specific applications.
Figure 27. Most significant heat exchange systems presented in literature driven by microwaves, infrared and chemical reaction.

When glancing at the tables, it is remarkable the dominance of literature concerning the Joule effect over other heating methods. During the last decades, scientists have regarded this heating method as a rapid and easy to control technology, and the different approaches are also numerous. Other systems with promising features have been also brought up, intended to overcome the difficulties when operating at microscale. However, the level of optimization is not as high as the encountered in Joule heating resistors, and more research and investment is needed to accurate such methods. The purpose of the majority of the systems proposed is aimed to control and optimize the increasingly important operation so called ‘polymerase chain reaction’, a method to duplicate DNA used mostly in biotechnology research. In spite of the disadvantage of the lack of background in such technologies, a weighting of their
potentials and limitations against the Joule heating will be accomplished within the following sections.

## 2.2.2 Temperature range balancing

One of the key factors of the performance of microdistillation, and distillation itself, is the temperature levels that are needed to accomplish satisfactory products. The device needs to be able to supply enough heat to the liquid feed for the operation to become successful. Therefore it can be stated that the temperature range that the heat source is capable to achieve is a critical parameter for the heating system design. Furthermore, a certain apparatus should not be intended to distillate only one type of mixture, with a certain boiling point, but a bundle of mixtures with different boiling points. For that reason, it is important for the heater to be capable to offer the widest possible temperature range. This feature will supply versatility and value to the system. Thus, the goal of the researchers is to accomplish the widest temperature range whilst maintaining an accurate temperature control. Figure 28 and Figure 29 depict the temperature range reported by the authors in their respective works.

<table>
<thead>
<tr>
<th>Author</th>
<th>Heating method</th>
<th>Range of temperatures [ °C ]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wu et al.(2009)[24]</td>
<td>Joule effect</td>
<td>20 / 96</td>
</tr>
<tr>
<td>De Mello et al.(2004)[9]</td>
<td>Joule effect</td>
<td>20 / 130</td>
</tr>
<tr>
<td>Lao et al.(2000)[22]</td>
<td>Joule effect</td>
<td>50 / 100</td>
</tr>
</tbody>
</table>

Figure 28. Temperature range reported by Joule effect heating systems presented in literature.
The bundle of temperatures achieved within the different works is varied. Higher temperatures are achieved by means of the Joule effect, and considerably wide ranges. The level of temperature achieved by microwaves is more varied, but generally lower than that encountered in Joule effect and with a smaller scope. Infrared technology has not yet achieved remarkable temperatures and more investigation in laser heating is needed. Eventually, glancing at the chemical reaction one can notice that it states potential features to become a feasible cooling system, demonstrated in [12] and optimized in [13].

2.2.3 Ramp rate and accuracy balancing

A fast and accurate temperature control is crucial for microdistillation to perform at its very maximum potential. Many applications, namely PCR, are strongly dependant on the temperature rate that the heater can supply in order to achieve an optimal performance. Accurate control is also vital because the more accurate the heating system, the more optimal might be the temperature profile along the microchannel. For that reason,
researchers have made big efforts in order to improve these features pointing towards a precise and fast temperature control. Figure 30 and 31 show the performance results obtained in other studies regarding the ramp rate, which are the increase of celsius grades per second, and for the accuracy, which is the minimum variance of temperature that the device allows to perform.

<table>
<thead>
<tr>
<th>Author</th>
<th>Ramp rate [ °C/s ]</th>
<th>Accuracy [ ± °C ]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wu et al.(2009)[24]</td>
<td>16</td>
<td>0,5</td>
</tr>
<tr>
<td>De Mello et al.(2004)[9]</td>
<td>0,1</td>
<td>0,2</td>
</tr>
<tr>
<td>Lao et al.(2000)[22]</td>
<td>15</td>
<td>1</td>
</tr>
<tr>
<td>Hsieh et al.(2008)[25]</td>
<td>15</td>
<td>0,2</td>
</tr>
<tr>
<td>Selva et al.(2010)[10]</td>
<td>20</td>
<td>0,6</td>
</tr>
</tbody>
</table>

**Figure 30.** Ramp rates and accuracy reported by Joule heating systems presented in literature.

<table>
<thead>
<tr>
<th>Author</th>
<th>Ramp rate [ °C/s ]</th>
<th>Accuracy [ ± °C ]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shah et al.(2010)[26]</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Kempitaya et al.(2009)[27]</td>
<td>7</td>
<td>Not stable</td>
</tr>
<tr>
<td>Shaw et al.(2010)[28]</td>
<td>65</td>
<td>0,1</td>
</tr>
<tr>
<td>Oda et al.(1998)[29]</td>
<td>16.000</td>
<td>1,4</td>
</tr>
<tr>
<td>Guijt et al.(2003)[12]</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>Maltezos et al.(2006)[13]</td>
<td>40</td>
<td>-</td>
</tr>
</tbody>
</table>

**Figure 31.** Ramp rates and accuracy reported by microwaves, infrared and chemical reaction heat exchange systems presented in literature.
2.2.4 Power needed balancing

Energy consumption is an important parameter when considering a system to operate at industrial scale. The energy costs should be kept as low as possible in order to increase the overall feasibility of the operation. That is why when designing a microdistillation system, the power needed to run the device needs to be taken into account. The following figures show an average power consumption of a certain device when operating at its optimal point.

<table>
<thead>
<tr>
<th>Author</th>
<th>Power consumption (watts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wu et al.(2009)[24]</td>
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<tr>
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<td>Lao et al.(2000)[22]</td>
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<td>Hsieh et al.(2008)[25]</td>
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<td>Kempitaya et al.(2009)[27]</td>
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<td>Shaw et al.(2010)[28]</td>
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<td>Oda et al.(1998)[29]</td>
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<td>Guijt et al.(2003)[12]</td>
<td>0</td>
</tr>
<tr>
<td>Maltezos et al.(2006)[13]</td>
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</table>

**Figure 32.** Average power consumption reported by Joule heating systems presented in literature.

**Figure 33.** Average power consumption reported by microwave, infrared and chemical reaction heating systems presented in literature.
3. Results and discussion

A deep study of the most significant previously developed microdistillation systems is developed within the past sections. In order to compare the features, advantages and weaknesses of them, a balancing of different key aspects in the operation's performance is carried out. A statement of which of the systems would have the most promising features based on experimental evidence, future possible applications, and greater advantages over the others, can be done.

On the other hand, a deep study of the most significant previously developed microheating systems is also developed within the past sections. In order to compare the features, advantages and weaknesses of them, a balancing of different key aspects in the heating/cooling performance is carried out. A seek of the most energy efficient, integrated and accurate device is the aim of the present section. A statement of which of the systems would have the most promising features based on experimental evidence, balancing the crucial aspects of a heat exchange device, can be done.

3.1 Microdistillation systems discussion

In the first instance, regarding the microdistillation systems, it is worth to mention that the bulk of literature is rather focused on studying and developing systems driven by capillary force, with no action of gravity. The fact that there exists more literature concerning capillary driven microdistillation is an advantage itself, given that the systems show a higher level of background and a greater optimization. Therefore, it could lead to an inherent improvement in the system’s performance.

Another key aspect regarding distillation in microfluidic environment is the dimension of the device. The sizes of the majority of them did not actually fall within the true definition of microscale systems (see Figure 20, and Figure 21). Over the years, the concern about the sizing reduction has increased and some of the researches did put an effort to reduce the size of their systems, such as of Tonkovich, MacInnes and Zhang, whom work shows a remarkable size reduction. However, it was not until the work of Lam who did put a great effort regarding the size reduction of the capillary driven
microdistillation device they proposed. The microscale condition was achieved in all dimensions of the working channel, whilst maintaining a satisfactory result. Regarding the efficiency of the systems, the improvement showed by the devices driven by capillary force is crystal clear (see Figure 23 and Figure 24). Such devices allow controlling the reflux by changing the outlet flow rates, and thus an optimal reflux can be established. Besides, sweep gas proposed configurations only allow for 1 single stage, due to its inherent performance condition.

When glancing at the level of purity achieved by the proposed systems, it is important to have one of the streams with a pure or almost pure composition of some of the agents of the initial mixture. That means that a pure or almost pure component would be obtained from the operation. The proposed microdistillation systems show a rather satisfactory level of the separation. All of them perform a high separation grade of the initial mixture and concentrated outlet streams are obtained (see Figure 25). However, the work of Seok and Hwang who obtained almost pure methanol and pure water is worth to remark. Also the device proposed by Lam offered an almost pure outlet stream. The device allowed obtaining almost pure ethanol in its bottom current.

Gathering all this information together, a statement can be done. Even though the difficulties encountered on integrating the heating and cooling systems to obtain a compact and accurate temperature control system, the design proposed by Lam shows a satisfactory performance in all the key aspects that determine the characteristics of a microdistillation system: the device is driven by capillary action, stated as the most efficient way to drive a microdistillation operation, and recognised as the most studied principle in literature. The high level of purity of the bottom stream is also satisfactory, obtaining an almost pure outlet product. The size reduction done pointing towards being the one and only device which is actually falling within the ‘micro’ condition is also worth to be taken into consideration.

For all those reasons, the design of device proposed within this work will be inspired in the design proposed by Lam. The extremely reduced dimensions of the channel, the optimization of a non-external microcontactor, namely the micropillars arrays sticked to the walls and the serpentine type channel in order to increase retention time, are firm
reasons to take this design as a basic idea to develop a novel microdistillation chip. However, the heat exchange system is not highly integrated, carried out by the heating of a ‘hot block’ placed at the evaporation part of the microchannel working as a reboiler. Within this system, the heat is not directly addressed to the working fluid inside the microchannel. The condensing is also carried out by the cooling of a ‘cold block’, not focusing only the interest part. Therefore, the energy consumption of the device is elevated, and the overall energy efficiency is reduced. The temperature measurement is performed by external sensors placed along the channel, in lieu of localised in situ temperature control, which would allow for a better continuous control. An innovative heat exchange system, intended to heat directly the working fluid to avoid energy losses as well as a more precise temperature control and integration aimed to achieve a better performed temperature profile will be investigated and designed within the next sections.

3.2 Microheating systems discussion

In the first instance, is worth to mention that the bulk of literature is rather focused on studying and developing systems ruled by the Joule effect (see Figure 26 and Figure 27). The fact that there exists more literature concerning this method is an advantage itself, given that the systems show a higher level of background and a greater optimization. Therefore, it could lead to an inherent improvement in the system’s overall performance. Most of the reported results in the literature involve either whole system heating or a heating zone of size much larger than the interest zone. Approaches to accurate temperature control within microfluidic systems have been proposed. De Mello et al. (2004)[9] demonstrated controlled ohmic heating of ionic liquids in a co-running channel that was external to the main fluidic system. However, precise control of Joule heating for large variations of temperatures remains difficult regarding the conductivity of ionic liquid proposed. Moreover, this method does not lead to uniformity due to boundary effects. Within the study of Hsieh et al. (2008)[25] the authors developed a novel architecture to generate a homogeneous temperature. However, a significant reduction of the interest area is needed.
Wider temperature ranges are encountered in Joule heating systems (see Figure 28 and Figure 29). That means that a certain device offer the chance to perform at a higher scope of temperatures. The work of De Mello et al. (2004)[9] heating by Joule effect of ionic liquids presents the widest temperature range observed, but still the other systems also present a significant performance, such as the device presented by Selva et al. (2010)[10]. The range showed in microwave, laser and chemical reaction heating methods are acceptable for certain applications, but the use of such devices is not yet applicable neither to a wide scope of operations nor to a wide temperature range.

When glancing at the ramp rate and accuracy that the systems offer, the results are extensively varied (see Figure 30 and Figure 31). However, all the results are highly satisfactory, given the inherent and novel advantages that these technologies present. Systems ruled by Joule effect present more than acceptable ramp rates with a precise accuracy. Microwave and chemical reaction heating also present satisfactory ramp rates, although some of them are still difficult to precisely determine an almost exact temperature. The power consumption is significantly lower than those encountered in traditional systems (see Figure 32 and Figure 33). Besides, given the underlying nature of some of them, there is no electrical power needed to operate them. However, other energy supplies are needed, such as chemical agents.

3.3 Microdistillation system with integrated micro heat exchange proposal

The novel propose of a microdistillation system is presented in Figure 35. The microdistillation chip consists of a serpentine microchannel 600 mm in diameter and 40cm in length. The channel shows a serpentine-like shape in order to obtain a greater residence time and the feed is located at the middle of the channel. The patterned wafers are etched by deep reactive ion etching. The etched depth of the microchannels is measured by a surface profiler while the microstructures inside the microchannel are examined by an optical microscope. The etched chip is bonded anodically with a glass plate with pre-drilled holes. NanoportTM fittings are attached to the glass surface for connection of fluidic conduits. The microchannel is endorsed on-chip, with three inlet/outlet points; one for the feed, and one for the distillate and bottom products. A data sheet of the main characteristics of the hereby designed system is presented in Figure 34.
### SPECIFICATIONS OF THE DEVICE

<table>
<thead>
<tr>
<th>PRINCIPLE</th>
<th>Capillary driven (Heat Pipe Principle)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MATERIAL OF CONSTRUCTION</td>
<td>Silicon-glass</td>
</tr>
<tr>
<td>PHASE CONTACTOR</td>
<td>20µm diameter x 300µm high micropillars</td>
</tr>
<tr>
<td>CHANNEL LENGTH</td>
<td>400 mm (Serpentine)</td>
</tr>
<tr>
<td>CHANNEL WIDTH</td>
<td>600 µm</td>
</tr>
<tr>
<td>CHANNEL DEPTH</td>
<td>300 µm</td>
</tr>
<tr>
<td>HEATING SOURCE</td>
<td>Chromium+Gold microresistor</td>
</tr>
<tr>
<td>COOLING SOURCE</td>
<td>Water bath</td>
</tr>
<tr>
<td>TEMPERATURE CONTROLLER</td>
<td>PC with LABVIEW (PDI)</td>
</tr>
</tbody>
</table>

**Figure 34.** Data sheet of the major characteristics encompassed by the proposed microchip. Those are the defining features which the device basically relies on.

### 3.4 Design approach

#### 3.4.1 Microdistillation system with a localized heat transfer system

In order to provide a concrete understanding of the operating principle and to comprehend the basic characteristics of the hereby designed microdistillation device, the following set of designs and outlines has been developed. It has been elaborated with the software *Autodesk Inventor 3D CAD*, both 3D and 2D views, and *KeyShot* to elaborate the renders.
Figure 35. Design of the microdistillation chip presented alongside with its different constructive parts.

Figure 36. Frontal view of the chip with the corresponding size of each part in millimetres.
The dimensions of the capillary driven microchip presented in this work are further decreased and the microchannel is 600 μm in width, 300 μm in depth and 400 mm in length in a serpentine shape. The separation performance is affected by the heating and cooling temperatures, due to the various effects that the temperature profile has on microdistillation, not only on VLE but also on surface tension and thus capillary forces, and thereby liquid flow. Given that in a true microscale distillation system the incorporation of a foreign mesh or wick material in order to work as the capillarity media is difficult, it is also necessary to overcome the challenge of incorporating a novel gas-liquid contacting medium in order to stabilise the gas-liquid interface. In the
presented device, the capillary action for liquid movement is induced by arrays of fabricated micropillars stucked along the walls of the microchannel, whilst the vapour from evaporation of the liquid flows counter-currently in the center of the microchannel. Both liquid feed and liquid reflux flow along the micropillars regions towards the hot end. Therefore, these micropillars work as the driving media to run the condensed liquid from the cold end back again to the hot end by means of capillary action, as well as the contactor where mass exchange occur between gas and liquid phase. The micropillars supply a feasible built-in solution to replace the foreign wick material for conducting liquid flow in the microdistillation device.

Controlling temperature in a lab-on-a-chip device, especially locally, constitutes a major constraint for chemical and biochemical applications. Within this work, a method to control heat using a heating resistance whose size is comparable to that of the cavity where it operates is presented. The heating will be based on Joule effect heating of a microresistor placed inside the microchannel, and the cooling will be based on water bath of the condensing zone of the chip. The process will be accurately controlled by a PC with the software LABVIEW, which contains a PDI controller, receiving information from sensors and giving orders to actuators in order to control temperature.

3.4.2 Contacting interface - Micropillars

In a distillation process, mass transfer between a liquid and a vapour phase is required. Inside a microdistillation system, a liquid film needs to be maintained in order to allow mass exchange to occur between vapour and liquid phases. When the operation is brought to microscale, the insertion of foreign wick materials becomes a significantly challenging task. A mesh or other wick contacting materials are not fitting inside such a small channel, and therefore the capillary action that they are intended to carry out is not actually possible. For that reason, given that the hereby presented microchip is significantly small, reaching the microscale condition, high aspect-ratio micropillars arrays are built on the wall of the microchannel to work as the phase-contactor. Thereby, the insertion of a foreign material is avoided. A continuous liquid–vapour
interface is formed at the pillars, thus allowing mass exchange between vapour and liquid during the distillation.

The configuration of the micropillars arrays stucked to the walls of the microchannel follows the pattern as shown in Figure 40. The liquid forms a thin film along the micropillars arrays when flowing back to the hot end by means of capillary action. The micropillars confine the liquid path without liquid flooding into the microchannel due to the effect of capillarity, thereby stabilising the film and forming the interface between gas and vapour phase, thus letting mass exchange occur.

**Figure 40.** Configuration of the micropillars structured along the microchannel wall of the microdistillation system device. The structures consist of high aspect-ratio micropillars (20 μm in diameter and 300 μm in height).
3.4.3 Heat exchange system

In order to carry out the heat exchange at the hot end of the device, a heating microresistor is spin-coated inside the heating area. The microresistor is endorsed inside the microchannel by evaporating an alloy of chromium and gold. The etching process comprises two steps: the first generates a connection between the heating wires composing the resistor and the power supply and the second step etches the wires of the resistor. This method provides a direct heating of the mixture, and furthermore, by changing the supplied voltage, the resistor releases more or less quantity of heat to the working mixture, allowing an accurate temperature control inside the channel. A micro thermal sensor is incorporated next to the microchannel in order to report the feedback to the CPU controlling the process. For the cooling operation, a water stream flowing next to the channel is aimed to condense the vapour at the cold end of the chip. The temperature control is equally carried out by the PDI control system receiving feedback from the micro thermal sensor placed and calibrated, next to the working channel. Thus, the system increases or decreases the water flow depending on the temperature needs.

A novel heating/cooling system is presented hereby. As aforementioned within this work, the temperature control of microdistillation chips has been a major challenge to overcome during decades. Researchers have made efforts to overcome the difficulties presented at such small scale. With the years of research, as well as the technologic improvement of the systems, several possibilities have been breaking through. Relying on the extensive review done in this work, and the balancing between the state-of-the-art of this specific field, an idea of a novel propose to carry out microdistillation has been brought out. Figure 42 is a representation of the operating heat control system of the microdistillation device that has been hereby designed.

The figure is a representation of how the temperature control is carried out in the system. At the hot end, on the left side of the chip, the microresistor formed by an alloy of chromium and gold is placed inside the working channel. The microheater is connected to a DC-Power supply at both ends aimed to apply the current which will provoke the Joule effect. When a current passes through the wires of the microheater, it will release a certain amount of heat, depending on the applied voltage, to the working fluid inside the microchannel.
Just next to such channel, a narrow wire is acting as a thermal sensor. Its resistance is variable with temperature. When an electrical current is passed through the microheater, the temperature rise affects the resistance of the nearby temperature sensor. This resistance variation can be precisely calibrated to determine the corresponding temperature inside the working channel. The microthermal sensor is connected to a multimeter, which will obtain a lecture of the resistance of the sensor. This value is reported to the PDI controller, and depending on the resistance value received, as well as the desired values that the user has previously established, it will give the order to the DC-Power supplier to increase, decrease or maintain the voltage applied to the microheater. This leads to a reciprocal system, meaning that the voltage
applied, and hence the temperature of the mixture, will always be under continuous accurate control. An increased view of the heating part of the system is showed in Figure 42.

![Figure 42](image)

**Figure 42.** Enlarged view of the heating zone of the microchip. The microheater (red) is placed inside the working channel (deep grey). The microthermal sensor (gold) is placed right next to the working channel.

Regarding the cooling system a microthermal sensor is also placed just next to the working channel in order to supply a resistance lecture for the multimeter. The resistance of the wires is extremely sensitive to the temperature, and therefore with a proper calibration a precise determination of the temperature of the working mixture can be done. The multimeter reports the resistance value to the PDI controller and depending on the lecture, throughout a DAQ card it gives the order to a solenoid valve to be at opened or closed position. This solenoid valve allows or restricts the cold water flow from a deposit. Given that the user has previously established the desired values of temperature on the PDI, when the temperature needs to be decreased, a signal will be sent to the valve and it will open allowing thus the flow and the cooling of the working mixture. If the mixture is too cold and needs to be increased, the order will be the opposite, and the solenoid valve will close and avoid the water flow. An increased view of the cooling area is shown in Figure 43.
The level of integration of this system is significant, taking into account that traditionally, the reboiler and condenser are outside the column walls, and with this design both of them are integrated on the chip. The on-chip microheater is capable to offer a range temperature range between 25°C and 96°C, which is appropriate to carry out almost all sorts of distillation. Besides, a great flexibility is also supplied, given that the certain input temperature value settled to the PDI can be chosen by the user. A power supply of 1.7 watts is needed in order to operate the microheater at its optimal conditions. A stream of cold flowing water is needed for the cooling operation. The temperature of the water as well as the flow can be accurately calibrated in order to condense the vapour at the cold end of the device. It is duty of a further work to perform a parametric study in order to determine the optimal balancing between water flow and its temperature. A similar system using compressed air as the cooling source was previously studied in literature but, given the higher cooling possibilities of water over air, improved results might be encountered with the system presented hereby. The throughput range of the device is between 0.05ml/h and 0.3ml/h for the feed, distillate and bottom product flow rates. The temperature ramp rate for the microheater is of 20°C/s with an accuracy of ±0.6°C. The temperature accuracy and ramp rate could be further improved within the novel control system.

**Figure 43.** Enlarged view of the cooling zone of the microchip. The cooling channels containing water (blue) condense the vapour conducted in the working channel (deep grey). The microthermal sensor (gold) is placed right next to the working channel.
3.5 Numerical approach

A study of the system’s theoretical efficiency will be carried out within this section in order to provide a better understanding of the system. Lam et al. (2011) [30] performed a parametric study on the separation of an acetone–ethanol mixture using a micro-fabricated distillation chip with a similar shape of the device presented in this work. The aim of the study was to identify the key parameters for optimal design and operation of the microdistillation device by varying the relevant operating parameters, including the temperatures of the heating and cooling regions, the flow rate and composition of the feed solution and the flow rate of the bottom stream. An extensive experimental analysis would be necessary in order to obtain a precise report of the system’s behaviour. However, in order to obtain a proper balancing of the hereby presented system, and given the absence of the manufactured device, a study of the theoretical efficiency is done under the same operating conditions as those encountered in previous works.

The studied mixture of 50:50 mol% acetone-ethanol has a set of underlying thermodynamic properties which will determine the whole separation behaviour.

3.5.1 Vapour-Liquid Equilibrium

As the desired levels of purity achieved by other works in literature are known, both for distillate and bottom streams, the number of theoretical plates (NTP) and the height equivalent of a theoretical plate (HETP) needed by the device presented hereby in order to achieve such compositions can be studied and balanced. By doing so, a statement of which systems performs a better theoretical efficiency can be done. In order to do so, the first step to take is to compute the vapour-liquid equilibrium (VLE) data of the actual mixture; 50:50 mol% acetone-ethanol. In this case, the data is extracted from ‘ASPEN +’, a chemical engineering computer based software, which has a database with the thermodynamic properties of the actual mixture. The first step to calculate such data is plotting the boiling point diagram, as shown in Figure 44.
Figure 44. Boiling point diagram for the liquid mixture acetone-ethanol computed with ‘ASPEN +’. The temperature is varying at a fixed pressure of 1 atm.

The equilibrium compositions of the components of the liquid mixture vary with temperature at a fixed pressure. The upper curve in the diagram is called the dew-point curve, which represents the temperature at which the saturated vapor starts to condense, while the lower one is called the bubble-point curve, which stands for the temperature at which the liquid starts to boil. The region above the dew-point curve shows the equilibrium composition of the superheated vapor while the region below the bubble-point curve shows the equilibrium composition of the sub-cooled liquid. The boiling point of the more volatile component (mvc) is that at which the mole fraction of such component is 1. The boiling point of the other component is that at which the mole fraction of the mvc is 0. In the mixture of acetone-ethanol, the mvc is acetone, which has a boiling point of 56° C when it is pure, whilst the boiling point of pure ethanol ascends to 78,4° C. Once the boiling diagram is performed, it is possible to extract the vapour and liquid mole fraction of acetone and to set the equilibrium table, which will lead to the equilibrium curve. Figure 45 is a table with the extracted values of molar fraction of liquid and vapour of acetone, the more volatile component (mvc) at a fixed pressure (P) of 1 atm.
**Figure 45.** Data for the VLE of an acetone-ethanol mixture at a fixed pressure of 1 atm. Computed with ‘ASPEN+’.

Once the VLE data of the mixture is available, the graph of the equilibrium diagram can be plotted. The equilibrium line and describes the compositions of the liquid and vapour in equilibrium at some fixed pressure. As can be seen in Figure 46, the slope of the curve is not very shaped and the actual binary mixture is not far from ideality, and therefore it would be relatively easy to separate.

**Figure 46.** VLE for the binary mixture of acetone-ethanol at a pressure of 1 atm.

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<tr>
<th>Liquid Mole Fraction - Acetone (x)</th>
<th>Vapor Mole Fraction - Acetone (y)</th>
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<table>
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<th>Vapor Mole Fraction – Acetone (y)</th>
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</tbody>
</table>
3.5.2 Efficiency: McCabe – Thiele

Once the vapour-liquid equilibrium characteristics (indicated by the shape of the equilibrium curve) of the mixture are available, it is possible to determine the number of stages, and hence the number of trays required for the separation. This is illustrated clearly by applying the McCabe-Thiele method to the separation of a binary mixture. This method is based on a graphic approach, and uses the equilibrium line to determine the theoretical number of stages required to carry out the separation of the binary mixture. The theoretical study of the separation of a 50 mol% acetone–ethanol mixture into 80 mol% acetone in the distillate and 2 mol% acetone in the bottom stream is computed and the theoretical efficiency of the designed device is obtained.

The following is the sequence of the steps taken to compute the TP and HETP of the actual system.

1. Location of the significant compositions

With a given purity for the distillate (\( x_D = 0.8 \)) and for the bottom product (\( x_B = 0.02 \)) the limits of the system are settled up in the graph previously found on the vapour-liquid equilibrium diagram. The feed composition (\( x_F = 0.5 \)) is also known, and thus, the feed line is also drawed.
2. Construction of the operating lines

Once the products and feed compositions are drawn, the next step to take is to represent the operating lines. The rectifying section operating line (ROL) in blue, the feed line (also known as the q-line) in yellow, and the stripping section operating line (SOL) in green. The ROL starts at the distillate point \([x_D, x_D]\) and points towards the point \([0, \frac{x_D}{Re+1}]\). Assuming a standard reflux ratio of 1.5 the obtained point is \([0, 0.32]\). The ‘q’ line, since the feed is a saturated liquid, is represented as a straight line following direction upwards. The SOL is drawn from the bottom product point \([x_B, x_B]\) until the intersection between the ROL and the ‘q’ line.

![Figure 48. Construction of the operating lines.](image)

3. Drawing of the plates

The last step to take is the drawing of the plates in order to achieve the separation of the actual mixture with the given specifications. It will be carried out by drawing a ‘stairs’ shaped figure. Each step is standing for a theoretical plate of the column. Plates are added from the distillate product to the bottom product, touching the VLE curve and the ROL and SOL lines. The number of needed steps represents the number of theoretical stages that the column will need to operate. In this situation, 6.75 theoretical plates are needed.
Note that in a traditional distillation column, a plate is counted as the reboiler. In our microdistillation chip, the reboiler is integrated within the device, and therefore it is also counted as a working plate to carry out the separation.

Once the number of theoretical plates (TP) is known, the height equivalent of a theoretical plate can be computed. This will be done by the relation:

$$\text{HETP} = \frac{\text{Column's length}}{\text{Theoretical plates}} = \frac{40 \text{ cm}}{6.75} = 5.92 \text{ cm}$$

Thus, the overall efficiency of the column is now available:

$$TP = 6.75$$

$$\text{HETP} = 5.92 \text{ cm}$$

Given the remarkable size reduction, such efficiency results are far more satisfactory than those of a traditional scale column, who's HETP typical values are around 30cm.
3.6 Experimental set-up operating the device

The configuration of the microdistillation chip with an integrated heat transfer system presented in this work has been extensively described within the latter sections. It describes a novel method to conduct a separation of a mixture by means of difference on the boiling points of the components, a distillation process. However, the microchip is not capable to work on its own; a complete set-up is needed in order to operate the device in a continuous regime at laboratory scale. Figure 50 is a scheme of the elements encompassed in an experimental set-up aimed to run the microdistillation chip.

The figure describes the whole set-up of elements in order to run the proposed microdistillation chip. Given that the device operates without gravitational force, the inlet and outlet are driven by a set of syringe pumps (1, 3, 19) connected to the ports of the device (2, 4, 18). This type of pumps allows setting the significantly low flows that are operating on the system, a range between 0.05ml/h and 0.3ml/h for the feed, distillate and bottom product flow rates. An accurate establishment of the flow rates can be conducted by means of the digital input that the user can introduce to each pump separately, as well as choosing the mode of the pump, either pumping or withdrawal, for the feed or the bottoms product and the distillate product, respectively. The two narrow wires working as the microthermal sensors, one on the hot (5) and the other on the cold end (15), give feedback in terms of ohmic resistance in order to control the temperature inside the working channel. Each of them is connected to a multimeter (6, 17), which makes the lecture of the resistance. These multimeters report directly to a PC (10) with an integrated PDI controller, i.e. LABVIEW software. Within this software, the computer is able to give the orders to the DC-Power supply (9) to increase or decrease the voltage applied and therefore increase or decrease the intensity of the joule effect on the microheater (7) for the heating zone, and for the cooling zone, the DAQ (11) card gives the order to a solenoid valve incorporated to a cold water reservoir (12) to open or close the flow. The water flows from the reservoir through the connected microchannels (13, 14, 16) whilst maintaining contact with the working channel. Thereby the cooling can be controlled by changing the water flow, as well as by changing the temperature of the cold water.
Figure 50. Experimental set-up operating the device. The configuration describes the operating principle of the system running the device. For further applications, it could be incorporated in a complete microchemical plant.
All these operations are dependent on the inputs received and read from the microthermal sensors, and on the indications that the user has previously established to the PDI software. By doing so, the heating and cooling temperatures are continuously and accurately controlled, and the product’s flow rate can be precisely established.

### 3.7 Prototype of the microdistillation device

In order to provide a more precise idea of the concept of the hereby proposed microdistillation apparatus, a prototype has been build. The design elaborated with the software *Auodesk Inventor 3D CAD* has been introduced to a 3D printing machine. The result is a prototype of the device made of plastic, which is aimed to proportionate a conceptual idea of the described microdistillation system. It is considered to be a support to achieve a better understanding of the configuration of the device, alongside with the detailed explanation carried out within the past sections. **Figure 51** shows the hereby mentioned prototype.

**Figure 51.** Photography of the build-up prototype aimed to provide a conceptual approach of the microdistillation device.
4. Conclusions and remarks

After the deep state-of-the-art review that has been developed within this work, the design of a novel microdistillation chip with an integrated and localized heat transfer system has been brought up. Microscale devices offer the possibility of intensifying separation operations by providing high ratios of contact areas to volume, high driving force gradients and considerably short transport distances. One of the major limitations to overcome is the heat loss that occurs within microscale devices due to the high surface to volume ratio. It is therefore essential to ensure good thermal control in a lab-on-a-chip device in order to precisely achieve a certain desired temperature profile. In order to do so, the most significant microdistillation and microheating methods have been studied and balanced, going through the main features that define the performance of a distillation operation.

One of the major challenges to overcome when operating a distillation at microscale is the increased heat-losses encountered due to the high surface-to-volume ratio of the channel as well as the temperature control inside the channel. In order to ensure a steady and efficient operation of microdistillation systems, it is of vital importance to have a precise control of the temperature profile described along the channel. The heating systems used thus far on microdistillation are not different than those used at traditional scale, namely a hot end and a cold end working as reboiler and condenser, respectively. Conventional heating and cooling methods offer a poor performance when operating at microscale. Given that the temperature control, when operating at microscale, has not yet an optimal solution, the study of the feasibility of novel integrated and localized heat exchange method has been of major importance within this work. The studied systems might not be intended to work as a reboiler or a condenser of a distillation column, but by adapting them to such purpose, a novel idea for a heat exchanger in a microdistillation chip has been brought up. Another key aspect that has been taken under significant consideration is the size of the device. In order to take advantage of the multiple applications that microdistillation technology offers, the size of the microchip needs to be reduced to a significantly small scale. The systems developed thus far are not actually falling within the limits of ‘micro’ system. That is why
big effort has been done in order to fulfil the sizing conditions of a truly microdistillation system, whilst maintaining a satisfactory result.

The system presented hereby is a novel idea in order to carry out microdistillation at an extremely reduced size with an accurate temperature control. It is based on scientific evidence and the study balancing between systems and designs previously brought up. The device is capillary driven with absence of gravity, which has been proven to be the most efficient driving force and it is indeed falling within the ‘micro’ condition. An accurate temperature control system has been also designed, with an integrated heating system relying on Joule effect. A cooling system based on cold water to condense the hot vapor at the cold end of the device has been chosen as the most appropriate system. Both of them are accurately controlled by a PDI controlling system, equipped with a set of syringe pumps, multimeters, power supply to heat and cold water to cool. The system is intended to overcome the difficulties encountered on other systems, and therefore allow an accurate and energy-efficient heat exchange within the device. The microchannel is 600 μm in width, 300 μm in depth and 400 mm in length in a serpentine shape, with inlet/outlet ports at the end, and the walls are covered by arrays of micropillars working as the phase contacting and the liquid conductor.

As the basic mechanisms and behaviours of microdistillation techniques become increasingly clear, tremendous opportunities exist for integrating micro-distillation devices with other unit operations in order to realize complex microchemical systems. This work aims to contribute on taking microdistillation technology a step further, by providing a novel proposition of the design of a device intended to carry out the operation. A further work to take under consideration would be to build a prototype of the device, and to perform a parametric study in order to optimize its operation.
5. Bibliography

5.1 Cited literature


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5.2 Figures

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