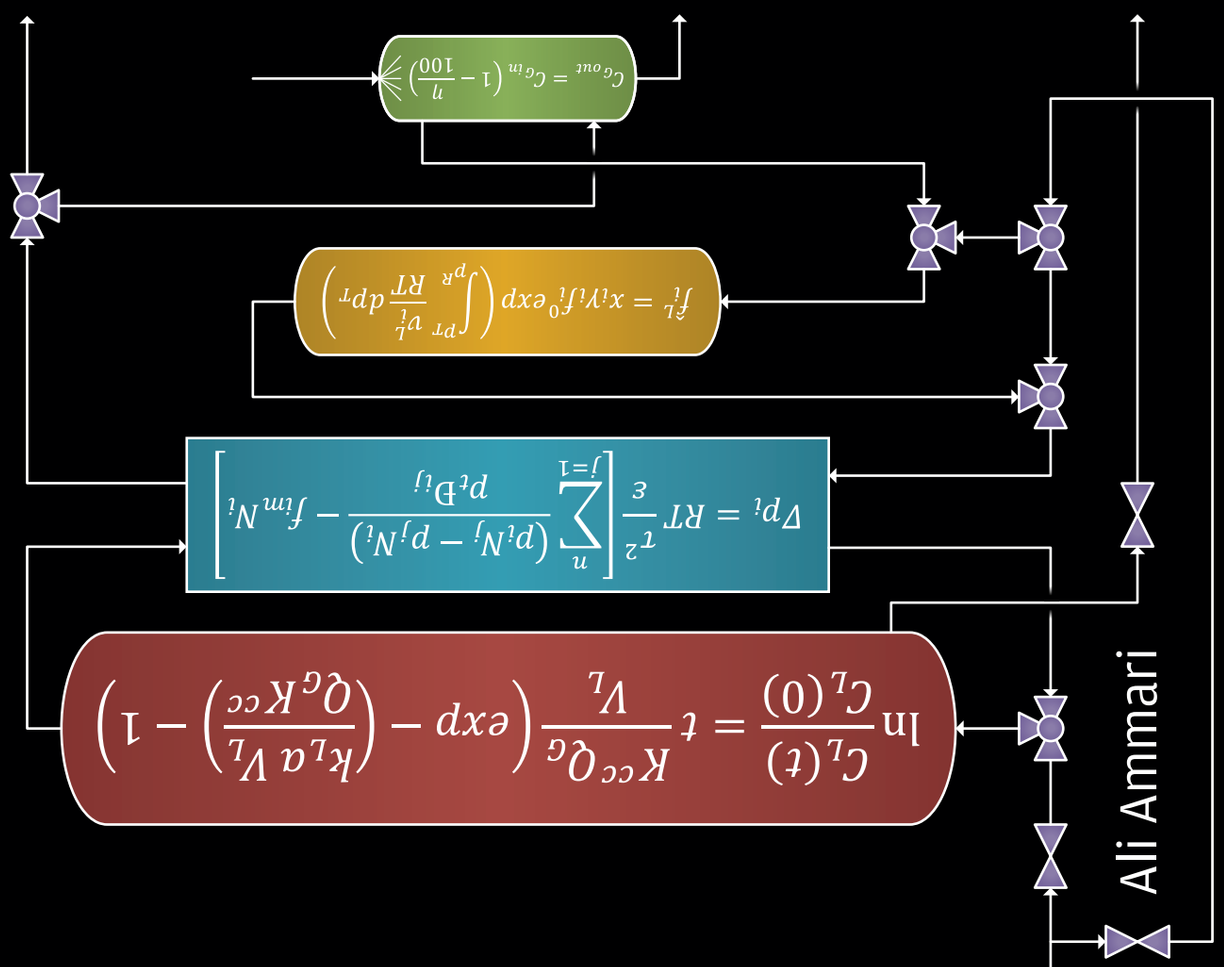
Separation Kinetics and Phase Behaviour of Volatile Flavour Active Compounds in Aqueous Food Streams



Separation Kinetics and Phase Behaviour of Volatile Flavour Active Compounds in Aqueous Food Streams

Ali Ammari

Propositions

1. To model behaviour of volatile flavour compounds in aqueous systems, unsymmetric standard state convention needs to be applied. (this thesis)
2. The challenge in the separation of flavour compounds is their physiochemical similarity, not their interactions. (this thesis)
3. Even chemistry is physics.
4. Scientific communication should be simple but not simplistic.
5. Science, art and literature are the human response to the world's imperfection.
6. If you are not able to write down what you argue, remain silent.
7. Doing a PhD is like a pregnancy: The first part, full of pleasure; the last push full of pain.

Propositions belonging to the thesis, entitled
Separation Kinetics and Phase Behaviour of Volatile Flavour Active Compounds in Aqueous Food Streams
Ali Ammari
Wageningen, 01 April 2020

Separation Kinetics and Phase Behaviour of Volatile Flavour Active Compounds in Aqueous Food Streams

ALI AMMARI

Thesis committee
Promotors
Prof. Dr CGPH (Karin) Schroen
Personal chair at the Laboratory of Food Process Engineering
Wageningen University and Research

Prof. Dr Remko Boom
Professor of Food Process Engineering
Wageningen University and Research

Other members:
Prof. Dr Michel Eppink, Wageningen University and Research
Dr Norbert Kuipers, Wageningen University and Research
Dr Marcel Ottens, Delft University of Technology
Dr Reinoud Noordman, Pentair, Enschede

This research was conducted under the auspices of the Graduate School VLAG (Advanced Studies in Food Technology, Agrobiotechnology, Nutrition and Health Sciences)

Separation Kinetics and Phase Behaviour of Volatile Flavour Active Compounds in Aqueous Food Streams

ALI AMMARI

Thesis
submitted in fulfilment of the requirements for the degree of doctor
at Wageningen University
by the authority of the Rector Magnificus,
Prof. Dr A.P. Mol,
in the presence of the
Thesis Committee appointed by the Academic Board
to be defended in public
on Wednesday 1 April 2020
at 11 a.m. in the Aula.

Ali Ammari
Separation Kinetics and Phase Behaviour of Volatile Flavour Active Compounds in Aqueous Food Streams
119 pages
PhD thesis, Wageningen University, Wageningen, the Netherlands (2020)
With references, with summary in English
ISBN: 978-94-6395-351-1
DOI: https://doi.org/10.18174/517903

Preface

After a successful appearance in biotechnology, pharmaceuticals, electronic device fabrication and environmental engineering, chemical engineers are pushing boundaries of food processing technologies in response to the global challenges in food safety and food security. Unlike classical careers in chemical, oil/gas and energy industries, which are fairly well-structured and well-developed, the presence of components with characteristics yet to be discovered in multiphase/component systems are challenges that chemical engineers are facing both in theory and practice.

The Wageningen University and Research as one of the leading institute in life science in the world have been one of the pioneers in exploring and introducing innovative solutions in food sciences. At the Food Processing Engineering (FPE) group, I had this privilege to employ my conventional engineering knowledge in comprehending and controlling volatile flavours and consequently manipulating their presence in complex aqueous systems. This report is the fruit of my service as a PhD candidate in that group.

This text is composed of six chapters. You will read a general introduction about this project, methodology and approach in Chapter I and the current status of what has been done by other scientists about flavour-food matrix interactions in Chapter II. The effect of ethanol on flavour active compounds are addressed in Chapter III and Chapter IV will offer a realistic case for flavour stripping from a beer model solution. First four chapters cover our comprehension and controlling part of this project. For manipulation and design, we discuss a conceptual investigation that will explore whether frictional diffusion method (FricDiff) can target a single volatile flavour or not in Chapter V. And finally, chapter VI will wrap up and highlights findings of this work.

Even though I have always been having my doubt in defining success let alone celebrating it, one thing is certain and that is the end of this chapter of my academic life. This could not be possible without the leadership of Professor Dr Karin Schroen whom I had the honour of working with. I extend my sincere gratitude to her for her kindness, patience and the trust she put in me allowing me to direct this project independently.

In this journey, I also saw people with brilliant minds, beautiful hearts, strong and respectful personalities. Lu Zhang, Sicong Zhu, Qinhui Xing, Qierui Zhang, Peijun Peng, Farahnaz Pashaei Kamali, Kambiz Farbod, Farnoosh Fasaei, Anja Schröder, Alime Cengiz, Patricia Duque Estrada, Jan-Eise Vuist, Dimitris Karefyllakis, Eline Both, Mauricio Alejandro Opazo Navarrete, Anne Walther, Linda Veldhuizen, Davide Papasidero, Lucille Chretien and Kay Moisan; you all are part

my life. I will always be thinking about you and I will hold your memories dear even if I do not see you again. I also would like to express my thanks to all support staff of the Food Process Engineering group (FPE) especially Marjan de Lange, Jarno Gieteling, Wouter de Groot, Maurice Strubel and Peter de Gijsel from food chemistry group (FCH).

Last but not least, dear Jos Sewalt, your unconditional support with word and deed has always been beyond your responsibilities. Words are too humble to show my respect towards your gracious and generous personality; so, the only thing that I can say is the biggest "thank you" I have ever told anybody during this project.

Ali

Wageningen

2020-01-01

Contents

Chapter I

Introduction

We are nowadays no longer surprised about the number of processed food products that we can put in our shopping baskets. Healthier foods that are developed as a result of legislation (e.g. alcohol-free beer in countries where alcohol is forbidden), or a desire for functional foods (such as energy drinks, meat analogues), and products for another experience (as with flavoured wine gums, ciders, etc.) are all a result of food processing. Flavours play a pivotal role in any food product. The amount and rate of release of flavours is a big factor in the sensory experience of the consumer, but it is highly dependent on the interaction with the food matrix, whether solid or fluid. Therefore, in most cases, the flavour balance has to be adapted, when a change is made to the food matrix. Thus, there are considerable interest methods to adapt the flavour composition using mild methods (see also review in chapter II for more information).

This thesis focusses on beverages, which are aqueous solutions of proteins, electrolytes and carbohydrates. In the case of alcoholic beverages such as beer, the presence of ethanol also needs to be taken into account. In general, flavours can interact with proteins, carbohydrates, while the presence of ethanol will change the solvent quality and enhance the solubility of flavours. This chapter introduces the challenges, the current knowledge, the research aim and the hypotheses on which we based the experiments reported in this thesis. The results are relevant not just for alcoholic beverages, but will also help develop processes for alcohol-free beer.

1.1 Beer production

Brewing is an ancient method to preserve food and has been performed since around the 6th millennium BC. There is archaeological evidence of beer brewing in the ancient Egyptian and Mesopotamian cultures. Water was generally not safe to drink, but the beer was safe because of

the heating step and production of antimicrobial ethanol in the brewing process. For the same reason, the right to brew beer was an important city right for medieval cities in Europe.

For brewing beer, mostly malted barley is converted into a wort, a liquid that is high in sugars and polysaccharides that are fermented by yeast resulting in alcohol and flavour. Although currently home brewing is gaining more interest, and the number of micro-breweries is rising, most of the beer is produced by large brewers or chains thereof. Large scale brewers produce international brands, that should comply with strict internal standards. Slight variations in flavour profile from one batch to another cannot be accepted and should be corrected. For small breweries, it is a much greater challenge to retain constant product quality. While for these small-scale breweries, fluctuations of flavour profile are more acceptable, also here, a relatively simple method to correct a flavour profile could be of benefit.

1.2 Flavours in beer

Flavour compounds present volatile and non-volatile forms. In beer, non-volatile compounds, such as polyphenols contribute to haze and astringent mouthfeel and hop-derived iso-α-acids to bitter flavour [1]. There are various volatile flavour compounds that they have a direct contribution to the flavour profile. On the other hand, various flavours are below the sensory level of human although their additive and synergistic sensory effects cannot be ruled out [2].

In general, the flavours originate from the malt and hops, some from heating, i.e., roasting of the malt and boiling of the wort. A large part of the flavours is the result of the secondary metabolism of the yeast using fermentation. Flavours may also result from the growth of contaminating micro-organisms (for example lactic acid bacteria). Finally, also storage, the influence of exposure to light and oxygen influence the overall ultimate flavour profile [3], [4]. Table 1.1 gives a very schematic overview of flavours prevalent in beers.

Table 1.1 Typical flavour compounds in beers [5]

Group	Chemical Name	Typical Level [mg/L]	Flavour Threshold [mg/L]	Flavour Description
Esters	Ethyl Acetate	10-60	30	Solvent-like, sweet
	Isoamyl Acetate	0.5-5.0	1	Banana, ester, solvent
	Ethyl Hexanoate	0.1-0.5	0.2	Apple, fruity, sweet
	Ethyl Octanoate	0.1-1.5	0.5	Apple, tropical fruit, sweet
	2-Phenylethyl Acetate	0.05-2.0	3.0	Roses, honey, apple, sweet
	Ethyl Nicotinate	1.0-1.5	2	Grainy, perfume
Alcohols	Methanol	0.5-3.0	10 000	Alcohol, solvent
	Ethanol	20 000-80 000	14 000	Alcohol, strong
	1-Propanol	3-16	700	Alcoholic
	2-Propanol	3-6	1500	Alcoholic
	2-Methylbutanol	8-30	65	Alcoholic, vinous, banana
	3-Methylbutanol	30-70	70	Alcoholic, vinous, banana
	2-Penthylethanol	8-35	125	Rose, bitter, perfumed
	1-Octan-3-diol	0.03	0.2	Fresh-cut grass, perfume
	2-Decanol	0.005	0.015	Coconut, aniseed
	Glycerol	1200-2000	-	Sweetish, viscous
	Tyrosol	3-40	200	Bitter, chemical
Aldehydes	Acetaldehyde	2-20	25	Green, paint
	Propanal	0.01 -0.3	5, 30	Green, fruity
	Butanal	0.03-0.2	1 .0	Melon, varnish
	trans-2-Butenal	0.003-0.02	8 .0	Apple, almond
	2-Methylpropanal	0.02-0.5	1 .0	Banana, melon
	C, Aldehydes	0.01-0.3	*ca.* 1.0	Grass, apple, cheese
	Hexanal	0.003-0.07	0.35	Bitter, vinous
	trans-2-Hexenal	0.005-0.0 1	0.6	Bitter, astringent
	Heptanal	0.002	0.075	Aldehyde, bitter
	Octanal	0.0014.02	0.04	Orange peel, bitter
	Nonanal	0.00 1-0.0 1 1	0.018	Astringent, bitter
	trans-2-Nonenal	0.00001-0.002	0.000 1	Cardboard
	cis-3-Nonenal [6]	-	0.0005	Soy-bean oil
	trans-2-cis-6-Nonadienal	-	0.0000 5	Cucumber, green
	Decanal	0.0.003	0.006	Bitter, orange peel
	Decadienal	-	0.0003	Oily, deep fried

Table 1.1 Typical flavour compounds in beers cont.

Group	Chemical Name	Typical Level [mg/L]	Flavour Threshold [mg/L]	Flavour Description
Ketones	3-Methylbutan-2-one	<0.05	10	Keton, sweet
	3-methylpent an-2-one	0.06	-	-
	4-Methylpentan-2-one	<0.013	1.5	-
	3,3-Dimethylbutan-2-one	-	-	-
	6-Methyl-5-hepten-2-one	0.05	-	-
	Heptan-2-one	0.04-0.11	2.0	Varnish, hops
	Octan-2-one	0.01	0.25	Varnish, walnut
	Nonan-2-one	0.03	0.20	Ketone, varnish
	Decan-2-one	-	-	Ketone, flowery
	Undecan-2-one	-	-	Ketone, green plant
	Oct-1-en-3-one [6]	-	0.0001	Metallic, mushroom
	Octa-l-cis,5-dien-3-one [7]	-	1×10^{-6}	Metallic, geraniums
Sulfur Compounds	Hydrogen sulfide	1-20†	5	Sulfidic, rotten eggs
	Sulfur dioxide	200-20 000†	> 25 000	Sulfitic, burnt match
	Carbon disulfide	0.0 1-0.3	> 50	-
	Methanethiol	0.2-1 5	> 20	Putrefaction, drains
	Ethylene sulfide	0.3-2.0	2.0	-
	Ethanethiol	0-20	1.7	Putrefaction
	Propanethiol	0.1-0.2	0.15	Putrefaction, rubber
	Dimethyl sulfide	10-100	30	Sweetcorn, tin tomatoes
	Diethyl sulfide	0.1-1.0	1.2	Cooked vegetables
	Dimethyl disulfide	0.1-3	7.5	Rotten vegetables
	Diethyl disulfide	0-0.0 1	0.4	Garlic, burnt rubber
	Dimethyl trisulfide	0.01-0.8	0.1	Rotten vegetables, onion
	Methyl thioacetate	5-20	50	Cabbage
	Ethyl thioacetate	0-2	10	Cabbage
	Methional(4-thia-1-pentanol)	0.1-1.0	2000	Raw potatoes
	Methional(4-thiapentanal)		250	Mash potatoes, soup-like
	3-Methyl-2-butene- 1 -thiol		0.01	Skunk, leek-like, light-struck
Vicinal diketone	2,3-Butanedione	0.01-0.4	0.07-0.15	Butterscotch
	3-Hydroxy-2-butanone	1-10	17	Fruity, mouldy, woody
	2,3-Butanediol	50-150	4500	Rubber, sweet, warming
	2,3-Pentanedione	0.01-0.15	0.9	Butterscotch, fruity
	3-Hydroxy-2-pentanone	0.05-0.07	-	-

† Total levels (free and bound) quoted.

The release of flavours depends on many factors, next to their abundance in the beer. The flavours have a certain affinity with the other components in beer. A strong affinity will cause a relatively low vapour pressure, and thus reduce the release of the flavour. Next to the affinity, the diffusion rate of a flavour from the beer towards air is important. Both the diffusion in beer towards the beer surface and the vapour-phase diffusion of the flavour from the surface towards the gas (air) bulk can be important. Generally, the liquid-phase diffusion from beer towards the surface is rate-limiting. The other components in beer, such as proteins, carbohydrates and ethanol, influence flavour release both by affinity (change of activity) and by influencing the diffusivity (e.g., by a change in viscosity).

Proteins have little flavour of their own but have an affinity for most aroma compounds. Depending on the nature and the strength of this affinity, the release of these aroma compounds to the gas phase will be influenced and this has an impact on the overall aroma release and perception. [8] Part of this effect is also caused by an effect on viscosity.

The *carbohydrates* in beer originate from starch-rich cereals, mainly malted barley, but also other cereals including wheat, rice, maize, oats, sorghum and sugar syrups may be used. [9] They comprise fermentable sugars such as glucose, maltose and maltotriose, but also longer dextrins and arabinoxylans. Typically, longer oligo- and polysaccharides may have an affinity for flavours, reducing their release.

Proteins and especially carbohydrates contribute to the mouthfeel through increasing the viscosity. Generally, a larger viscosity also reduces the rate of release of flavours.

Ethanol is the major volatile in beer and since it reduces the hydrophilicity of the solvent, it lowers the partial vapour pressure of flavours, and therefore reduces their release. Besides, it is a flavour by itself and has a relatively sweet odour. [10]

1.3 Flavour readjustment through separation

The flavour profile of a beer may vary slightly from batch to batch, due to slight variations in ingredients or exact process conditions. For brewing on a smaller scale (such as in micro-breweries), the variation may be larger. On both large and small scales, one of the options is to adjust the flavour profile by selectively, partially removing some of the flavours.

With the current state of the knowledge, there is no single-step solution for selective targeting of a volatile flavour compound and it originates from the fact that flavours in beer present at very low concentrations sensitive for operational conditions and more importantly physiochemical similarities that strongly affect the selectivity of any separation method. However, depending on

the quality of the separation one may choose either single-step separation through distillation or membrane separation, or to obtain higher selectivity one may first strip the beer with for example carbon dioxide, and then remove the flavours from this strip gas, for example through adsorption, membrane separation, or other methods.

Distillation of beer to separate components with high vapour pressure should be done at vacuum condition to protect beer nutrients such as protein from denaturation. As the selectivity is toward lighter compounds such as volatile flavours and ethanol, a second step must be coupled with the effluent vapour to fractionate the desired component and return to the beer. Both operations under vacuum conditions and condensation are energy-intensive without considering the inherent of secondary fractionation step. Another option is the use of membrane separation, for example, the use of reverse osmosis [11], which however selectively mostly removes the ethanol. Nanofiltration would allow separation of flavours next to ethanol [12]. This would also require the separation of the ethanol from the flavours and returning the ethanol to the beer. Pervaporation allows more selective removal of flavours, depending on the membrane, but is relatively intensive in energy, and the separation is mostly dependent on the properties of the membrane; hence it does not leave much flexibility for adaptation of the separation from batch to batch [13], [14].

Therefore in most cases, the beer is first stripped with a carrier gas, such as carbon dioxide [15]. This gas takes up hydrophobic flavours and some ethanol that stripped from the beer. If the stripping gas is emitted, this may not only cause environmental complications but also does not give any selectivity against the specific flavours that are removed. Therefore again, it is possible to regenerate the strip gas feeding for a secondary separation stage in the liquid condensate phase or gas phase without condensation. The condensate can go under various separation steps such as distillation in which the desired fraction may be returned to the beer [16]. This distillation process is however relatively complex and energy-intensive. One may also choose to use a vapour permeation membrane, often made of hydrophobic rubbery polymers such as poly(dimethyl siloxane) [17]. These allow the removal of more hydrophobic vapour-phase components such as flavours and ethanol. Membrane vapour permeation is a relatively simple process, but removal is mostly dependent on the membrane material. Therefore, the process does not leave much flexibility to adapt the separation from batch to batch. Recently, Saffarionpour et al. [18] proposed using adsorption, for example with active carbon or zeolites, to selectively remove the flavours from the carbon dioxide. While this does allow flexibility in terms of separation, it is a semi-batch process, in which the columns regularly need to be regenerated, which complicates process operation.

An interesting option is the concept of frictional diffusion, which was originally developed by Geboers et al. [19], which was originally developed for the separation of ethanol/H2O mixtures using CO_2 .

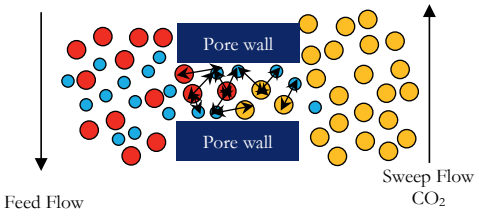


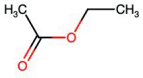
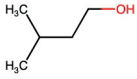
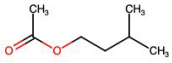
Figure 1.1 Schematic representation of the separation mechanism of FricDiff in a single pore meso/macro pore.

The process uses a microporous barrier, which allows the diffusion and convection of gases through its pores. This barrier separates the feed stripping phase (in our case carbon dioxide with flavours and ethanol) and a sweep gas, which could consist of carbon dioxide and ethanol as well. The separation of flavours then rests on differences in diffusion of the flavours trough the barrier pores, but this can be adapted by applying a small convective flow of the carrier gas through the barrier pores. This allows adapting both the flavour fluxes and the selectivity of the process very easily. At the same time, the process is mild, its operation and system are quite simple, being a continuous process, and using a simple, inert microporous barrier, which is only in contact with gases.

1.4 Aim of this thesis

This thesis will, therefore, assess the use of this frictional diffusion (FricDiff) process for the separation of flavours from beer, which have first been stripped with a carrier gas (CO_2) that is recycled after being regenerated with a FricDiff system. We expect that this FricDiff process will be able to separate different flavour components, with the convective flow as an independent process parameter. To limit the complexity, we will focus on a few flavour components, which represent the most important classes of flavours from beer: ethanol, ethyl acetate, isoamyl alcohol and isoamyl acetate.

Table 1. 2 Flavours used in this research (the solubility values are from our work, those between brackets are from literature)

Component	Structure	Formula	Boiling point [K]	Mw [g/ml]	Solubility in water [mg/L]
Ethanol		C_2H_6O	351.2	46.07	Fully miscible
Ethyl acetate		C_4H8O_2	350.2	88.10	74.35 (92.76) [20]
Isoamyl Alcohol		$C_5H_{12}O$	404.2	88.15	33.72 (34.74) [21]
Isoamyl Acetate		$C_7H_{14}O_2$	415.0	130.19	2.268 (2.98) [22]

In practice, these flavour components will have interaction with all components in beer that were mentioned before. In this thesis, the focus is laid upon the interaction with ethanol, as this is the strongest effect in the system.

1.5 Outline of the thesis

In the current chapter, the starting points for investigation were defined, and in **Chapter II** an overview is given of various food systems in which flavours play an important role, with emphasis on liquid food systems and flavour-matrix interactions. In **Chapter III**, the equilibrium behaviour of flavours is discussed, especially the effect of ethanol on the partition coefficient of flavours. **Chapter IV** focuses on the rate of mass transfer, via mass transfer coefficients and the effect of other beer constituents on these. **Chapter V** combines these into a model that describes the fluxes and selectivity of flavours during FricDiff as a function of process design and conditions. Finally, the main conclusions from each chapter are compiled into general conclusions, and an outlook towards application and further research is given in **chapter VI**.

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Chapter II

Flavour Retention and Release from Beverages: a Kinetic and Thermodynamic Perspective (review)

For the investigation of retention and release of flavour components, various methods are available which are mostly used on a case to case basis depending on the raw material. These effects that originate from kinetics and thermodynamics could be put in a much wider perspective, if these fields were taken as a starting point of the investigation, in combination with rigorous data analysis. In this review, we give an overview of experimental techniques and data analysis methods, and also predictive methods using mass transfer techniques are discussed in detail.

We use this as a foundation to discuss the interactions between volatile flavours and the matrix of liquid foods/beverages. Lipids present in the form of an emulsion, are the strongest volatile retainers due to the lipophilic nature of most of the volatile flavours. Proteins also have flavour retention properties whereas carbohydrates hardly have a retention effect in beverages. Smaller components, such as sugars and salts can change the water activity therewith facilitating flavour release. Alternatively, salts can also indirectly affect binding sites of proteins leading to release (e.g. NaCl and Na_2SO_4) or retention (NaCSN and $Cl_3CCOONa$) of flavours. Furthermore, the effects of temperature and pH are discussed. The review is wrapped up with a critical section on the determination of parameters relevant to flavour release. We highlight the importance of accurate determination of low concentrations when using linearization methods, and also show that there is an intrinsic preference for non-linear regression methods that are much less sensitive to measurement error.

This chapter was published as:
Ammari, A., Schroen, K., 2019. Effect of Ethanol and Temperature on Partition Coefficients of Ethyl Acetate, Isoamyl Acetate, and Isoamyl Alcohol: Instrumental and Predictive Investigation. J. Chem. Eng. Data

2.1 Introduction

Aroma, taste, texture, and mouthfeel all contribute to the perception of flavours.[1] When removing off-flavours or adding flavour to a product, separation of these components highly depends on their physicochemical interactions with other molecules, which are complex as discussed in various reviews.[2]–[16]

Flavour retention and release are mostly studied to design healthier food products (low-fat milk, alcohol-free beer etc.) without compromising on traditional product acceptability, functional beverages (including drinkable meal replacers or sports supplements) and beverages with exotic features (exotic fruit tastes, cocktails, and fusions etc.). In skim milk, loss/lack of hydrophobic flavours challenges consumer's acceptability compared to high-fat milk, whereas the potential health benefit of soymilk suffers from beany off-flavour [17] originating from lipoxygenase activity.[18], [19]

Flavour release or retention, generally, is affected by the intrinsic chemical properties of the flavour (hydrophobicity, hydrophilicity, (log P value) and volatility), the composition of the medium (lipid, protein, salt, sugar, etc.) and finally environmental conditions (temperature, pH). In other words, the interaction between flavour compounds and other food ingredients at given environmental condition determines the intensity of flavour retention or release from a product. In this paper, we cover the thermodynamics and kinetics of flavour-matrix interactions in aqueous food systems, starting with experimental and theoretical approaches; the actual human flavour perception is considered outside the scope of this review.

In general, the driving force for flavour release from an aqueous phase is determined by the deviation from the thermodynamic equilibrium conditions between aqueous and gas phase. Such thermodynamic equilibrium obeys the following relationship:

$$K^{cc} = \frac{1}{H^{cc}} = \frac{C_G}{C_L} \tag{2.1}$$

Where K is the partition coefficient or dimensionless Henry's volatility coefficient, which is the reciprocal value of Henry's solubility coefficient H, with C_G and C_L, the concentrations of the flavour in gas and liquid phase, respectively. The superscript cc indicates that concentrations are used. Although these coefficients are tabulated for binary aqueous systems (e.g. Sanders [20]), the available information is limited to simple systems, and even moving from binary to ternary systems makes the behaviour quite complex.[21] In the current review, we will use the thermodynamic background to link the intrinsic chemical properties of flavours, matrix, and environmental conditions, starting with measurement methods.

2.2 Methods to Determine Flavour Retention

Thermodynamics and transport phenomena can be investigated experimentally or mathematically to predict the equilibrium and kinetics of flavour-matrix interactions. Understanding retention of flavours in a product requires measuring the variation of flavour present in at least one of the phases, liquid and/or gas, for which ample experimental methods are available for food matrices. For example, binding of volatiles to β-lactoglobulin has been investigated by O'Neill & Kinsella [22] by equilibrium dialysis, Andriot et al. [23] by headspace analysis, Relkin et al.[24] by spectrofluorometric measurement, and Rogacheva et al. [25] used a diffusion cell. In the food field, interpretation of data is complex, leading to the use of (over-) simplified systems, whereas predictive methods have gained relevance due to experimental limitations or high costs.

First, we focus on experimental methods, after which data analysis is touched upon, followed by the mathematical models in use. In a dedicated section, specific liquid foods are discussed.

2.2.1 *Experimental approach*

Flavour behaviour can be assessed by sensory or instrumental analysis. Sensory analysis (performed by trained experts or ordinary assessors), gives an overall picture of the perceivable flavours, which implies that only a limited number of components play a role; the concentrations of a vast amount of volatile chemicals are simply below the limit of detection of the human sensory system. For example in wine, with more than 1000 identified compounds [26], only a few flavours contribute to sensory experiences. For the current review, we consider aspects related to sensory perception outsize our scope and focus on instrumental methods.

The current analytical methods are capable of tracking flavour behaviour in great detail. Liquid chromatography [27], dynamic coupled liquid chromatography [28] and affinity chromatography [29] have been used for different aqueous flavour systems often in combination with headspace analysis. One of the important parameters that may be obtained using chromatography is the octanol/water partition coefficient (log P) that can be used to parameterize hydrophilicity or lipophilicity of compounds.[30], [31]

2.2.2 *Static Headspace Analysis (SHS)*

It is a standard procedure of collecting samples from the gas phase in equilibrium with a second phase (liquid or solid). [19] Samples are collected by syringe, solid-phase micro-extraction [32], or single-drop micro-extraction [8], [33], and mostly analysed by GC equipped with flame ionization detector (FID), or mass spectrometry (MS), thermal conductivity detector (TCD), proton transfer reaction mass spectrometer (PTR-MS), that may be equipped with a switchable reagent

(SRI-PTR-MS). For quantitative measurement of the concentration in the gas phase, the total vaporization technique is particularly used for the preparation of calibration standards.[34] The effective parameters in static headspace analysis are temperature, sample volume [35] and incubation time that can easily be controlled using an incubator and standard vials. In the case of micro-extraction methods, the selection of adsorbent fibre or solvent has a significant effect on the quality of measurement.

2.2.3 *Dynamic headspace (DHS)*

In this method, volatile is continuously removed from the headspace by sweeping with inert gas or taking multiple samples in time, leading to depletion of the matrix. The most important parameters are the sweep or purge gas volume and the extraction temperature.[35]

Multiple Headspace Extraction (MHE) was introduced by McAuliffe [36] and uses multiple gas phase withdrawal steps. This method was originally used to find the total concentration of a component in a matrix; since sampling times are not carried out ad infinitum, regression is used. The concentration in the headspace and consequently peak area decrease exponentially

$$C = C_0 \times e^{-at} \tag{2.2}$$

Where C is volatile flavour concentration in time t, the proportionality parameter, and C_0 the initial concentration. Transforming this into peak area results in:

$$A_i = A_1 \times e^{-a(i-1)} \tag{2.3}$$

Where A_1 is the peak area of the first measurement and i the sample number. In linear form:

$$\ln A_i = -a(i-1) + \ln A_1 \tag{2.4}$$

Just like any linear regression, the equation heavily depends on A_1, the first measurement taken, which can be prone to experimental error. Therefore, the quotient $q=e^{-a}$ has been introduced, leading to a new intercept A_1^*. The sum of all peak areas for a component defined as:

$$\sum A_i = \frac{A_i^*}{(1-q)} \tag{2.5}$$

Phase Ratio Variation (PRV) is an indirect method to determine the partition coefficient that is independent of liquid volume. The following constants are derived:

$$\alpha = \frac{V_V}{V_S} \tag{2.6}$$

$$\beta = \frac{1}{A_P} \tag{2.7}$$

where V_V and V_S are vial and sample volume, respectively, and A_P the peak area. By linear regression of α against β, the partition coefficient follows from the slope and intercept:

$$K^{cc} = \frac{slope}{intercept} \tag{2.8}$$

Because this method depends on the peak size differences resulting from changing the phase ratio, it is not suitable for components with high partition coefficients K^{cc} that give large peaks already at low concentrations of which the difference is hard to measure, leading to issues with linear regression. For more details on the method, we refer to the book of Kolb & Ettre.[37]

Exponential dilution technique (EDT) is a method where the liquid phase is exhausted by the continuous flow of an inert gas. The concentration in the liquid usually decreases exponentially (similarly as described for dynamic headspace analysis), and extraction kinetics can be compared between different liquid samples that contain flavour retainers or enhancers.

Multi Volatile Method (MVM) is a sequential dynamic headspace method in combination with adsorption using different adsorbent traps.[38] The first and second sampling sequence target components with high (>20 kPa) and moderate (1–20 kPa) vapour pressure using carbon-based material at 25°C. The third and final sequence uses a Tenax TA trap at 80°C to target components with low vapour pressure (<1 kPa) and/or hydrophilic characteristics. The three traps are sequentially thermally desorbed, trapped and concentrated in a programmed temperature vaporizing (PTV) inlet, and analysed in a single GC-MS run.

Batch stripping is used if the direct gas-phase analysis is not possible. Since Henry's coefficient is an important design parameter for stripping columns, this equipment can be used to derive its' value from liquid samples taken as a function of time [39] (see also data analysis section). Based on our experience (figure 2.1) significant separation takes place early on; therefore, measurement time intervals need to be tuned accordingly.

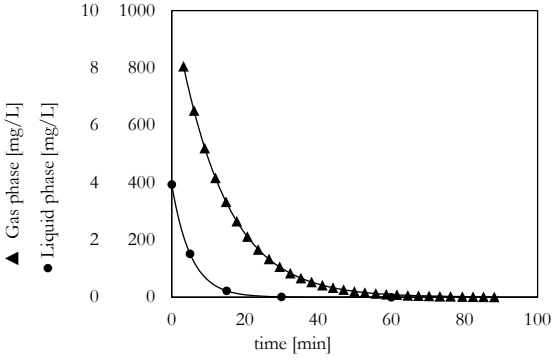

Figure 2. 1 Concentration depletion in gas and liquid phase during stripping of 0.5 mL/L isoamyl acetate solution in water with CO_2.

2.2.4 *Equilibrium Dialysis*

It is one of the oldest methods [40]; two cells of equal volume separated by a membrane are filled with e.g. a buffer containing flavour, and a protein solution, and allowed to equilibrate. The key points are to ensure true equilibrium, the absence of adsorption to the membrane [15], and the sample container (relevant at low solubility). For this appropriate blank measurements can be used.[41] Equilibrium analysis suffers from comparatively higher uncertainty: Beyeler & Solms [42] investigated binding between 12 ligands and soy protein and bovine serum albumin and found similar binding constants, whereas Mills & Solms [43] found notable differences using headspace analysis. Most probably, protein-membrane interactions are responsible for this.

2.2.5 *High-performance liquid affinity chromatography (HPLAC)*

Sostmann & Guichard [27] introduced this method to investigate the interaction of β-lactoglobulin (BLG) with flavour compounds. They immobilized BLG on a silica support, and by injecting flavour compounds, differences are observed related to protein-flavour interactions. One of the drawbacks is that the support materials are not inert to all flavours.

These are the most common methods used for food, but there are others applied in e.g. biology, biophysics or biochemistry. For example, the Hummel and Dreyer method are used by Pelletier et al. [29] to determine the number of binding sites in β-lactoglobulin for selected flavours, but these methods are too specific for this review and considered out of scope.

2.3 Data Analysis

In most methods mentioned earlier, gas chromatography is used to measure headspace composition. The GC peak areas are used in different ways, for instance, Weel et al. [44] took peak area variation to report the effect of whey protein gel on diacetyl and ethyl butyrate release, whereas Nahon, Roozen & de Graaf [45] used sum of the average peak area to investigate possible interactive effects between sweetness and aroma compounds. Mostly, a flavour in an aqueous food matrix is reported relative to a standard such as a flavour-water system.[46]–[48] Nahon et al.[49] reported partition coefficients for ethyl acetate, methyl butanoate, ethyl butanoate, hexanal, and octanal as a function of sucrose concentration, which is much more generally applicable.

Next, we describe various characterization parameters. Wang & Arntfield [50] used "binding percentage" and expressed it as a function of their gas chromatograms peak area A as:

$$binding\ \% = \left(1 - \frac{A_{with\ protein}}{A_{without\ protein}}\right) \times 100\% \tag{2.9}$$

Landy et al. [51] replaced peak area values with vapour-liquid partition coefficient expressed in molar fraction and called it "retention percentage".

In various investigations [22], [40], [52], [53] the "double reciprocal equation" is used to analyse equilibrium dialysis data using:

$$1/\nu = 1/n + 1/(n \cdot \kappa \cdot C_f) \tag{2.10}$$

With ν moles of bound flavour per mole protein, C_f the free flavour concentration, n the number of binding sites in the protein, and $\varkappa$ the global binding constant. This method heavily depends on measurement accuracy at low concentration; non-linear fitting is preferred (see conclusions).

The amount of bound component [54] can be determined using:

$$bound\ component = \left(\frac{C_G^{bb} - C_G^{pb}}{C_G^{bb}}\right) \times C \tag{2.11}$$

where $C_G^{bb}$is the headspace concentration for the buffer blank, C_G^{pb} the headspace concentration for protein-buffer solution and C the flavour concentration. Seuvre et al. [55] used the Henry coefficient as a starting point and derived the "retention percentage" defined as:

$$retention\% = \frac{\left(K_{GW}^{xy} - K_{GM}^{xy}\right)}{K_{GW}^{xy}} \times 100 \tag{2.12}$$

In which K_{GW}^{xy} and K_{GM}^{xy} are Henry's volatility parameters of a volatile in water and solution, respectively. Landy et al.[51]reported the vapour-liquid partition coefficient of aroma compounds in a solution containing non-volatile constituents through:

$$K^{xy} = \frac{1}{t}\frac{RTN}{\dot{Q}_G P}\ln\frac{A_t}{A_{t_0}} \tag{2.13}$$

Where t is the time, A_{t_0} and A_t are the peak area of volatiles at time t=0 and t, respectively, T is the temperature (K), N is the number of moles of the liquid phase, $\dot{Q}_G$ is the carrier gas flow rate, P is the total pressure and R , is the gas constant.

Using activity coefficients, Fares et al. [56] and Langourieux & Crouzet [57] derived:

$$\ln A = \ln A_0 + \frac{\dot{Q}_G}{RT}\frac{p_i}{N}\gamma_i^{\infty} t \tag{2.14}$$

where p_i is the vapour pressure of the pure solute and γ_i^{∞} the activity coefficient at infinite dilution.

As mentioned, if there is a limitation in gas phase sampling, the partition coefficient can be measured with a batch stripping column. For the flavour concentration in the liquid phase at known stripping gas flowrate [39] the following equation is used:

$$\ln \frac{C_L}{C_L^0} = -\frac{K_H^{pc} . \dot{Q}_G}{V_{column} . R . T} \times t \tag{2.15}$$

With C_L^0 and C_L the initial and sequential liquid phase concentration respectively, K_H^{pc} Henry's volatility coefficient (pc indicates dimension pressure over concentration in the phase), $\dot{Q}_G$ the gas flowrate, T the temperature, V_{column} the column volume, R the universal gas constant, and t is time. From a linear plot of $ln\, C$ versus time, K_H^{pc} is determined. Please note, the system needs to be (i) isothermal, (ii) liquid phase well-mixed, (iii) vapour phase ideal, (iv) Henry's law valid, (v) volume of liquid constant, (vi) partial pressure of the solute low compared to the total pressure, and (vii) exit vapour at equilibrium with the liquid. Gosset et al. [58] mentioned that equilibrium in the outlet and well-mixed system are difficult to warrant, and we believe that the liquid volume is not that constant when taking multiple samples.

For high-performance liquid affinity chromatography, the flavour-protein interactions are reported as a "binding constant" [27], [29], [59]–[61]

$$\mathcal{K}_B = \frac{t_R - t}{C_P \times t_0} \tag{2.16}$$

Where t_R and t are retention time of the compound with protein and without protein present on the column, respectively, C_P protein concentration, and t_0, the void time.

2.4 Predictive Approach

Various modelling approaches have been successfully applied; here we focus on phase equilibria and mass transfer starting with the partition coefficient that underlies both.[62] We give special attention to experimental work in the conclusions, since it forms the basis for fully theoretical concepts such as UNIFAC [63], NRTL [64] or the interaction-parameter-based Wilson method.[65]

2.4.1 Phase equilibrium

Buttery et al. [66] estimated partition coefficients (equation 2.17) for aliphatic aldehydes in water-oil mixtures starting from binary air-to-water partition coefficients, air-to-oil partition coefficients, and the oil, and water fraction in the product :

$$K_{GM}^{cc} = \frac{C_G}{C_M} \tag{2.17}$$

Where C_G and C_M are the concentration of flavour in gas and liquid mixture, respectively. The overall concentration of the flavour in the liquid mixture can be expressed through a component mass balance with F_W and F_O the fraction of water and oil respectively.

$$K_{GM}^{cc} = \frac{C_G}{(C_W F_W + C_O F_O)} \tag{2.18}$$

Thus:
$$K_{GM}^{cc} = \frac{1}{(F_W/K_{GW}^{cc} + F_O/K_{GO}^{cc})} \tag{2.19}$$

Doyen et al. [46] used the same expression to investigate volatile release from emulsified lipids based on concentrations, Roberts et al. [48] investigated the effect of lipids on flavour retention in milk-based liquids using oil-to-water partitioning.

$$C_M = (1 - F_O)C_W + F_O C_O \tag{2.20}$$

$$K_{GM}^{cc} = \frac{K_{GW}^{cc}}{1 + (K_{OW}^{cc} - 1)F_O} \tag{2.21}$$

For systems containing proteins instead of lipids, Andriot et al. [23] reformulated the partition coefficient based on available unbound flavours by introducing an effective partition coefficient.

$$C_M = C_b + C_f \tag{2.22}$$

Where C_b and C_f are the concentrations of bound and free flavour in the liquid phase, respectively. At equilibrium, the concentration of bound flavour is a function of binder concentration C^B, the concentration of free flavour in the liquid phase C_f^{eq}, and global equilibrium binding constant $\mathcal{K}_b$.

$$C_b^{eq} = \mathcal{K}_b C^B + C_f^{eq} \tag{2.23}$$

These authors assume that protein reduces available flavour for transport to the gas phase by a factor $(1 + \mathcal{K}_b C_b)$ or in other words, they assumed irreversible binding to the protein and:

$$K_{GM}^{eff} = \frac{C_G^{eq}}{C_f^{eq}} = \frac{K_{GM}^{cc}}{1 + \mathcal{K}_b C_b} \tag{2.24}$$

The equations mentioned above form a good basis. If the flavour compounds interact, this will complicate the situation [67] and some factors need to be treated with caution, such as temperature, acid-base equilibria, sorption to suspended particles, and other phase transitions such as crystallization [62], as described next.

Temperature, pressure and phase composition

We discuss these factors together because they are linked: equilibrium is established when the chemical potential of a component in the two phases is equal. For gas and liquid:

$$\mu_i^{Gas} = \mu_i^{Liquid} \tag{2.25}$$

and by definition:

$$\mu_i^0(p_i^{sat}, T) + RT \ln\left(\frac{p_i}{p_i^{sat}}\right) = \mu_i^0(p, T) + RT \ln(a_i) \tag{2.26}$$

Where μ is chemical potential p vapour pressure, R and T universal gas constant and temperature, respectively. Superscript 0 and "sat" are indicators of values in standard and saturated conditions, respectively. The chemical potential is not only affected by temperature, and pressure but is also a function of the activity of the flavours in the liquid phase.

If the temperature, pressure, and composition were the only factors to consider, modelling should not be complicated, since commercial software such as Aspenplus® can predict gas-product equilibria. However, some components affect the activity of volatiles without binding, such as ethanol [68], [69], salt [18] and sugar [45], [70], and this is not yet covered in this software. These components can also influence the equilibrium indirectly e.g. by changing the binding constant of proteins[71], or through denaturation.[40] Furthermore, phase transitions, such as crystallization [16] can reduce the phase volume for flavours to interact with [72], which consequently leads to higher gas-to-mixture partitioning. To be complete, for sugars comparative effects were reported: sugar hydration reduces free water and increases flavour concentration (some observations are in the next section).

Flavour binding and entrapment

Flavour binding to a food matrix is "sorption" in its broadest sense, so adsorption, absorption, physicochemical and chemical binding.[1] Bound, free, and total concentration can be distinguished, and only the freely dissolved components contribute to the gas phase concentration. Exchange of flavour compounds between bound and free state is often faster in liquid foods than flavour transfer to the gas phase [73]; transport across the water-gas interface is thus the rate-limiting step. Flavours can also be entrapped in small regions e.g. created by carbohydrates [74], and suspended solid particles can have binding properties albeit that the rate of equilibration is often slow because of diffusion limitation [62], therefore we only mention this to be complete.

2.4.2 Interfacial mass transfer

Transfer of flavours from the aqueous phase to either air or another liquid phase such as saliva can be described using theoretical concepts from chemical engineering.[3] As early as 1855, Fick expressed the mass transfer rate as a linear function of a molar concentration gradient.[75] By introducing h_M and h_G as mass transfer coefficients for mixture and gas phase, mass flux J for either side can is given by:

$$J_M = h_M\left(C_M^i - C_M\right) \tag{2.27}$$

$$J_G = h_G\left(C_G - C_G^i\right) \tag{2.28}$$

where C_M, C_M^i , C_G and C_G^i are concentration of flavour in mixture bulk, and interface and gas bulk, and interface respectively. $\left(C_G^i - C_G\right)$ is the driving force for mass transfer on the gas side which is often smaller than that on the liquid side $\left(C_M^i - C_M\right)$.[73], [76], [77] The concentration C_M^i at the interface determines the concentration in the bulk air phase $C_M^i = C_G/K_{GM}^{cc}$ (see also figure 2.2) so equation 2.27 can be re-written to:

$$J_M = h_M\left(\frac{C_G}{K_{GM}^{cc}} - C_M\right) \tag{2.29}$$

The value of mass transfer coefficient h_M depends on how we describe mass transfer phenomena in the interface (see Coulson et al. [78] for a review). Two classic theories, the two-film theory [77] and the penetration theory [79], are still extensively used in prediction of flavour release, and later we introduce them briefly.

Mass transfer is a process resulting from either the random movement of molecules (molecular diffusion) or convective eddies present in turbulent fluids (eddy diffusion), and both are relevant

for food research. Eddy diffusion is much faster than molecular diffusion and independent of flavour type.[62] Doyen et al. [46] showed that eddy diffusion can be used to predict ethyl hexanoate release from an emulsion with low-fat content, while molecular diffusion is suited to predict ethyl octanoate release, whereas the headspace behaviour of ethyl butyrate can be described by eddy diffusion. In general, eddy diffusion gives better predictions for systems with high partition coefficients, and molecular diffusion for systems with a low partition coefficient (see figure 2.2 [80] for corresponding headspace concentration profiles).

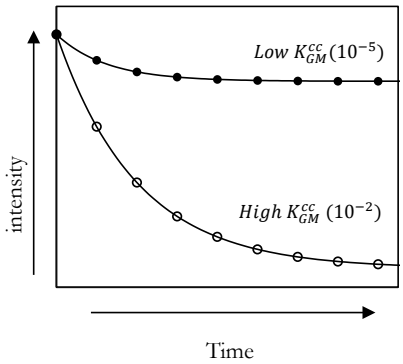

Figure 2. 2 Schematic representation of headspace depletion for compounds with different partition coefficients [80]

The Two Film Theory

In this theory, it is assumed that turbulence creates concentration uniformity in gas and product, while bringing molecules close to the interface where eddies die out, and form a laminar stagnant region where the resistance to transfer is located. In these regions, diffusion is molecular, and the mass transport coefficient h_M is given by:

$$h_M = (\frac{D_M}{\delta_M}) \tag{2.30}$$

Where D_M and δ_M are molecular diffusivities of flavour and film thickness on the mixture side.

Penetration Theory

This theory suggests that eddies in the bulk bring an element to the interface for a finite time, exposing it to the second phase, after which it returns to the bulk. In this way, the bulk is exposed to the second phase, and equilibrium is established immediately through molecular diffusion.[62] The short exposure time does not restrict components to reach the surface layer [78], and the mass transfer coefficient is given by:

$$h_M = 2\sqrt{D/\pi t_e} \tag{2.31}$$

With D the average diffusion coefficient and t_e the exposure time to the second phase. Van Elk et al. [81] introduced a modified theory for finite liquid bulk, to which we refer the interested reader.

In both the film and the penetration theory, the resistance in the liquid phase controls mass transfer, which is valid if there is no concentration gradient in the gas phase. For stagnant water phase and a turbulent gas, this holds for high partition coefficients $K_{GM}^{cc} > 10^{-3}$.[62] If mass transfer resistances in both phases exist, this can be taken into account using the following relationship [82]:

$$J = h_O(K_{GM}^{cc} C_M - C_G) \tag{2.32}$$

Mass flux across the interface is related to the bulk concentrations of the flavour in both phases that can be derived from an overall mass transfer coefficient h_O defined as:

$$\frac{1}{h_O} = \frac{1}{h_G} + \frac{K_{GM}^{cc}}{h_M} \tag{2.33}$$

Since no concentrations build up in the boundary layers at the interface, this gives:

$$J = h_M\left(C_M^i - C_M\right) = h_G\left(C_G^i - C_G\right) = h_O(C_G - K_{GL}^{cc} C_M) \tag{2.34}$$

Non-Equilibrium Partition Model

De Roos & Wolswinkel [83] described partitioning of volatile compounds in matrices for eddy diffusion in highly agitated systems to allow exchange between product volume element V_P^* and gas volume element, V_G^*. Furthermore, the whole liquid boundary layer is considered at equilibrium with the gas boundary layer.[3] Equation 2.35 shows the amount of released volatile M'_P after n extraction steps relative to M_P^0 , the initial concentration.

$$\frac{M'_P}{M_P^0} = 1 - \left\{\left(\frac{V_P^*}{V_P}\right)\left\{\frac{\frac{1}{K_{GM}^{cc}}}{\left(\frac{1}{K_{GM}^{cc}} + \frac{V_G^*}{V_P^*}\right)}\right\} + \left(1 - \frac{V_P^*}{V_P}\right)\right\}^n \tag{2.35}$$

The term V_G^*/V_P^* is indicative of mass transfer resistance; for high product resistance, the product element in equilibrium with a fixed volume element of gas is smaller leading to higher V_G^*/V_P^*. De Roos & Wolswinkel [83] showed that their approach also holds for some less agitated systems.

Mathematical models for predicting flavour equilibration in the headspace above aqueous mixtures

In 1997, Harrison and colleagues [76] presented a mathematical model for diacetyl release from water-sunflower oil emulsion using equilibrium partitioning [66], and the penetration theory:

$$C_G(t) = \frac{K_{GM}C_M(0)}{\left(\frac{K_{GM}V_G}{V_M} + 1\right)}\left[\left(1 - exp\left\{-\left(1 + \frac{V_M}{K_{GM}V_G}\right)\frac{h_D A_{GM}}{V_M}t\right\}\right)\right] \quad (2.36)$$

where A_{GM} is a gas-liquid mixture surface area. This correlation dates back to McNulty's PhD thesis [84] that focused on flavour transport from emulsions to saliva.[85]–[87] For a long exposure time $t \to \infty$, the headspace concentration reaches equilibrium, thus:

$$C_G(\infty) = \frac{K_{GM}c_M(0)}{\left(\frac{K_{GM}V_G}{V_M} + 1\right)} \quad (2.37)$$

Andriot et al. [23] state that $C_G(\infty)$ must be the same as that used for the effective partition coefficient in equation 2.24. For a short exposure time $t \to 0$, equation 2.36 results in:

$$C_G(t) = \frac{c_M(0)h_D A_{GM}t}{V_M} \quad (2.38)$$

In the early stages of flavour transfer, the partition coefficient K_{GM} does not affect the release (see equation 2.38). Harrison et al. [76] conclude based on equation 2.36, that the effect of emulsion composition and microstructure on initial flavour release, is through an effect on the interfacial mass transfer coefficient h_D that they used as a fitting parameter. They also found that surfactant or protein had no effect on flavour diffusion between the phases, and could successfully describe the release of 2-heptanone from 60/40 oil-in-water emulsion. Despite these interesting finds, we believe that a case by case evaluation is needed, using the thermodynamic kinetic models as a reference. Seuvre et al. [55] showed that increasing lipid (miglyol) concentration from 0.5% to 1% completely masks flavour binding to β-lactoglobulin, while McNulty & Karel [86] saw a drop in overall mass transfer coefficient for long-chain alcohols as the surfactant is added to the oil/water emulation. A similar observation by Guichard & Langourieux [61] shows that even if the addition of fat-induced a greater change in favour retention than the addition of protein, β-lactoglobulin at the oil/water interface does limit the transfer of hydrophobic compounds from oil to water. In the next section, the effects that have been attributed to the various food components are discussed based on their category.

2.5 Flavour-matrix Interaction in Beverages

Except for water, the majority of drinks are complex mixtures of water, carbohydrates, lipids, proteins and other organic compounds, and all of them can interact with and/or bind flavours.[88] The duality of health and acceptability of a beverage usually has contradicting aspects; e.g. separation of fat from milk or ethanol from beer leads to loss of desirable flavours,

whereas the product as such could be healthier. In this section, we will look at flavour-matrix interactions in liquid food products. Due to the massive amount of research [12], [89], [90], it is not feasible to address all flavour-matrix interactions, therefore we present relevant categories below.

2.5.1 Lipids

In beverages, oils and fats may be dispersed as droplets [91] that are thermodynamically unstable; therefore, surfactants (emulsifiers), such as proteins, are added to protect oil drops from coalescence.[92], [93] Lipids can accommodate hydrophobic components [1], [46], [94], [95], and consequently, have high flavour retention (depending on the logP value of the component) compared to other food ingredients (see later sections).[94] The physical state of the lipid also affects aroma retention. [96] McNulty & Karel [86] using stirred diffusion cells showed that hydrogenated vegetable oils decreased flavour release rates by one order of magnitude when going from oil to a solid fat index of 66; therewith influencing the overall partitioning coefficient as discussed before. Roberts et al. [48] used headspace sampling with a solid-phase microextraction fibre and investigated this further using a milk-based emulsion with 1.36% lipid content consisting of hydrogenated palm fat and milk fat. Investigations at various temperatures showed lower flavour release at higher solid fat content for practically all systems, with the exception of 2-pentylfuran and limonene in milk fat, which may be due to crystal exclusion effects.

2.5.2 Proteins

Protein-containing beverages have a broad spectrum, dairy, soft drinks, sports drinks, and fermented beverages, and may contain proteins from animal and plant origin. Even though proteins do not contribute to the flavour of products directly [97] they can interact with flavours either reversibly [22], [27] or irreversibly [98], [99] (if hydrolyzed proteins are known to form peptides that can be extremely bitter depending on their size and hydrophobicity[100]). Covalent chemical linkage such as amide and ester formation, condensation of aldehydes with sulfhydryl (SH) groups [101] are irreversible, non-covalent hydrophobic and electrostatic interactions, hydrogen bonds, or van der Waals interactions are reversible.[14] E.g. β-lactoglobulin is known to have reversible interactions with flavours [27], while aldehyde flavours can bind reversibly and irreversibly to proteins.[97], [102]

Proteins may also convey undesirable off-flavours to foods, especially soy protein is known for this. [103], [104] Furthermore, proteins can change food structure, which reduces flavour perception due to inhibited mass transfer.[105]–[107] Flavour-protein interactions are more

diverse than those with lipids or carbohydrates due to the variability of the chemical structure, including varying amino acid side chains, terminal ends, and more hydrophobic regions.[89]

Whey protein was long considered a by-product of cheese formation, but is now highly valued, and contains amongst others α-lactalbumin, bovine serum albumin BSA, immunoglobulins, and most abundantly β- lactoglobulin.[108]

β-lactoglobulin of which the characteristics and structure are well known [14], [109], is also known to bind various flavours such as alkanones [22], esters [29], methyl ketones [110] alcohols [61] and lactones [14] reversibly through hydrophobic interactions.[27] The binding capacity increases going from alcohols to ketones and aldehydes [14], and within a chemical class, the affinity constant increases with increasing hydrophobic chain length [61], except for terpenic compounds [60], acids and pyrazines.[29]O'Neill & Kinsella [22], [111] using equilibrium dialysis method observed a reduction of binding capacity as a consequence of structure loss due to urea treatment (disulphide bonds, or ethylation). Further, it was reported that β-lactoglobulin at the oil/water interface limits the transfer of hydrophobic compounds and reduces flavour release.[61] Furthermore, by using headspace analysis and exponential dilution technique, Seuvre et al.[55] showed that the relative volatility of 2-nonanone in a mixture of water with 3% β-lactoglobulin and 0.5% miglyol is higher when using an emulsion, while isoamyl acetate was not affected, which could hint at cooperative effects.

α*-lactalbumin* has lower binding capacity compared to other whey proteins even though it can bind ketones and aldehydes.[112], [113] Charles et al. [114] used static headspace analysis and compared flavour release of ethyl hexanoate and allyl isothiocyanate from emulsions with β-lactoglobulin and α-lactalbumin; the flavour retention of the latter emulsion was significantly less.

Bovine serum albumin (BSA) binds a variety of compounds: retinol [115], long-chain fatty acids [116]–[119], alkanes [120]–[122], aldehydes and ketones.[40], [41], [112] By using liquid-liquid partition equilibrium method Damodaran & Kinsella [123] found that the binding constant for ketones depends on chain length, functional group, and protein structure. In general binding constants for BSA decreases in the order aldehydes > ketones > alcohols.[124] Compared to casein BSA binds larger amounts, using as many as 5-6 out of 21 primary carbonyl binding sites.[90], [113]

Caseins are less ordered and more flexible than the globular whey proteins that have secondary and, tertiary structure.[125] In aqueous solutions, caseins show retention of several flavour compounds: limonene, linalool, terpinyl acetate, β-ionone and 2-octanone.[126] Caseins are used in a wide variety of food emulsions [127], and the effects are diverse: aqueous phase mass

transfer resistance increases for ethyl acetate, whereas interface resistance is higher for ethyl butanoate and ethyl hexanoate.[128]

Flavour retention depends on aroma compounds and the protein content, as was the case for the other proteins. For a homologous series of ethyl esters (ethyl acetate, butanoate, and hexanoate), Landy et al. [51] using either headspace analysis or exponential dilution method showed that retention increased with carbon chain length from 0 to 38% and 0 to 61% for caseinate contents of 5 and 50 (g/L), respectively. For diacetyl, the corresponding increase is 0 to 23%, which is in line with data for ethyl acetate.[129]

Fares et al. [56] employed exponential dilution and equilibrium dialysis and compared activity coefficients of aroma compounds in casein solution (25 and 75 g/L) and found no retention for acetone, ethyl acetate, and 2-propanol, but diacetyl and benzaldehyde interacted through strong and weak bonds. The binding behaviour of diacetyl is in agreement with findings of Landy et al. [51]; activity coefficients of selected aroma compound in an aqueous casein solution (25 g/L) gave no significant change for acetone and ethyl acetate, but for diacetyl, benzaldehyde, and 2-propanol the activity coefficient increased with 360, 150 and 130% respectively, which we interpret as an increase in volatility. At higher casein concentration (75 g/L) significant binding for benzaldehyde acetone and ethyl acetate is found, and volatility of diacetyl and 2-propanol increased. In another work done by Le Thanh et al. [130], this increase in activity coefficient was observed for acetone and ethyl acetate they used head-space analysis and sorption

Soy protein consists of four protein fractions: 2S, 7S, 11S, and 15S according to their Svedberg units. The main protein fractions are the globulins 7S or β-conglycinin (37-39% of total protein) and 11S or glycinin (31-44% of total protein).[131] Damodaran & Kinsella [132] studied binding of 2-nonanone using equilibrium dialysis method and found that 11S has a very weak affinity compared to 7S, that acted similarly to whole soy protein, suggesting preferential interaction with the 7S fraction.

Gremli [133] and co-workers used headspace sampling method along with what they named high vacuum transfer method and investigated flavour interactions with soy protein; unsaturated aldehydes strongly interact (a percentage is permanently bound, due to irreversible bonds) compared to saturated ones. Furthermore, at 100 mg/L, no evidence of flavour-flavour interaction of aldehyde and ketones were found in 5% protein solution. From the maximum number of volatiles bound to the protein they concluded that at conventional dosage levels, around 70% of added heptanal and 60% of 2-nonanone might be lost in soy protein containing beverages.

By using micropartitioning method Li et al. [134] studied interactions of vanillin with soy, casein, and whey proteins. At 12° C, they found that the enthalpy and entropy of binding for casein and whey protein are negative so enthalpy-driven, whereas for soy protein this is highly positive and entropy-driven. Protein-flavour binding is strongest in the following order: Soy > Gelatine >Ovalbumin > Casein > Corn.[89] Beyeler & Solms [42] also found that soy protein, β-lactoglobulin, and bovine serum albumin showed increased binding with chain length, which points to hydrophobic interactions.[22], [28], [40]

2.5.3 Sugars

In food products such as ice cream, beverages, jellies and sauces, carbohydrates are used as a sweetener, thickeners, stabilizers, and gelling agents. The impact of carbohydrates on aroma compounds is quite diverse and difficult to predict since they are able to induce both retention and release effects, depending on the conditions used and on the actual flavour molecules.[135] In beverages small sugar molecules (mono- and disaccharide), affect flavour partitioning via binding with water molecules, leaving flavours to be concentrated in the remaining available water [45], [136], [137] as reflected in increased activity coefficients of acetone, ethyl acetate, and octanol in solution in the presence of glucose [130] and sucrose.[36] Cyclic oligosaccharides such as cyclodextrin, and polysaccharides (starch, gum, and pectin) are known for their ability to form inclusion complexes with aromatic compounds, making them good flavour carriers and encapsulation materials.[138]–[140] These interactions have been investigated [141]–[143] and reviewed [144], but are considered outside the scope of the current paper.

In Expresso coffee beverage, the addition of sucrose, fructose or lactose, was shown to lead to a significant release of some furan compounds and a lower release of pyrazines[145] while in Ready-to-Drink coffee, the presence of sugars induced either no change or a retention effect depending on the sugar type. Even though salting-out should not be excluded, Paravisini and Guichard believe that retention can be a result of interactions between other non-volatile compounds and aroma compounds. For example, the non-volatile matrix of coffee contains up to 30% of brown polymers called melanoidins that are known to interact with aroma compounds.[135]

Using headspace analysis technique, Kieckbusch & Judson King [146] showed that for esters, partition coefficient increases in maltodextrin solutions with increasing carbon number, as later on, Nawar [147] observed for sucrose/water solutions and ketones using the same method. Nawar also reports a radical increase in headspace concentration when the flavour was added to the water/sugar solution compared to adding sugar to water/flavour solution. Bredie et al. [148]

showed that in 20% glucose/water solution, the volatility of compounds with low water solubilities, such as menthol and limonene increased, while isoamyl acetate and diacetyl which have some solubility were not affected. The activity of flavours with low solubility is much more affected by the addition of sugars.

2.5.4 Ethanol

Ethanol odour is described as sweet [6] and the concentration ranges from 2.5% to 70% in commercial beverages. Ethanol is polar and fully miscible with water which increases the solubility of hydrophobic flavours, and thus, enhances flavour retention [149]–[151], which can be traced back to a book written by Young [152] that shows that partitioning of esters and higher alcohols is reduced with an increasing volume percentage of ethanol. Bakker et al. [153] showed this also for 10mg/L isoamyl acetate, and Conner et al. [154] using headspace analysis showed that activity coefficients of esters decreased for ethanol concentration > 17% (v/v), depending on their acid chain length. At concentrations below 17% (v/v), the activity is not affected because of the limited solubility of these hydrophobic compounds.

Indirectly, ethanol is involved in structural changes of certain proteins [155], [156]; in 13 %(v/v), ethanol denaturation of β-lactoglobulin was observed, which influences flavour interactions [157] through reduction of accessible binding sites.[158] Andriot et al. [157] used two complementary static headspace and HPLC techniques found that heat treatment did not affect the retention of benzaldehyde in β-lactoglobulin solution, whereas, in the presence of NaCl or ethanol, retention of benzaldehyde decreased, which was attributed to aggregation of the protein.

2.5.5 Salts

Salts are known to influence flavour compounds in aqueous systems [159]–[161] often referred to as salting in and salting-out effects, and in emulsions, they are known to influence the partition coefficient because of this. Although most foods do not contain large amounts of salt, it can still be relevant, also since some salts have much greater effects than others (e.g. $CaCl_2$). We here mention a number of effects that were reported to be complete. Saturation of paraffin oil/water emulsion with sodium sulfate increases the partial pressure of volatiles 12 to 20 times.[18] Salts can also alter protein conformation, possibly exposing hydrophobic binding sites, leading to changes in their binding capacity [162], [163], and even aggregation may occur. Damodaran & Kinsella [53] using equilibrium dialysis investigated NaCl, Na_2So_4, NaSCN, and $CL_3CCOONa$ in relation to binding of 2-nonanone, 2-octanone, and 2-heptanone to bovine serum albumin. They found that NaCl and Na_2So_4 increased the activity coefficient of 2-nonanone, leading to its' removal from the protein phase to the salt solution. Wang & Arntfield

[50] using headspace analysis investigated pea protein isolate and rated the effect of different salts on flavour binding strength as Na_2SO_4 >> NaCl > $NaCH_3$ = no salt > NaSCN. By using solid-phase microextraction (SPME) and GC/MS analysis for porcine protein Pérez-Juan et al. [164] observed that KCl and NaCl increased branched aldehydes, hexanal and methional concentration in the headspace by 5–10 times, whereas no effect was found for octanal and 2-pentanone, while $MgCl_2$ and $CaCl_2$ showed no effect for all flavours, with the exception of branched aldehydes that were completely released in the presence of 1.0 M $MgCl_2$. Last but not least, Bortnowska [165] used static headspace analysis and studied the effect of salt in oil/water emulsions with dried egg yolk (DEY) or starch sodium octenylsuccinate (SOE) as emulsifiers and observed a decrease in diacetyl retention with increasing salt concentration, regardless of emulsifier type.

From the above is clear that salts can have various effects, starting from a direct effect on the activity of flavour components present in the water phase (depending on their solubility), to indirect effects, mostly on proteins. Salt can influence charges of binding sites for flavours, lead to exposure of more hydrophobic patches, and even lead to aggregation of proteins. All these effects can influence the release and retention of flavours, and what we see in literature is that often the more complex explanations are preferred while overlooking the direct thermodynamic effects on activity, which is a true omission.

2.5.6 Environmental Conditions

Viscosity is internal friction of a fluid and acts on molecular diffusion as suggested by the Stokes-Einstein and Wilke-Chang equations. De Roos [62] reports that adding 1% carboxymethylcellulose (CMC) to an aqueous flavour solution, and observed lower release rates from the viscous CMC solution than from water; differences being highest for the most volatile compounds. By using headspace SPME, Rabe et al. [166] studied the effect of viscosity using sucrose solutions on the release of thirteen flavours and found very diverse behaviours. In general, highly volatile flavours are most affected by viscosity compared to less volatile ones [70], which is logical, because highly volatile compounds hardly experience resistance from the gas phase, and the movement across the liquid phase is rate-limiting for mass transfer. Marin et al. [167] found little effect on the mass transfer coefficient of flavours in water, but the temperature and the viscosity play a critical role. Hansson et al. [136] suggested that binding with viscosity enhancers also need to be considered.

Starting from the penetration theory, it is clear that the diffusion coefficient is influenced by viscosity [12], and this is the case for both molecular and eddy diffusion, which is a complex

matter since diffusion of small molecules does not obey the Stokes-Einstein relation. The macroscopic viscosity of the system dramatically differs from the microscopic viscosity as "sensed" by the diffusing molecules.[168] McClements [169] offers an interesting example from Basaran et al. [170], who used an ultrasonic imaging technique and showed that sugar molecules move through xanthan solutions at almost the same rate as they move through pure water. The macroscopic viscosity of the xanthan solutions (measured at low shear rates) is much higher than that of water but the sugar molecules can pass through the pores rather unhindered.

Temperature affects the retention of aroma compound either directly or indirectly. At higher temperature, more flavour will be found in the headspace, which is a direct effect. Fares et al. [56] used exponential dilution and equilibrium dialysis and show that temperature increases the activity coefficient of flavours, and this can be further influenced by the presence of small molecules as discussed earlier. Indirectly, temperature influences binding sites, e.g. soy protein binding of hexane to glycinin occurs at 5°C but not at higher temperatures [171], while carbonyls interacted independent of temperature at temperatures above 25°C, but binding increased drastically at 5°C.[40] These findings were attributed to changes in the tertiary and quaternary structures; more examples can be found in the protein section. In general, binding is favourable at low temperature for β-lactoglobulin[111], casein and whey protein [134]; bovine serum albumin and model wine solution. [172]. As mentioned in the fat section crystallization of lipids [127] can also influence the distribution of flavours.

pH is one of the main reasons for protein denaturation, and through that also influences flavour binding. Emulsions stabilized by proteins are particularly sensitive [173]; β-lactoglobulin undergoes several conformational changes between pH 2 and pH 9 [174] and these changes affect the affinity for flavours, and also the emulsification strength of the protein. Jouenne & Crouzet [28], [175] show that binding of β-ionone, limonene, ketones systematically increased going from pH 3 to 9, with the sharpest increase going from pH 6 to 9, which diminishes at pH 11 where denaturation takes place. Binding of hydrocarbons by proteins was investigated by Mohammadzadeh et al. [121] using lysozyme, ovalbumin, ovotransferrin, α-chymotrypsin, and α-chymotrypsinogen. For all proteins, there was a noticeable increase in binding of heptane at lower pH values except for α-chymotrypsinogen.

2.6 Concluding remarks

From the previous sections, it is clear that retention and release of flavour components are a complex matter, but at the same time, there is a theoretical background that can help interpretation of experimental data using thermodynamics as a starting point, and as

schematically illustrated in figure 2.3. A flavour will partition between liquid and gas (2nd panel), and this partitioning can be influenced by the presence of small components (1st panel) that affect the chemical activity of the flavour. When introducing a binder such as protein, depending on its state (native or denatured) the flavour will bind more or less to it while obeying sorption relations (3rd panel), whereas introduction of an additional phase (4th panel) such as oil, will lead to redistribution of the flavour over all available phases depending on partitioning coefficients.

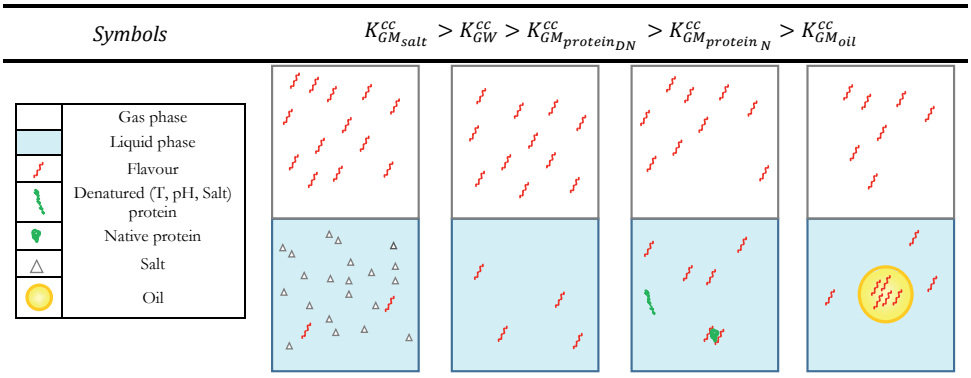

Figure 2. 3 Schematic representation of the effect of different beverage ingredients on the partition coefficient of flavours

Although a lot of investigations have been done on flavours, application of models in food design is still a step to take. We have shown that there are ample methods, and also thermodynamic insights, and kinetic models. We think that the theoretical background is not used that often due to the peculiarities of the components: they are mostly present at a very low concentration, while the models are validated for conditions in which the ratio of components is not that extreme.

This is also linked to the analysis threshold, that can induce a relatively large measurement error at the low flavour concentrations in foods. To that needs to be added that even the smallest loss of flavour to e.g. adsorption to a wall can influence the measured concentration greatly, and through that also, for example, the partition coefficient. We want to stress that the methods that are standardly used to derive parameter values (as described in that session), either through linearization in a log plot or taking reciprocal values are very prone to small differences in concentration. For example, in a reciprocal plot, those measurements that are done at low concentration give a lot of weight to the parameter values that are derived from for example the slope because they would be positioned at the high end of the x-axis. Because these concentrations are also prone to the highest experimental error (often in the range as the measured values), this can very rapidly lead to misinterpretation. Because of these aspects, we

recommend the use of fitting procedures that are non-linear and are directly applied to measured data. This is a well-established fact in for example enzyme kinetics research in which linearization was traditionally used in, for example, the Lineweaver-Burke approach, which leads to over- and underestimation of parameters, while when using a non-linear approach this does not occur.

We already mentioned the analysis threshold, and we think that this is an undervalued aspect of flavour research, especially in combination with interaction analysis that makes the situation as described above even more complex. The concentrations that are to be measured will in most cases be lower than in a system that contains liquids and flavour, which puts even more relevance to the measurement method. It cannot be ignored that this may also have led to misinterpretation of parameter values, and consequently models that are unable to capture the observed release behaviour. We thoroughly believe that more attention needs to be paid to how concentrations are measured, and their influence on parameter values, and model predictions.

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Chapter III

Effect of Ethanol and Temperature on Partition Coefficient of Ethyl Acetate, Isoamyl Acetate, and Isoamyl Alcohol: Instrumental and Predictive Investigation

For alcoholic beverages such as beer, downstream processing for either dealcoholisation or off-flavour removal requires both quantitative data and suitable predictive methods. Along with experimental investigations, we use a method initially developed for studying the solubility of gases in two or more miscible liquid solvents to monitor the effect of ethanol on the air-water partition coefficient of three major flavours found in beer namely isoamyl alcohol, ethyl acetate, and isoamyl acetate. In the ethanol concentration range between 0 and 0.1 mole fraction a slight rather linear increase in Henry's solubility coefficient was observed. This overall behaviour can be captured well using Henry coefficients for aqueous binary, and ternary systems together with the Wohl expansion for excess Gibbs free energy coupled with the one-parameter Margules equation. Based on the developed model, Wohl's expansion parameter for ethanol-water is introduced as the solvent-solvent interaction parameter. Van 't Hoff parameters for the temperature dependence of Henry coefficients for binary water-flavour solutions is determined in the range of 30 to 60°C.

This chapter was published as:
A. Ammari and K. Schroen, "Effect of Ethanol and Temperature on Partition Coefficients of Ethyl Acetate, Isoamyl Acetate, and Isoamyl Alcohol: Instrumental and Predictive Investigation," J. Chem. Eng. Data, vol. 64, no. 8, pp. 3224–3230, Aug. 2019.

3.1 Introduction:

Volatile flavour compounds are small molecules with relatively similar physiochemical characteristics, such as hydrophobicity or boiling point. These molecules are present at low concentration in a complex matrix present in beverages; therefore, separation or addition of these compounds to enhance flavour profiles or develop new products is challenging.

The market for alcohol-free beers is growing rapidly in Western Europe; with a worldwide market projected to reach 25 billion US dollars by 2024.[1] Alcohol-free beers can be produced using yeasts that do not produce alcohol, which affects the flavour composition compared to regular beers due to different bioconversion. Alternatively, alcohol may be removed from regular beers, but in the process, flavours are expected to be removed as well, depending on their physiochemical interaction with the aqueous matrix. For more information on process details, we would like to refer through to a recent review on production processes by Brányik *et al.* [2]

In current processes for the preparation of low alcohol beer, two approaches are mostly used: single-stage and cost-effective dealcoholisation, and multistage ethanol separation and flavour recovery followed by reconstitution of the beer.[2] In brewing industries, stripping is a popular post-production technique for both flavour control and dealcoholisation due to its well-defined and mild operational temperature and other conditions. Depending on the stripping gas polarity, different volatiles can be separated. For example, esters have a higher affinity for carbon dioxide whereas components with an alcoholic group can be removed through steam stripping.

Through stripping it is (almost) impossible to target one single component due to physiochemical similarities between volatile compounds. This implies that control of beer flavour needs to take place in multistage processes. For instance, a stripping column separates the component of interest that gives an off-flavour and a consecutive stage recovers and recycles the 'on-flavour' components that are removed with the target molecule. It is evident that the effectiveness of the latter stage depends on the previous stages, and the interaction of compounds needs to be charted in order to monitor retention of flavours.

Methods for the prediction of non-ideality and the phase behaviours of simple systems comprising of liquid, gas or vapour have been reasonably well-documented. For aqueous mixtures, comprising of electrolytes and flavours even commercial chemical engineering software can be used to predict non-ideality; although these databases use binary interaction parameters, of which it is questionable whether they are valid for such dilute systems or not. Furthermore, the effect of the food matrix on flavour has been limited to sensory evaluation. Data on quantitative analytical methods are very scarce and limited in scope.

In the current work, we quantify the effect of ethanol and temperature on the partitioning of three major flavours found in typical pilsner beers produced in the Netherlands and Belgium (light ale). When considering a gas/liquid system at equilibrium, the ratio of the concentration of flavours in the gas phase and the liquid phase is constant. This constant is called Henry's law constant (HLC) and can be defined in either solubility or volatility terms:

$$K^{cc} = \frac{1}{H^{cc}} = \frac{C_G}{C_L} \tag{3.1}$$

Where K and H are volatility and solubility coefficients respectively, superscript cc indicates a dimensionless value based on concentrations, and C_G and C_L are the concentration of the flavour in the gas and vapour phase, respectively. Binary HLC has been tabulated for various components [3] and the database is still expanding. By definition, in a binary water-flavour system at equilibrium, the chemical potential (μ) of flavour i is equal in both phases.

$$\mu_i^G = \mu_i^L \tag{3.2}$$

and by definition:

$$\mu_i^0(p,T) + RT\ln\left(\frac{y_i p_T}{p_i^s}\right) = \mu_i^0(p,T) + RT\ln(\gamma_i x_i) \tag{3.3}$$

Where p, p_T, and p^s are the given, total and saturated pressures, respectively, R is the gas constant, T is temperature, x and y are mole fractions in liquid and gas phase respectively and γ is the activity coefficient. Partition coefficient based on mole fraction can be defined as follows:

$$K_i^{yx} = \frac{y_i}{x_i} = \frac{p_i^s \gamma_i}{p_T} \tag{3.4}$$

and Henry's solubility coefficient H^{cc} as follows:

$$H_i^{cc} = \frac{C_L^i}{C_G^i} = \frac{\left(\frac{x_i \times \rho_{sol}}{\sum x_j \times Mw_j}\right)}{\frac{p_T \times y_i}{RT}} = \frac{\left(\frac{\rho_{sol}}{\sum x_j \times Mw_j}\right)}{\frac{p_i^s \gamma_i}{RT}} \tag{3.5}$$

Where ρ is solution density and Mw is a molar mass of compounds. Equation 2.5 will be used in this work to derive HLC from activity coefficients available in the literature, and databases.

To determine activity coefficients, *Excess Gibbs free energy* is one of the useful approaches. Wohl presented a general expression for the Gibbs free energy based on a power series expansion of the effective volume fractions of the solution combinations. [4] Several methods have been developed based on simplified Wohl expansion such as Wilson, van Laar, UNIQUAC and Margules etc. in which interaction parameters (A) of components i and j, are used. In this work, Wohl's expansion is coupled with the one-parameter (two-suffix) Margules equation for a ternary system of water (1), flavour (2) and ethanol (3) and defined as follows: [5]

$$\left(\frac{G^E}{RT}\right)_{123} = A_{12}x_1x_2 + A_{13}x_1x_3 + A_{23}x_2x_3 + (\beta_0 + \beta_1x_1 + \beta_2x_2)x_1x_2x_3 \tag{3.6}$$

where x is the mole fraction of components, β_0, β_1, and β_2 are adjustable parameters.[6] As indicated in literature[7], this approach does *not* lead to an invariance problem for a system consisting of water, ethanol, and ethyl acetate (one of our selected flavours), and we expect that given the low flavour concentration used, this will hold for all flavours under investigation.

Gibbs energy and hence chemical potential is defined in relation to internal energy and entropy, for which absolute values are unknown but can be approached using the fugacity concept.[8] For a system at equilibrium condition the fugacity in the liquid phase $\hat{f}_i^L$ is defined as:

$$\hat{f}_i^L = x_i\gamma_i f_i^0 exp\left(\int_{p^R}^{p_T} \frac{v_i^L}{RT} dp_T\right) \tag{3.7}$$

Where p^R is the reference pressure, f_i^0 the liquid reference fugacity of species i, and v, the partial molar volume of the species in solution. Since water (1) is present in the largest quantity followed by ethanol (3) as a secondary solvent, the symmetric standard state convention is assumed to be valid to find their activity coefficients. This means fugacity for solvents in their pure state is taken as a reference, complying with Raoult's law. The flavour (2) is referenced to the state of "infinite dilution" therewith complying with Henry's law [9] through an unsymmetric fugacity referencing method. For our three components, equation 2.7 now becomes

$$\gamma_1 \equiv \frac{\hat{f}_1^L}{x_2 f_1^0} exp - \int_{p_1^s}^{p_T} \frac{v_1 dP}{RT} \tag{3.8}$$

$$\gamma_2^* \equiv \frac{\hat{f}_2^L}{x_2 H_{21}^{cc}} exp - \int_{p_1^s}^{p_T} \frac{v_2 dP}{RT} \tag{3.9}$$

$$\gamma_3 \equiv \frac{\hat{f}_3^L}{x_3 f_3^0} exp - \int_{p_1^s}^{p_T} \frac{v_3 dP}{RT} \tag{3.10}$$

The asterisk denotes that the activity coefficient is normalized using the unsymmetric convention. The reference pressure for all components is taken equal to the dominant solution vapour pressure, which is water. For solute molecules, O'Connell-Prausnitz [10] showed that:

$$\gamma_2^* = \gamma_2 \times exp\,(-A_{12}) \tag{3.11}$$

and

$$A_{23} = A_{12} + \frac{H_{23}^{cc}}{H_{21}^{cc}} \tag{3.12}$$

Since for flavour compounds by definition: $G^E/RT = \sum_i [x_i \ln(\gamma_i)]$, integration of equation 3.6 gives:

$$\ln \gamma_2^* = A_{12}[x_1(1-x_2) - 1] + A_{23}x_3(1-x_2) - A_{13}x_1x_3 \tag{3.13}$$

By assuming $x_2=0$ substitution of equation 2.12 in 2.13 yields:

$$\lim_{x_2 \to 0} \ln \gamma_2^* = x_3 ln \frac{H_{23}^{cc}}{H_{21}^{cc}} - A_{13}x_1x_3 \tag{3.14}$$

By recalling the definition of the activity coefficient of the flavour in solution (eq. 3.9) and considering $H_{2M}^{cc} = f_2/x_2$ in a dilute system, HLC of the flavour H_{2M}^{cc} can be found using the following equation:

$$H_{2M}^{cc} = (H_{21}^{cc})^{x_1} \times (H_{23}^{cc})^{x_3} \times exp(-A_{13}x_1x_3) \tag{3.15}$$

Equation 3.15 suggests that HLC of a flavour is a function of the mole fraction of both water and ethanol as well as solvent-solvent interaction (A_{13}), which in itself is a function of ethanol concentration.

3.2 Materials and Methods:

3.2.1 Chemicals

All chemical are listed in table 3.1 and used as supplied without further purification.

Table 3. 1 Chemicals and their properties

Chemical name	CAS	Purity (GC)	Molecular Wt. [g/mol]	Boiling Point [C]	Log P†	Supplier
Ethanol	64-17-5	≥99.9	46.07	78.37	-0.31	Merck
Ethyl Acetate	141-78-6	≥99.7	88.11	77.1	0.73	Sigma-Aldrich
Acetone	67-64-1	≥99.8	58.08	56	-0.24	Merck
Isoamyl Alcohol	123-51-3	≥99	88.148	131	1.42	Merck®
Isoamyl Acetate	123-92-2	≥99	130.19	141	2.25	Merck®
Water	-	-	18.013	100	-	Milli Q-Plus system

† *Experimental data* [11]

3.2.2 Static headspace analysis

All HLC were determined using Phase Ratio Variation (PRV). This method is based on the fact that the partition coefficient of a volatile compound in a solution is not a function of the volume of the solution. However, a larger volume of a solution creates more concentrated volatiles in the headspace. This change in concentration can be detected by various headspace analysis. By using gas chromatograph method, change in the reciprocal value of peak areas against the ratio of vial total volume over the liquid phase volume becomes a linear plot with a slope of a' and intercept of b'.

As described by Kolb and Ettre [12] HLC can be determined though:

$$H^{cc} = \frac{a'}{b'} \tag{3.16}$$

Therefore, in this work, various sample volumes: 0.1, 0.2, 0.5, 1, 2 and 5 mL were transferred to standard 20 mL headspace screw neck vials supplied by VWR and incubated for 60 min. After that, 1 mL of headspace sample was taken by CombiPAL autosampler equipped with Hamilton-Gastight 1002 syringe and injected into the same GC mentioned earlier. The syringe was heated 10°C above injection temperature to avoid condensation of vapour. To create the -100 °C trap required for analysis, the GC was coupled with a CryoFocus-4 cold trap. The initial temperature of the GC oven was kept at 40 °C for 30 seconds and increase to a maximum 160 °C with a temperature increase rate of 10°C per second. We used DB-WAXetr a high polarity polyethene glycol (PEG) column from Agilent with flame ionization detector (FID).

All flavour concentrations in this study were produced by mixing 0.5 mL of a flavour taken by 1 mL (±1%) GSM gas-tight syringe with water in 1000 mL (±0.4) volumetric flask creating 0.05 v%. HLC was determined at 30, 40, 50, and 60°C for the binary flavour-water systems.

3.3 Results and discussion

Effect of ethanol on Henry solubility coefficients of flavours

Figure 3.1 is constructed by experimental data and the proposed model (eq. 3.15) with parameters presented in Table 3.2. It illustrates the effect of ethanol concentration on Henry solubility coefficients of flavour compounds with corresponding regression lines and ethanol-water interaction parameters A_{13} (using equation 3.15). In the range of 0-0.05 mole fractions the effect of ethanol on retention of flavours is minor which was in accordance with Conner et al.[13] who reported that activity coefficients for esters were not affected significantly by ethanol concentrations below 17%(v/v) ≈(0.0622 mole fraction) whereas they decrease at higher

ethanol concentrations which means higher Henry's solubility constant H^{cc} in our case. They attribute this to the formation of ethanol clusters that reduce hydrophobic interactions, leading to partitioning into these ethanol-rich clusters.[14]–[18]

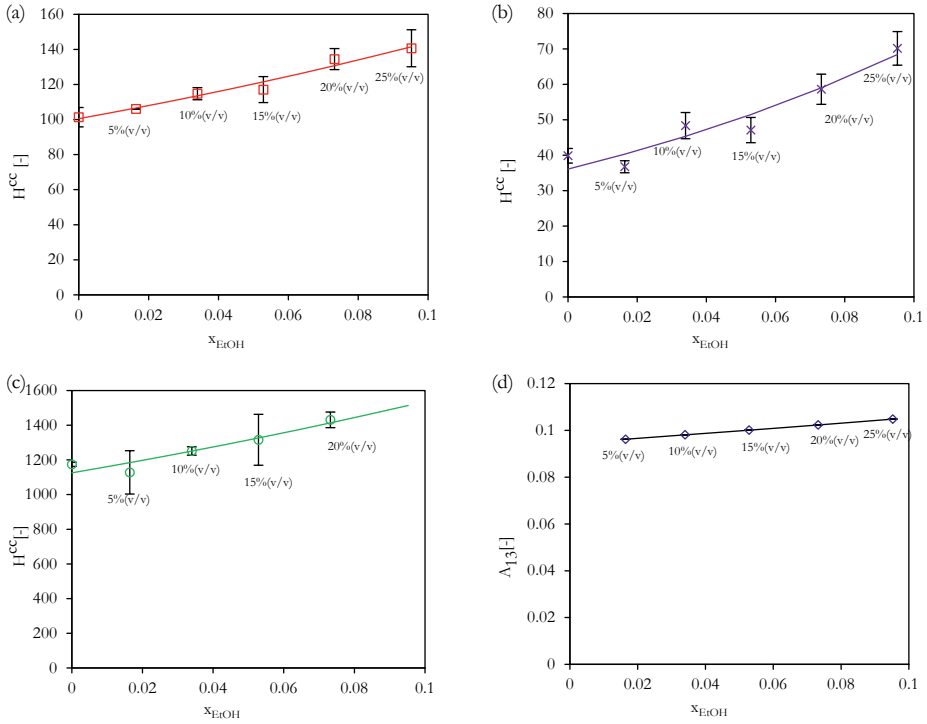

Figure 3. 1 Effect of ethanol on HLC of (a) ethyl acetate, (b) isoamyl acetate, (c) isoamyl alcohol regressed by equation 3.15 using experimental data. (d) Ethanol-water interaction parameter A_{13} as a function of ethanol mole fraction. Markers are experimental data and the values beneath them concentrations as volume percentage

The value of the interaction parameter A_{13} showed a fairly linear increase with ethanol volume fraction. Please note that for all components attention must be paid to the fact that the H_{23}^{cc} values are extrapolated (ultimately to a volume fraction of 1 for ethanol) as illustrated in the appendix (Fig. A.3.1). This co-determines the slope of A_{13}; however, because we did not see any significant difference in the value of A_{13} when comparing flavours, we expect that these values are reliable. It is important to note that applying binary parameters for multicomponent systems by extending the usual quadratic mixing rules in equations of state to higher-order polynomials potentially suffer from the fact that these models are not invariant when a component is divided into two or more identical subcomponents. [19] there are modified mixing rules for multi component systems to overcome this problem [7]. In this work composition $A_{1,3}$ serves not only

as a so-called solvent-solvent interaction parameter in the model but also carries structural characteristics of ethanol-water mixture. Even though we can argue about the degree of linearity of that we believe that this parameter is immune to the above-mentioned complications because of two main reasons. First flavour-matrix systems are such dilute that hardly have any interactions with the solvents and each other; therefore, mixtures can be considered as ternary. Second, dissimilarity between two solvent (water and ethanol) and solute (flavour) is large enough that does not fall in the category of what was called *"identical subcomponents"* addressed by Michelsen and Kistenmacher.[19]

Table 3. 2 Parameters for equation 3.15 at T =30°C, determined using: (i) experimental data; (ii) extrapolated (iii) equation 3.5; (iv) literature[20]; (v) UNIFAC (Dortmund) standard uncertainty values for experimental points $u(H_{21}^{cc})$ are in the table

		Experimental values				*Predicted data*				
	$x_{flavour}$	$H_{21}^{cc\,i}$	$H_{23}^{cc\,ii}$	${\gamma_{21}}^{iii}$	${\gamma_{23}}^{iii}$	$H_{21}^{cc\,iv}$	$H_{21}^{cc\,v\&iii}$	$H_{23}^{cc\,v\&iii}$	${\gamma_{21}}^{v}$	${\gamma_{23}}^{v}$
Ethyl Acetate	9.182×10^{-05} *(1.836×10^{-06})*	100.49 *(5.53)*	965.3	63.7	6.6	107.3	128.4	3197.5	66.4	2.66
Isoamyl Acetate	6.015×10^{-05} *(1.203×10^{-06})*	36.10 *(1.79)*	1181.3	2578.8	76.4	34.4	62.4	35453.7	1945.8	3.42
Isoamyl Alcohol	8.269×10^{-05} *(1.654×10^{-06})*	1125.31 *(12.01)*	8237.6	147.6	20.1	1142.2	1722.7	192787.7	129.2	1.15

Temperature dependence of Henry's law constant

Temperature is known to significantly alter the HLC particularly for those components with a low enthalpy of dissolution. Figure 3.2 shows HLC of the flavour compounds at four experimental temperatures, 30, 40, 50, and 60 ºC, together with their corresponding regressed and predicted data. As it is also shown in table 3.3, the HLC has a higher standard deviation at low temperatures, and this may originate from the relatively low solubility of the flavours, which influences equilibrium quality. Figure 3.2 compares our experimental data with that of Kutsuna et al.[21]and Fenclová et al.[22] both using the column-stripping method. the method of Hilal et al.[20] which uses SPARC (SPARC Performs Automated Reasoning in Chemistry)[23] vapour pressure coupled with activity coefficient models relatively underestimates the HLC of ethyl acetate in water; however, is in a good agreement with the prediction method of Mackay et al.[24] which is based on ratio of vapour pressure over the solubility of isoamyl acetate in water. Our data –especially at higher temperatures– is in better agreement with Meylan and Howard[25] predictive methods which is based on bond contribution values.

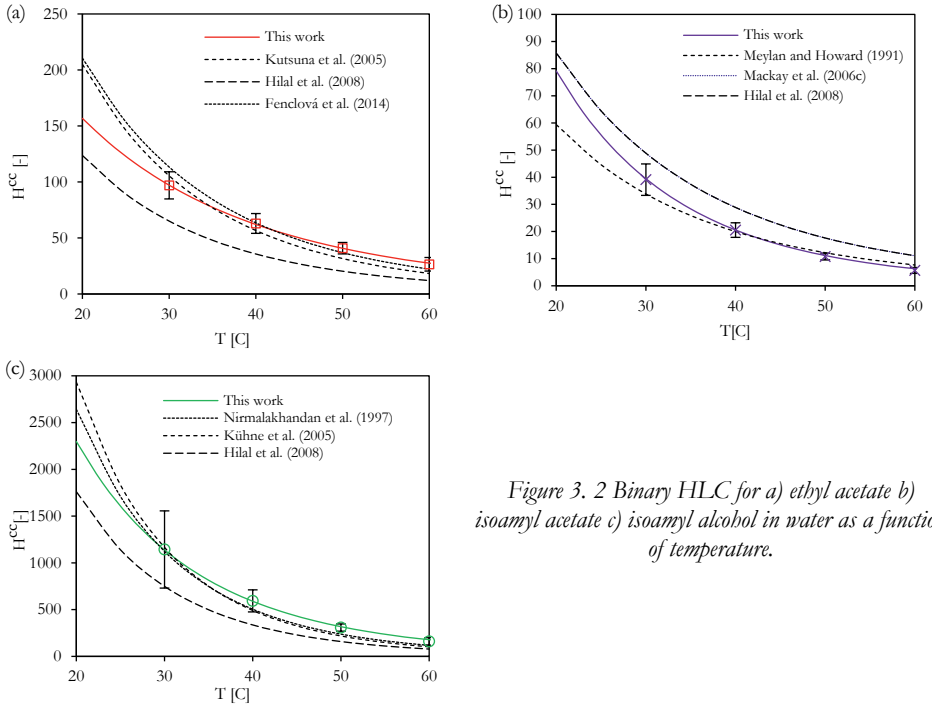

Figure 3. 2 Binary HLC for a) ethyl acetate b) isoamyl acetate c) isoamyl alcohol in water as a function of temperature.

In the absence of experimental data we compared three different predictive methods. Nirmalakhandan and Speece[26] using quantitative structure-activity relationship (QSAR), Kühne *et al.* [27] using their novel model based on two-dimensional structure for organic compounds and Hilal et al.[20], which has already been mentioned above.

Table 3. 3 Experimental HLC data using headspace analysis binary water+ flavour at different temperatures; the standard uncertainties for temperature of the incubator u(T)=0.5 ºC and u(H^{cc}) are given in the table

		H^{cc} [-]			
	$x_{flavour}$	30ºC	40 ºC	50 ºC	60 ºC
Ethyl Acetate	9.182×10^{-05}	*100.49*	*62.98*	*40.89*	*26.55*
	(1.836×10^{-06})	*(12.12)*	*(8.84)*	*(5.10)*	*(6.03)*
Isoamyl Acetate	6.015×10^{-05}	*36.097*	*20.52*	*10.77*	*5.65*
	(1.203×10^{-06})	*(5.79)*	*(2.68)*	*(1.26)*	*(1.09)*
Isoamyl Alcohol	8.269×10^{-05}	*1125.31*	*593.56*	*308.20*	*160.03*
	(1.654×10^{-06})	*(412.01)*	*(117.95)*	*(38.63)*	*(39.52)*

Classically the temperature dependence of Henry's law constant is described by the approaching van 't Hoff introduced for equilibrium constants. The definition of H^{cc} was as follows:

$$H^{cc}(T) = H^{cc\ominus} \times \exp\left((-)\frac{\Delta_{sol}H}{R}\left(\frac{1}{T}-\frac{1}{T^{\ominus}}\right)\right) \tag{3.17}$$

Where $H^{cc\ominus}$ is the HLC at the reference temperature $T^{\ominus}$, $\Delta_{sol}H$ enthalpy of dissolution and R is the universal gas constant. The negative or positive value in the exponent depends on how the

HLC is defined. When applying nonlinear regression to the experimental data (fig. 3.2) using the least squares method, the values tabulated in Table 3.4 were obtained.

Table 3. 4 Henry's law constants at reference temperature (25 ºC) for binary water-flavour system regressed from gas-liquid equilibrium data given in table 3.3

	This work		Literature		
Component	$H^{cc\ominus}$	$\frac{\Delta_{sol}H}{R}$	$H^{cc\ominus}$	$\frac{\Delta_{sol}H}{R}$	Reference
Ethyl Acetate	123^{i}	4500^{iv}	146	5900	[21]
			154	5500	[22]
			89	4800	[20]
Isoamyl Acetate	49^{ii}	5500^{v}	45	5000	[25]
			64	5000	[24]
			64	5000	[20]
Isoamyl Alcohol	1628^{iii}	7000^{vi}	1710	7600	[26]
			1834	8200	[27]
			1140	7600	[20]

To investigate the effect of experimental uncertainties on the uncertainty of driven parameters using equation 3.17 the concept of the propagation of uncertainties [29] is applied and presented in table 3.5.

Table 3. 5 The uncertainty of propagation for driven van 't Hoff parameters (see Appendix B).

Component	Temp ºC	$W(H^{cc\ominus})$	$W(\frac{\Delta_{sol}H}{R})$
Ethyl Acetate	30	6.09	1057.73
	40	18.46	883.73
	50	16.64	487.05
	60	29.56	647.02
Isoamyl Acetate	30	2.11	1048.24
	40	6.63	830.74
	50	5.38	463.49
	60	7.63	552.75
Isoamyl Alcohol	30	45.91	684.35
	40	368.98	1252.84
	50	245.90	497.34
	60	469.40	705.89

3.4 Conclusion

The applied predictive method allows us to describe air-water partition coefficients of flavours in ethanoic solutions. The retention of isoamyl acetate and ethyl acetate increased slightly with an increasing amount of ethanol, whereas these effects were much stronger for isoamyl alcohol (that eventually was completely retained in ethanol). We found that the ethanol concentration dependency of parameter A_{13} plays a pivotal role in describing Henry's law constants, and found similar dependency for the flavours tested, which may help translate our findings to that of other

flavours. The observed dependence of A_{13} may originate from the structural changes reported by others [13]–[17]. As expected, temperature affected partition coefficient of flavours, which we successfully covered through a Van 't Hoff approach.

Appendix A3:

Comparison of using binary HLC of compounds in water and ethanol driven from activity coefficient models with that of extrapolated from experimental data.

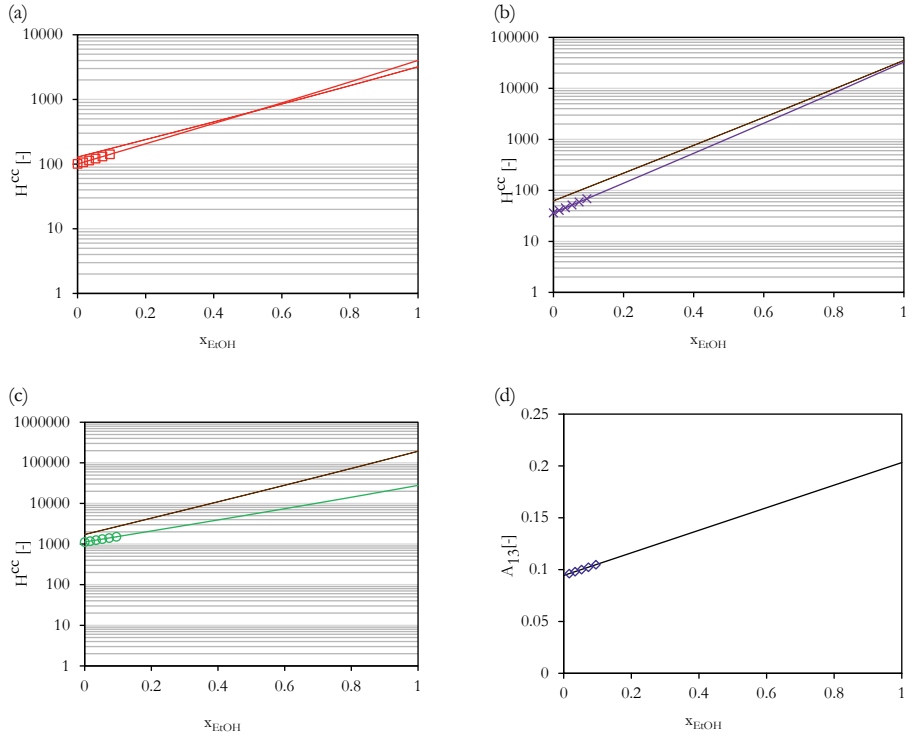

Figure A.3.1. Effect of ethanol on HLC of (a) ethyl acetate, (b) isoamyl acetate, (c) isoamyl alcohol using (—) experimental data (extrapolated from 0.25) or (--) driven from equation 3.5 using UNIFAC (Dortmund). (d) change in interaction parameter between water and ethanol A_{13} as a function of ethanol concentration regressed by equation 3.15. Markers indicate the experimental data range.

Table A.3.1. HLC of flavours at T =30(±0.5)℃ based on the ternary gas-liquid equilibrium of water+ethanol+flavour; the standard uncertainties for experimental HLC, u(H^{cc}), interaction parameters u(A_{13}), ethanol volume fraction u(φ_{EtOH}) ethanol mole fraction u(x_{EtOH}) are given in the table.

		$H_{21}^{cc}: experiment;\ H_{23}^{cc}(x_{Ethanol}=1): extrapolated$				$H_{21}^{cc}: Predicted;\ H_{23}^{cc}(x_{Ethanol}=1): predicted$		
φ_{EtOH}	x_{EtOH}	A_{13}	Ethyl Acetate	Isoamyl Acetate	Isoamyl Alcohol	Ethyl Acetate	Isoamyl Acetate	Isoamyl Alcohol
0	**0**	**0.094**	**100.49**	**36.09**	**1125.31**	**128.36**	**62.40**	**1722.73**
			(5.53)	***(1.79)***	***(12.01)***			
0.05	0.0164	0.096	106.59	40.29	1184.27	135.10	69.13	1858.38
(6.00E-05)	*(1.967E-05)*	*(7.870E-06)*	*(0.12)*	*(1.04)*	*(124.98)*			
0.1	0.0340	0.098	113.53	45.34	1250.89	142.72	77.15	2015.64
(1.00E-04)	*(3.397E-05)*	*(4.212E-05)*	*(3.45)*	*(3.37)*	*(23.94)*			
0.15	0.0529	0.100	121.50	51.48	1326.67	151.38	86.82	2199.52
(1.50E-04)	*(5.285E-05)*	*(6.053E-05)*	*(7.41)*	*(3.56)*	*(146.84)*			
0.20	0.0732	0.102	130.72	59.02	1413.51	161.31	98.59	2416.59
(2.00E-04)	*(7.321E-05)*	*(6.592E-05)*	*(6.00)*	*(4.26)*	*(45.19)*			
0.25	0.0952	0.105	141.48	68.43	undetected	172.78	113.13	2675.55
(2.50E-04)	*(9.523E-05)*	*(7.200E-05)*	*(10.55)*	*(4.74)*				
1	**1**	**0.203**	**4012.13**	**32824.05**	**27858.87**	**3197.52**	**35453.67**	**27864.96**

Appendix B3:

We used experimental data (e.g. H_{21}^{cc}) as input values to calculate other values (e.g. A_{13}) using the model proposed in the main text. These measured values have an experimental uncertainty presented in the tables as u in the subscript and graphically as error bars. The uncertainty related to the extrapolated Henry's solubility constant of flavours in pure ethanol (H_{23}^{cc}) is the main source of uncertainty, which also indirectly affects the water-ethanol interaction parameter (A_{13}). However, as (A_{13}) is constant for all flavours, the standard deviation can be reported from their regression (in this work three values for A_{13}). The propagation of uncertainties for the temperature dependency of Henry's law constant can be found using the following description [29]:

$$R = R(x_1, x_2, \dots, x_n) \tag{B.3.1}$$

$$w_R = \left[\left(\frac{\partial R}{\partial x_1} w_1\right)^2 + \left(\frac{\partial R}{\partial x_2} w_2\right)^2 + \cdots + \left(\frac{\partial R}{\partial x_n} w_n\right)^2\right]^{1/2} \tag{B.3.2}$$

R is a result of independent variables $x_1, x_2, \dots, x_n$, w_R is the uncertainty in the results and $w_1, w_2, \dots, w_n$ are uncertainties in the independent variables.

B1. Example for Ethyl Acetate at 60 ºC assuming $H^{cc\ominus} = f(H^{cc}(T), T, \frac{\Delta_{sol}H}{R})$

$$H^{cc\ominus} = \frac{H^{cc}(T)}{exp\left(\frac{\Delta_{sol}H}{R}\left(\frac{1}{T} - \frac{1}{T^{\ominus}}\right)\right)}$$

$$\frac{dH^{cc\ominus}}{d(H^{cc}(T))} = exp\left(\frac{-\Delta_{sol}H}{R}\left(\frac{1}{T} - \frac{1}{T^{\ominus}}\right)\right) = 4.88$$

$$\frac{dH^{cc\ominus}}{d\left(\frac{\Delta_{sol}H}{R}\right)} = -H^{cc}(T)exp\left(\frac{-\Delta_{sol}H}{R}\left(\frac{1}{T} - \frac{1}{T^{\ominus}}\right)\right)\left(\frac{1}{T} - \frac{1}{T^{\ominus}}\right) = 0.046$$

$$\frac{dH^{cc\ominus}}{dT} = \frac{\frac{\Delta_{sol}H}{R}H^{cc}(T)exp\left(\frac{-\Delta_{sol}H}{R}\left(\frac{1}{T} - \frac{1}{T^{\ominus}}\right)\right)}{T^2} = 5.255$$

$$\frac{dH^{cc\ominus}}{dT^{\ominus}} = \frac{\frac{-\Delta_{sol}H}{R}H^{cc}(T)exp\left(\frac{-\Delta_{sol}H}{R}\left(\frac{1}{T} - \frac{1}{T^{\ominus}}\right)\right)}{T^{\ominus 2}} = -6.562$$

$$w\left(H^{cc}(T)\right) = H^{cc}(T) \times w\left(H^{cc}(T)\right) = 26.55 \times 0.23 = 6.030$$

As the term $\Delta_{sol}H/R$ itself is a regressed value we treat it as a constant.

$$w\left(\frac{\Delta_{sol}H}{R}\right) = \frac{\Delta_{sol}H}{R} \times w\left(\frac{\Delta_{sol}H}{R}\right) = 4500 \times 0 = 0$$

$$w(T) = T \times w(T) = (60 + 273.15) \times 0.015 = 0.5$$

$$w\left(T^{\ominus}\right) = T^{\ominus} \times w\left(T^{\ominus}\right) = 298.15 \times 0 = 0$$

$$W(H^{cc\ominus})_{60℃} = \sqrt{4.88^2 \times 6.03^2 + 0.046^2 \times 0^2 + 5.25^2 \times 0.5^2 + -6.56^2 \times 0^2} = 29.54$$

B2. For $\frac{\Delta_{sol}H}{R}$ rearranging equation 3.15 yields:

$$\frac{\Delta_{sol}H}{R} = \frac{\ln\left(\frac{H^{cc}(T)}{H^{cc\ominus}}\right)}{\left(\frac{1}{T} - \frac{1}{T^{\ominus}}\right)}$$

$$\frac{d\frac{\Delta_{sol}H}{R}}{dH^{cc}(T)} = \frac{1}{H^{cc}(T)\left(\frac{1}{T} - \frac{1}{T^{\ominus}}\right)} = -106.90$$

$$\frac{d\frac{\Delta_{sol}H}{R}}{dH^{cc\ominus}} = \frac{-1}{H^{cc\ominus}\left(\frac{1}{T} - \frac{1}{T^{\ominus}}\right)} = 23.07$$

$$\frac{d\frac{\Delta_{sol}H}{R}}{dT} = \frac{ln\left(\frac{H^{cc}(T)}{H^{cc\ominus}}\right)}{T^2\left(\frac{1}{T} - \frac{1}{T^{\ominus}}\right)^2} = -111.26$$

$$\frac{d\frac{\Delta_{sol}H}{R}}{dT^{\ominus}} = \frac{-ln\left(\frac{H^{cc}(T)}{H^{cc\ominus}}\right)}{T^{\ominus 2}\left(\frac{1}{T} - \frac{1}{T^{\ominus}}\right)^2} = 138.91$$

$$w\left(H^{cc}(T)\right) = H^{cc}(T) \times w\left(H^{cc}(T)\right) = 26.55 \times 0.23 = 6.03$$

Using calculated $H^{cc\ominus}$ results:

$$w\left(H^{cc\ominus}\right) = H^{cc\ominus} \times w\left(H^{cc\ominus}\right) = 0.296$$

$$w(T) = T \times w(T) = (60 + 273.15) \times 0.015 = 0.5$$

$$w\left(T^{\ominus}\right) = T^{\ominus} \times w\left(T^{\ominus}\right) = 298.15 \times 0 = 0$$

$$W\left(\frac{\Delta_{sol}H}{R}\right)_{60℃} = \sqrt{-106.90^2 \times 6.03^2 + 23.60^2 \times 0.2588^2 + 109.69^2 \times 1^2 + 136.95 \times 0^2}$$

$$= 647.02$$

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Chapter IV

Batch Stripping of Flavour Active Compounds from Beer: Effect of Dry Matter and Ethanol on Equilibrium and Mass Transfer in a Packed Column

Physiochemical similarities of volatile compounds and their interactions with the beer matrix are the main challenging factors in selective separation of ethanol for the production of non-alcoholic beer and removal of excess (off-)flavours produced during fermentation, such as isoamyl acetate. In this paper, we are especially interested in the effect of beer dry matter, a complex mixture of carbohydrates and proteins, and of ethanol on flavour behaviour during treatment with a packed bed column using CO_2 as a stripping agent. By analysing the gas phase at different dry matter concentrations, we observed that its' presence is a facilitating factor for ethyl acetate and isoamyl acetate release, whereas isoamyl alcohol is retained in the liquid phase. These effects are a result of combined mass transfer effects and affinity for carbon dioxide, which are both affected by the presence of ethanol in the feed stream. Mass transfer analysis of isoamyl alcohol and ethanol revealed that the resistance is not controlled by their solubility in water but the affinity to CO_2.

This chapter was published as:
Ammari, A., Schroen, K., 2019. Batch Stripping of Flavour Active Compounds from Beer: Effect of Dry Matter and Ethanol on Equilibrium and Mass Transfer in a Packed Column. Food Bioprod. Process.

4.1 Introduction:

Flavours are present in beverages at ppm level; therefore, any interaction they may have with the food matrix can influence their release greatly. Flavour compounds can be physically trapped in microstructures [2] (large carbohydrates), or adsorb to the surface of a non-volatile compound (proteins) [3], or be affected by physiochemical effects such as a change in water activity. [4]

On the other hand, one of the frequent problems associated with food processing is the loss of flavour, which results in flavour profile distortion or even in a complete lack of flavour. [5] This is of course not desired, and flavour composition needs to be controlled, ideally through mild processing considering temperature sensitivity of foods in general. For example, in the brewing industries, the taste of beer determines its quality to a large extent, and this also holds for alcohol-free beer. One of the prerequisites to achieve control over product quality is a mild-temperature treatment to protect nutrients such as proteins from denaturation. One of the methods of choice is stripping [6] which is an industrially established technique for the separation of volatile organic compounds (VOCs) from aqueous systems [7], [8]. Basic principles of this method have been examined for separation of terpene hydrocarbons from orange juice [6]. However, this method has poor selectivity and affects all volatile flavours and also ethanol, so to design this system properly, insights are needed that relate flavour and ethanol transfer to any additional effect that matrix components may have.

In general, two aspects need to be considered to understand the migration of flavours, mass transfer kinetics in a gas-liquid system, and thermodynamic equilibria of flavour with gas and possibly also the matrix. Thermodynamics determines the maximum achievable migration of a component from one phase to another in a closed system whereas kinetics show how fast that equilibrium can be achieved. Although equilibrium is often not reached, it is still needed as an upper-boundary in modelling approaches, as also used here.

It is well-understood that the presence of various components in food may have a significant effect on the behaviour of flavours, as recently reviewed by us [9]. We showed that, for example, volatile flavours with hydrophobic characteristics tend to concentrate in the emulsified lipid phase [10] therewith acting as the main rate-limiting factor for flavour migration from the liquid-gas interface.

In the current work, we will investigate beer dry matter and report on how it affects mass transfer resistance and partition coefficients of beer flavours in ethanol-water mixtures, by determining overall mass transfer coefficients and Henry's law constants (HLC) using a batch stripping column.

4.2 Materials and Methods:

4.2.1 Beer composition

The beers of choice are all pilsner beers (light ale) and available in the Dutch supermarkets. We evaluated 4 alcoholic beers (Amstel, Heineken, Jupiler, Hertog Jan), and one alcohol-free beer (Amstel 0%) that were purchased in glass bottles of 0.30 L. The concentration of volatile compounds was determined by dissolving 1 mL of beer in 4 mL of acetone containing a trace amount of n-butanol as an internal standard. Next, 1 μL of this liquid was injected into a gas chromatograph (Interscience FID, type Finnigan Trace GC connected to a DB-WAXetr Agilent® capillary column (30 m length, 0.25 mm inner diameter, coated with 0.25 μm thick polyethylene glycol film and 7-inch cage)). The volatile composition is given in Appendix B.4; figure B.4.1.

Non-volatile compounds were determined by freeze-drying (Epsilon 2-6D LSCplus from Christ® with the built-in program shown in figure B.4.3) and gravimetry was carried out on at least five independent samples to determine dry weight. Protein content was measured by the Dumas method using FlashEA® 1112 NC Analysers (Thermo Fisher Scientific, Breda, The Netherlands). Ash content was determined after treatment in a Carbolite® ashing furnace at 550°C for 24 hours and represents the sum of all minerals. More information can be found in Appendix B.4; figure B.4.2. The alcoholic beer typically contains 35-37 g dry matter per litre of which 5 [w%] is protein. The non-alcoholic beer was significantly lower in flavours compared to its' alcoholic counterparts.

The protein size distribution was determined by HP-SEC equipped with UV @ 214nm detector and columns: TSKGel G3000SWXL 5 μm 300×7.8 mm and TSKGel G2000SWXL 5 μm 300×7.8 mm. Eluent was 30% Acetonitrile in MilliQ + 0.1% trifluoroacetic acid at a flow rate of 1.5 ml/min. The column temperature was 30°C for 20 minutes runtime.

The composition of carbohydrates was determined by Thermo Scientific UltiMate 3000 UHPLC equipped with Shodex KS-802 300×8 mm column and refractive index detector using MilliQ water as eluent at a flow rate of 1 mL/min. The column temperature was set at 80°C for 15 min. The viscosity of the samples was measured using Anton Paar Rheometer MCR301 equipped with double-gap measuring systems (according to DIN 54453) at constant 20 °C.

4.2.2 Chemicals and sample preparation

All chemical are listed in table 4.1 and used as supplied

Table 4.1. Chemicals and their properties. † Experimental data [11]

Chemical name	Purity (GC)	Molecular Wt. [g/mol]	Boiling Point [C]	Log P†	Supplier
Ethanol (SeccoSolv®)	≥99.9	46.07	78.37	-0.31	Merck
Ethyl Acetate (Chromasolv®)	≥99.7	88.11	77.1	0.73	Sigma-Aldrich
Acetone (SupraSolv®)	≥99.8	58.08	56	-0.24	Merck
Isoamyl Alcohol (Emsure®)	≥99	88.148	131	1.42	Merck®
Isoamyl Acetate (Emplura®)	≥99	130.19	141	2.25	Merck®
Water		18.013	100	-	Milli Q-Plus system

All solutions are prepared in either 250(±0.15), 500(±0.25), or 1000(±0.4) mL volumetric flasks using MilliQ water mixed with 0.5 mL flavours taken with a 1 mL (±1%) Hamilton 1000 series syringe. Two different 'model beers' were investigated consisting of (1) water-flavours-dry matter and (2) water-flavour-ethanol.

4.2.3 Stripping column

The stripping column had an inner diameter of 5 cm and was packed with Salzer® Mellapak M750Y with the specific interfacial area a =746 m^2/m^3 (Figure 4.1). The constant inflow of gas was controlled by a unit from Convergence® and injected from the bottom. The effluent gas was analyzed every three minutes by Agilent® 490 Micro GC with a thermal conductivity detector (TCD). The gas-phase was calibrated using a mixture provided by Air Liquide the Netherlands. As the column did not have heating or cooling jacket, the temperature variation during the experimentation was monitored and logged every second. The column was filled with 500 mL water-flavour-dry matter solution (which foams) and 750 mL non-foaming ethanolic solutions. The column content was recirculated by a centrifuge pump with a revolution per minute scaled from 0 to 100 set on 50. Initial flavour concentrations in the column were 0.5 mL/L for all experiments.

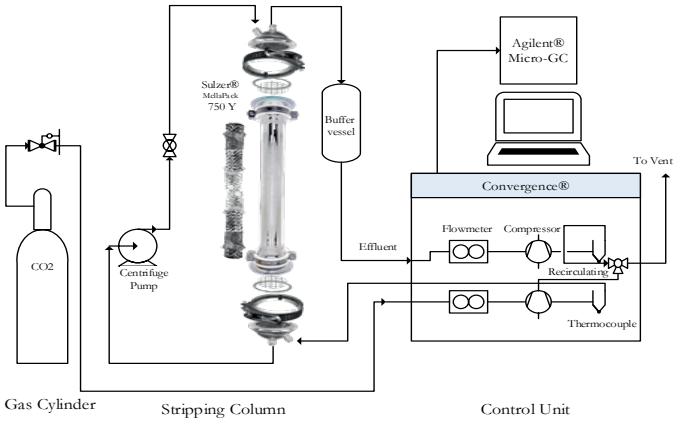

Figure 4.1. Schematic overview of the setup with the stripping column and internals.

4.3 Theory

Mathematical models describing flavour release from aqueous systems should address at least three general phenomena; namely, diffusion in the liquid phase, diffusion in the gas phase, and partitioning characteristics of the flavour in both phases. These stages have already been studied and reviewed extensively [12]–[14] and here we summarize them.

Equilibrium: In 1803, William Henry found that dissolution of a gas in a liquid with a constant volume is proportional to its pressure [15]. This proportionality is called Henry's law constant (HLC) and can be expressed as equation 1.

$$K^{cc}(-) = \left(\frac{C_G}{C_L}\right)_e = \frac{1}{H^{cc}} = \frac{R.T}{K^{pc}} = R.T.H^{cp} \tag{4.39}$$

Where K and H are Henry's solubility and volatility coefficients, respectively, C_G and C_L are gas and liquid concentrations, respectively, R is the ideal gas constant and subscript e denotes equilibrium. Superscript cc indicates HLC is concentration based and dimensionless, pc indicates that HLC has a dimension of the partial pressure of headspace over the liquid molar concentration and cp indicates the liquid molar concentration over the partial pressure of headspace. HLC is an essential value in designing stripping columns. For a batch operational conditions, the following correlation can be expressed:

$$\frac{dM}{dt} = -V_L \frac{dC_L(t)}{dt} = Q_G C_G(t) = Q_G C_L(t) K^{cc} \tag{4.40}$$

where M is the total transported mass of flavour, Q_G is the gas volume flow rate, V_L is the liquid volume of the column. If the effluent gas is in equilibrium with the liquid phase: $C_G(t) = C_L(t) \times K^{cc}$. A numerical solution for the second and last term of equation 4.2 yields: (Appendix A.4.1):

$$\ln\frac{C_L(t)}{C_L(0)} = -t\frac{K^{cc}Q_G}{V_L} \tag{4.41}$$

where $C_L(0)$ is the initial flavour concentration. Assuming equilibrium, eq. 4.3 can be rearranged to predict equilibrium gas phase concentration (eq. 4.4):

$$C_G^e(t) = C_L(0)_t K^{cc} exp\left(-t\frac{K^{cc}Q_G}{V_L}\right) \tag{4.42}$$

In this correlation, the partition coefficient is temperature-dependent but assumed to be concentration-independent and saturated concertation of the effluent gas at time the t is a function of its corresponding concentration at the same time in the liquid phase. There are various methods to monitor if the flavour leaving the column in the gas phase in equilibrium with the liquid phase, as discussed in detail by Gosset *et al.* (1985); however, we compared the effluent concentration behaviour with a well-known activity coefficient method which will be discussed later.

Kinetics: When equilibrium is not established and the gas phase is not saturated, the concentrations need to be approached using mass transfer rate expressions that are described next for well-mixed conditions. According to Fick's first law, the rate of unidirectional diffusion from the liquid phase to the gas phase is as follows determined by the concentration gradient in each phase:

$$\frac{dM}{dt} = -D_{AB}\frac{\partial C}{\partial x} \tag{4.43}$$

D_{AB} is the diffusion coefficient of a flavour A into solvent B and $\partial C/\partial x$ is concentration gradient which is the driving force for mass transfer. If we assume that the boundary layer thicknesses are constant (but not necessarily equal), and there is no concentration build-up in at the interface; equation 4.5 for the mass transfer through the interface in the direction from liquid to gas phase can be rewritten as follows:

$$\frac{dM}{dt} = k_L.a\big(C_L(t) - C_L^i(t)\big) = k_G.a\big(C_G^i(t) - C_G(t)\big) \tag{4.44}$$

where $k_L=(\partial C/\partial x)_L$ and $k_G=(\partial C/\partial x)_G$ are mass transfer coefficients in liquid and gas phase, respectively, a is the effective area of contact between the two phases per unit of bed

volume with units of reciprocal length, and superscript i denotes the concentration at the interface. Resistance to mass transfer may be present in both liquid or gas phase for which overall mass transfer coefficients can be used and arranged as in equation 4.7:

$$\frac{dM}{dt} = k_{OG}.a(K^{cc}C_L(\mathrm{t}) - C_G(\mathrm{t})) \tag{4.45}$$

According to the two-film theory of Lewis and Whitman (1924), the overall mass transfer coefficient is the result of two resistances in the liquid and gas phase boundary layers. This

model assumes steady-state diffusion, so the concentration of solute at the interface for one phase is in equilibrium with the other phase. For the liquid phase, this is expressed by eq 4.8:

$$\frac{1}{k_{OL}} = \frac{1}{k_L} + \frac{1}{K^{cc} k_G} \tag{4.46}$$

and for the gas phase in eq 4.9:

$$\frac{1}{k_{OG}} = \frac{K^{cc}}{k_L} + \frac{1}{k_G} \tag{4.47}$$

This correlation suggests that the overall mass transfer coefficients are a function of solute-solvent partition coefficient, which itself is a function of temperature, the characteristics of the stripping gas, and the liquid phase composition. For example, the partition coefficient K^{cc} of ethanol in steam stripping is much higher than in CO_2-stripping, which implies that in the latter case, mass transfer resistance is much more determined by the liquid phase. Furthermore, the actual flow conditions and the measurement system seem to play a role. De Roos [12] states that for a system consisting of a stagnant water phase and a turbulent gas $K^{cc} > 10^{-3}$ is required to assume that the whole resistance is in the liquid phase. Whereas Munz and Roberts [18] suggest a value larger than 0.55 for their mechanical surface aeration system.

Mackay *et al.* [19] integrated the third term in Eq. 4.2 along with the last term of Eq. 4.7 with boundary conditions based on the interfacial area in column A to quantify the degree of removal as follows:

$$\frac{C_G(t)}{C_G^e(t)} = 1 - exp\left(\frac{-k_L A(t)}{Q_G K^{cc}}\right) \tag{4.48}$$

$C_G(t)/C_G^e(t)$ indicates the degree to which equilibrium is achieved at time t. Numerical calculation of the second and third term of the equation 4.2 (see appendix A.4.2) yeids:

$$\ln\frac{C_L(t)}{C_L(0)} = t\frac{K^{cc} Q_G}{V_L}\left(exp - \left(\frac{k_L a\, V_L}{Q_G K^{cc}}\right) - 1\right) \tag{4.49}$$

This correlation is similar to that of Cho and Wakao [20] and suggests that if $k_L a/Q_G K^{cc} > 5$ the exponential value is small enough to reduce equation 4.11 to 4.3; if $k_L a/Q_G K^{cc} < 0.1$ equation 4.11 will reduce the following equation:

$$\ln\frac{C_L(t)}{C_L(0)} = -t\frac{k_L a}{V_L} \tag{4.50}$$

Because the area across which mass transfer occurs (a) and the overall mass transfer coefficient (k_L) cannot be determined independently, it is a common practice that the two terms are combined and referred to as the volumetric mass transfer coefficient.

4.4 Results and discussions

4.4.1 Beer compositions

Table 2 shows that the proteins in our sample beers are smaller than 2 kDa which means they are mainly peptides.

Table 2 Protein size distribution of the beers [w%]

	>50kD	50-10kD	10-4kD	4-2kD	<2kD
Amstel 0%	12.1	7.7	6.2	6.4	67.7
Amstel 5%	6.5	7.0	6.7	7.4	72.4
Heineken	4.0	7.9	7.4	8.0	72.8
Jupiler	3.8	8.7	8.0	8.4	71.1
Hertog Jan	5.3	9.9	8.2	8.1	68.5

Except for alcohol-free beer, which was rich in maltose, all of the other beers contained more or less the same size distribution range as shown in Table 4.3 (DP is the degree of polymerization).

Table 4.3. Carbohydrate composition of the beers % (mg/L) (w/v)

	>DP6	DP6	DP5	DP4	Maltose	Glucose	Fructose
Amstel 0%	21.93	1.11	2.38	12.53	52.07	7.49	2.49
Amstel 5%	59.04	6.91	15.29	12.60	4.86	0.31	0.99
Heineken	61.68	6.76	16.21	9.34	5.12	0.44	0.45
Jupiler	63.39	8.31	16.69	7.09	3.56	0.62	0.33
Hertog Jan	63.15	7.34	15.17	8.61	4.70	0.39	0.64

4.4.2 Partition coefficient

To investigate the equilibrium condition of the column we compared experimentally detected effluent gas concentration with predictive methods. To do so we used the following correlation between the partition coefficient and activity coefficient.

$$K_i^{cc} = \frac{C_G^i}{C_L^i} = \frac{\frac{p_T \times y_i}{RT}}{\left(\frac{x_i \times \rho_{sol}}{\sum x_j \times Mw_j}\right)} = \frac{\frac{p_i^s \gamma_i}{RT}}{\left(\frac{\rho_{sol}}{\sum x_j \times Mw_j}\right)} \tag{4.51}$$

where ρ is the solution density p_T, and p^s are the total and saturated pressures, respectively, Mw is the molar mass of the compound, x and y are mole fractions in liquid and gas phase respectively, and γ is the activity coefficient predicted with UNIFAC (Dortmund). The density and the partition coefficient of flavours in water-ethanol solution with different ethanolic strength are listed in Appendix C.4.1.

It is evident that all effluent gasses are leaving the column above their thermodynamic equilibrium values if we assume UNIFAC our benchmark of equilibrium (Appendix C4, fig. C.4.2-C.4.4). During the first few minutes of operation, the gas-phase concentration of isoamyl acetate might be above equilibrium in the absence of matrix components most probably due to its' high partition coefficient [21]. Because the partition coefficient of compounds does not change with the gas flow, we can assume that the system operates under equilibrium conditions (fig. C.4.5). It is also good to mention that relatively high flavour concentrations were used in this work to prevent detection limitations.

To monitor the effect of matrix composition on the partition coefficient of flavours, we used a normalized Henry's solubility coefficient expression as follows:

$$\widehat{K}^{cc} = \frac{K_{GW}^{cc}}{K_{GM}^{cc}} \tag{4.52}$$

Where subscripts GW and GM indicate gas-water and gas-liquid mixture partition coefficients, respectively. In Figure 4.2, the normalized Henry's solubility coefficient is shown as a function of dry matter content for major beer esters namely ethyl acetate and isoamyl acetate. Figure 4.2 suggests that at lower dry matter concentrations the volatility of flavours is not affected, but at 35-40 g dry matter per litre, a range that our typical beers contain a slight increase of the Henry coefficient may be observed. Because of low concentration of proteins (~4 g/L) and minerals compare to that of carbohydrates (~32 g/L) the observed effect on flavour release is most probably related to hydration of carbohydrates which leads flavours to concentrate in the remained available water. This concentration creates a larger driving force for flavours to transfer from the interface to the gas phase.

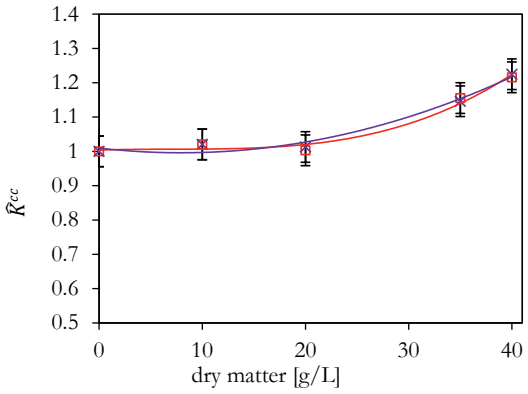

Figure 4.2. Effect of dry matter on relative Henry coefficient of flavours □ ethyl acetate and × isoamyl acetate determined by gas sampling and equation 4. Gas flow rate 3000 mL/ min (±10) initial flavour concentration 0.5(±0.005), feed volume 500 mL (±0.25), column temperature 294.87 K (±0.17) and operating time 120 min; values in parenthesis are standard errors.

After 120 min stripping, the concentration of esters that remained in the liquid phase in the column (fig.3a) was in accordance with their partitioning strength. The hydrophobic and long-changed isoamyl acetate was removed completely, whereas ethyl acetate still remained in the liquid phase, and isoamyl alcohol showed some degree of retention (fig. 4.3b).

We used MacKay's method (eq. 4.3) to determine partition coefficients (fig. 4.2&4.5). Because this method uses the slope of the logarithmic concentration depletion of volatiles; it is suitable for systems with sufficiently high partitioning characteristics. Isoamyl alcohol as we can see in fig. 4.3b has a concentration gain in the liquid phase. That is why the relative partition coefficient cannot be determined through this method and is absent in figure 4.2.

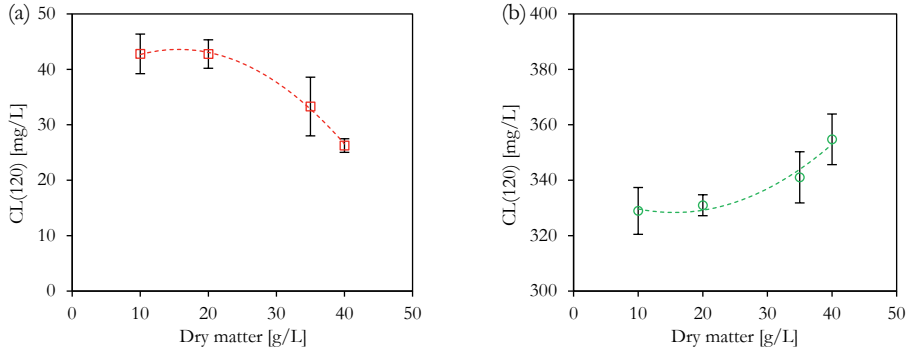

Figure 4.3. Effect of dry matter on the residual concentration of flavours a) □ ethyl acetate and b) ○ isoamyl alcohol after stripping with an operational condition similar to that of fig. 4.2.

Beer is a Newtonian fluid [22] and its viscosity change during stripping might influence the mass transfer characteristics during stripping. This is investigated further, and in line with this also the

ethanol concentration is investigated, not only as an effect on viscosity but also for its' co-solvent effect (fig. 4.4).

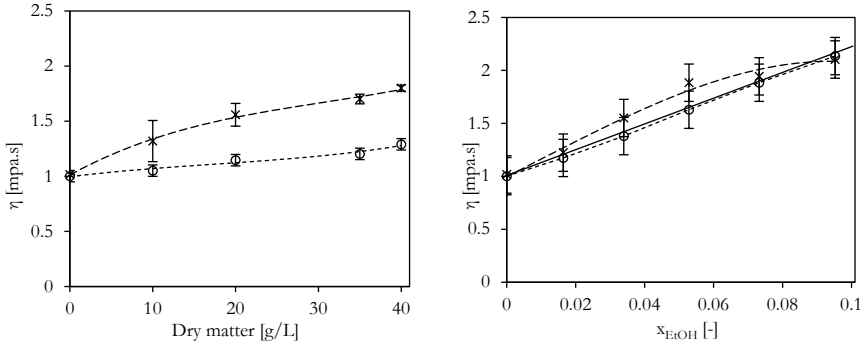

Figure 4.4. Measured viscosity of feed(--) and column residue (––) at 293.15 K a) dry matter, water, flavour; b) water, ethanol, flavour, at operational conditions similar to fig. 2. (—) NIST, the values are driven from AspenPlus

The effect of dry matter on the viscosity of the column feed was up to ~ 30% in the studied concentration range, whereas ethanol affected viscosity up to ~200% (Figure 4.4).

Ethanol also influences the partition coefficient of volatile organic compounds (VOCs), and retains flavours in the liquid phase (see Figures 4.5 constructed based on the relative partition coefficient correlation introduced in eq. 4.12, and Figure 4.6).

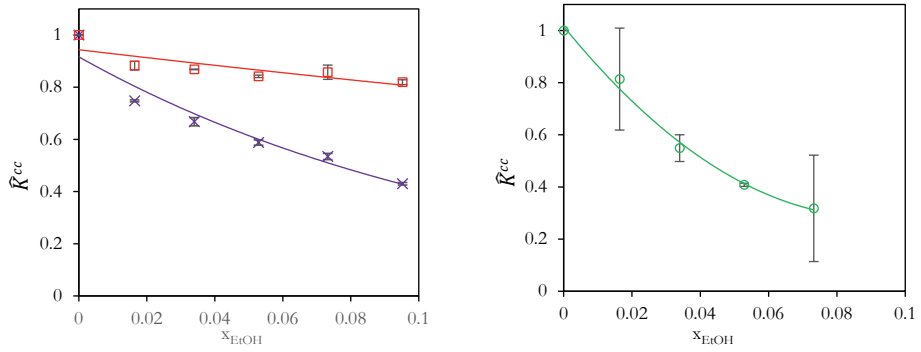

Figure 4.5 Effect of ethanol on relative HLC determined by gas sampling and equation 4; a) □ ethyl acetate, × isoamyl acetate b) ○ isoamyl alcohol; Gas flow rate 3000 mL/ min (±10) initial flavour concentration 0.5 mL (±0.005), feed volume 750 mL (±0.25), column temperature 294.80 K (±0.09) and operating time 120 min; values in parenthesis are standard errors.

From the results in Figure 6 that relates the composition of the feed after treatment, we concluded that the components followed their Log P characteristics. Again, the concentration of the components with an alcoholic group (ethanol, isoamyl alcohol) did not change significantly due to the relatively low affinity for CO_2. Isoamyl acetate is much less polar making it more

favourable for separation with CO_2 whereas the presence of ethanol has a larger retention effect on the heavier ester isoamyl acetate.

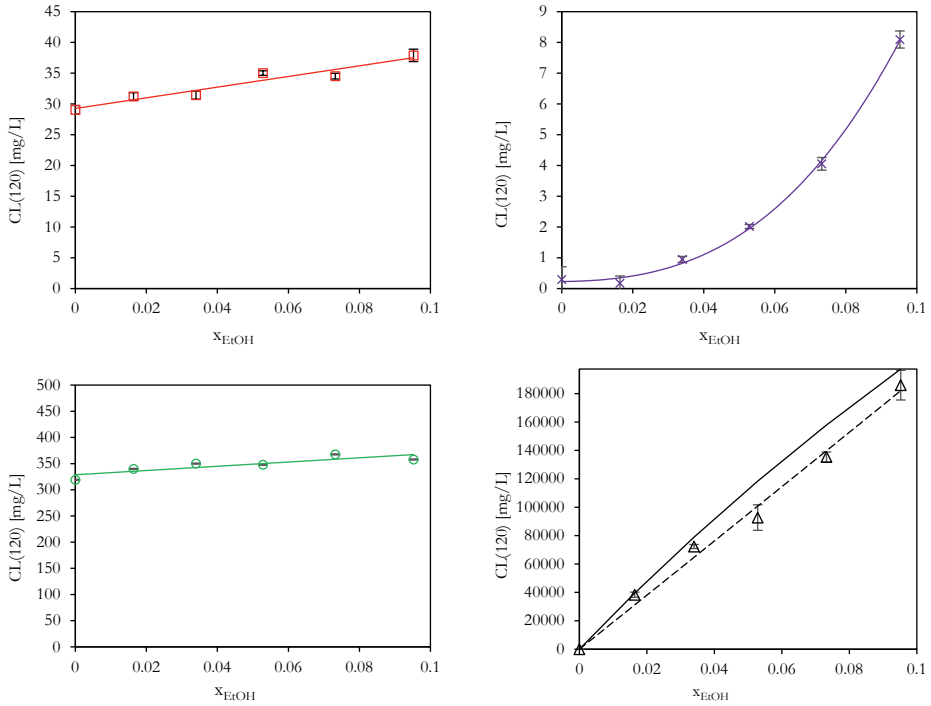

Figure 4.6. Effect of ethanol on the concentration of volatiles in column residue after 120 min operational time $C_L(120)$ a) □ ethyl acetate, b)× isoamyl acetate c) ○ isoamyl alcohol, d) △ ethanol and (--) parity line for mole fraction to mg/L conversion.

4.4.3 Mass transfer coefficient

Using the second term of equation 4.1 along with equation 4.3, the flavour concentration in the gas can be determined, starting from a constant $C_G^e(0)$ equation 4.8 is used to predict overall mass transfer coefficients for $C_G(t) < C_G^e(0)$. Figure 4.7 is constructed to represent the effect of K^{cc} on mass transfer as function a of time. Given the changes in concentration (especially in ethanol) during the stripping process, the 'partition coefficient' was determined using equation 4.13, and $C_G^e(t)$ through equation 4.4. Figure 4.7 is a graphical representation of equation 4.10 in the region where $C_G(t)/C_G^e(t) < 1$.

From figure 4.7, which includes a change in ethanol concentration as a function of time, it is clear that the mass transfer coefficient is greatly influenced by the values used for K_{ox} and more so by the amount of ethanol present (so going from left to right in the figure). The presence of ethanol increases the solubility of all flavours, leading to the lower volatility of compounds.

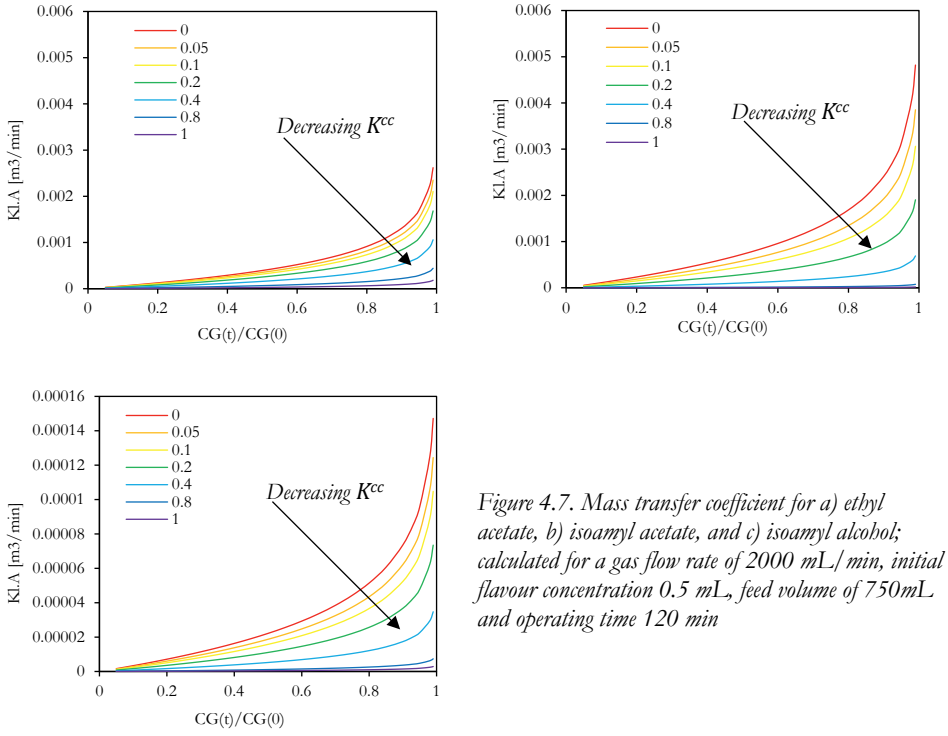

Figure 4.7. Mass transfer coefficient for a) ethyl acetate, b) isoamyl acetate, and c) isoamyl alcohol; calculated for a gas flow rate of 2000 mL/min, initial flavour concentration 0.5 mL, feed volume of 750mL and operating time 120 min

Furthermore, it is already been discussed that the retention effect of ethanol on short-chain esters is lower than that of a longer chain. [23] This behaviour was true in this work(fig. C.4.5) comparing ethyl acetate and isoamyl acetate (fig. C.4.5). Besides, the determined Henry coefficients did not show strong dependency with gas flow rate when going from 2000 to 3000 mL/min (fig. C.4.5) especially for highly hydrophobic isoamyl acetate; however, mass transfer coefficient increased significantly (fig. 4.9). Even though shorter residence time at higher gas flowrates the turbulence enhances gas-liquid interfacial mass transfer leading fast equilibrium condition.

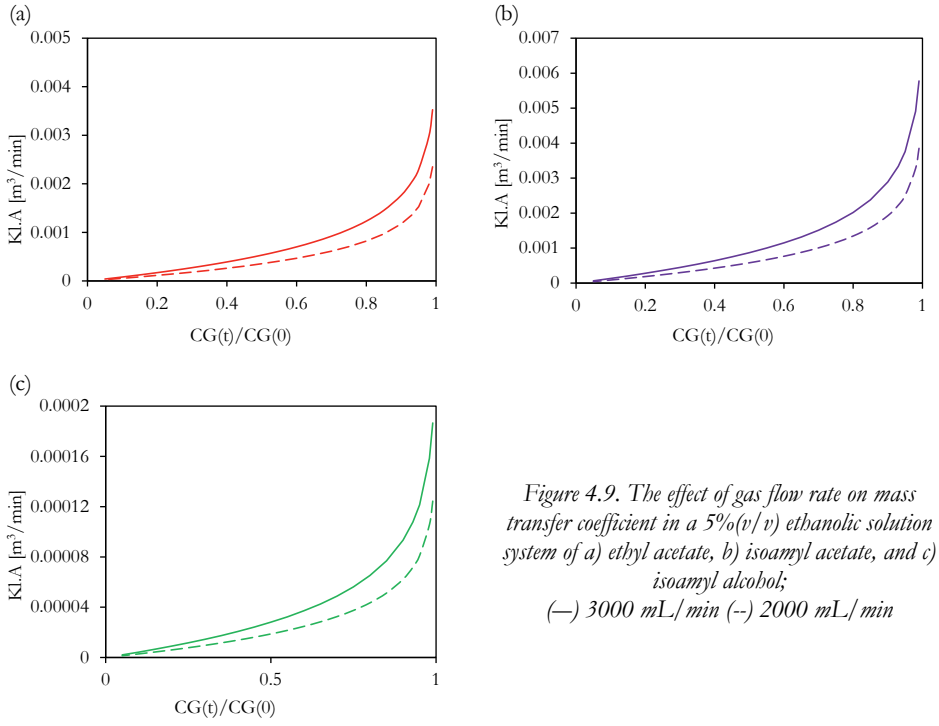

Figure 4.9. The effect of gas flow rate on mass transfer coefficient in a 5%(v/v) ethanolic solution system of a) ethyl acetate, b) isoamyl acetate, and c) isoamyl alcohol;
(—) 3000 mL/min (--) 2000 mL/min

4.5 Conclusion

We investigated the effect of volatile and non-volatile compounds on flavour stripping using a packed bed column. We chose to use CO_2 as a stripping gas, because of good affinity for esters, and also because it is present in breweries as a by-product. The non-volatile components (dry matter) slightly influenced flavour separation at high concentrations suggesting effects on the chemical activity of flavours. We found that the flavour stripping process is controlled by mass transfer resistance in the liquid phase for esters, and the gas-phase for isoamyl alcohol. Furthermore, ethanol greatly influences the stripping process because it enhances flavour retention; the values that we found are thus that they imply that it is very hard to establish and maintain a flavour profile in a non-alcoholic beer. We identified the various influences, and present a theoretical framework that can be used to quantify effects, such as the ethanol concentration on flavour retention for various process conditions.

Appendix A4:

Numerical analysis to derive equation 4.4

$$V_L \frac{dC_L(t)}{dt} = Q_G C_L(t) K^{cc} \qquad A.4.1$$

Laplace transform of the equation A.4.1 yields:

$$L(s) = V_L(C_L(0) - s \cdot L) - K^{cc} Q_G L \qquad A.4.2$$

Solving for L

$$L(s) = \frac{V_L \cdot C_L(0)}{s \cdot V_L + Q_G K^{cc}} \qquad A.4.3$$

Inverse Laplace of equation A.4.3

$$L(s) = C_L(t) = exp\left(\frac{-t \cdot Q_G K^{cc}}{V_L}\right) C_L(0) \qquad A.4.4$$

Rearranging delivers:

$$\ln\left(\frac{C_L(t)}{C_L(0)}\right) = \frac{-t \cdot Q_G K^{cc}}{V_L} \qquad A.4.5$$

Solving for K^{cc} yields:

$$K^{cc} = \frac{-V_L}{t \cdot Q_G} ln\left(\frac{C_L(t)}{C_L(0)}\right) \qquad A.4.6$$

And solving for saturated gas-phase concentration prediction yields:

$$C_G^e(t) = C_L(0) K^{cc} exp\left(-t \frac{K^{cc} \cdot Q_G}{V_L}\right) \qquad A.4.7$$

Numerical analysis to derive equation eq.4.11

$$V_L \frac{d}{dt} C_L(t) = Q_G C_G(t) \qquad A.4.8$$

Recalling Mackay equation (eq.4.10) and rearranging for saturated condition yields:

$$C_G(t) = K^{cc} C_L(t) \left(exp\left(\frac{-k_L A\, V_L}{Q_G K^{cc}} \right) - 1 \right) \qquad A.4.9$$

Replacing A.4.9 in A.4.8 yields:

$$V_L \frac{d}{dt} C_L(t) = Q_G K^{cc} C_L(t) \left(exp\left(\frac{-k_L A\, V_L}{Q_G K^{cc}} \right) - 1 \right) \qquad A.4.10$$

Laplace transform of Eq. A.4.10 yields:

$$C_L(s) = \left(Q_G K^{cc} - K^{cc} Q_G exp\left(\frac{-k_L A\, V_L}{Q_G K^{cc}} \right) \right) \cdot \mathrm{L} \cdot\ V_L \cdot (C_L(0) - s \cdot L) \qquad A.4.11$$

Solving right-hand side for L yields:

$$C_L(s) = \frac{V_L C_L(0)}{s \cdot\ V_L + K^{cc} Q_G - K^{cc} Q_G exp\left(\frac{-k_L A\, V_L}{Q_G K^{cc}} \right)} \qquad A.4.12$$

$$C_L(t) = L(s) \qquad A.4.13$$

Inverse Laplace of L(s) yields:

$$C_L(t) = exp\left(-t \frac{K^{cc} Q_G}{V_L} \left(exp\left(\frac{-k_L A}{Q_G K^{cc}} \right) - 1 \right) \right) C_L(0) \qquad A.4.14$$

$$\ln\left(\frac{C_L(t)}{C_L(0)} \right) = t \frac{K^{cc} Q_G}{V_L} \left(exp\left(\frac{-k_L A}{Q_G K^{cc}} \right) - 1 \right) \qquad A.4.15$$

Appendix B4:

Beer composition (volatile compounds).

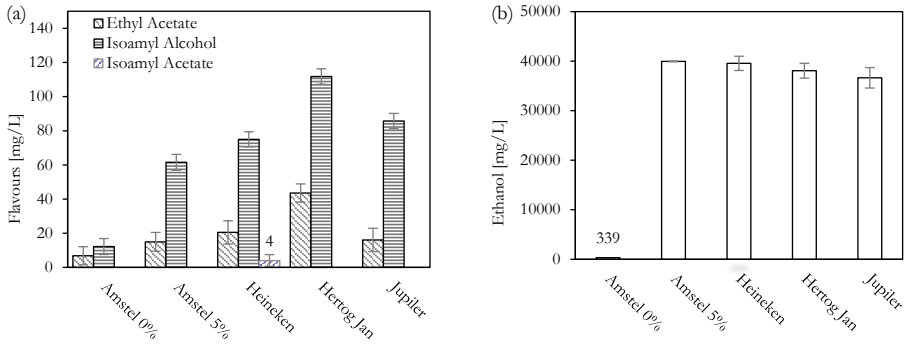

Figure B.4.1 Composition of the pilsner beers (a) major volatile flavours (b) ethanol.

Beer Composition (non-volatile compounds).

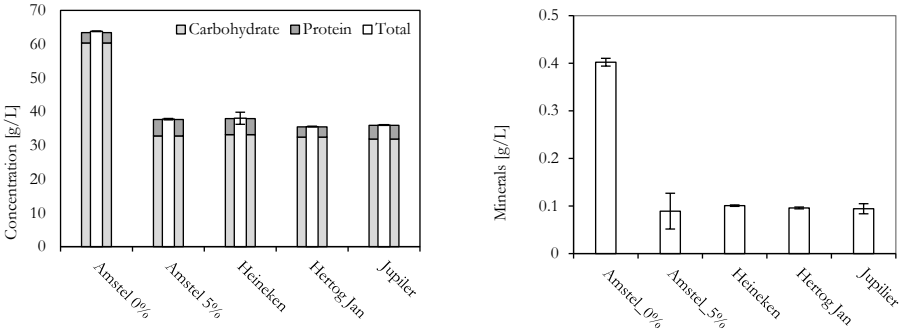

Figure B.4.2 Composition of the pilsner beers (a) dry matter concentration (b) mineral concentration.

Freeze –drying operational profile.

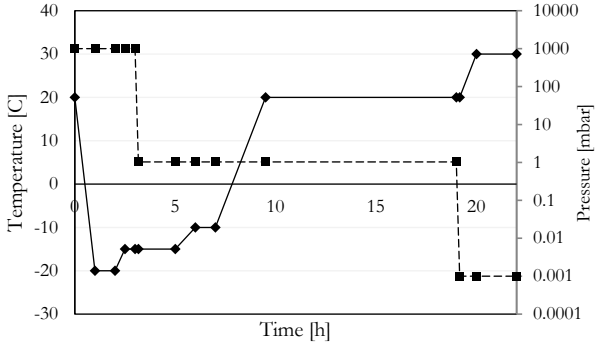

Figure B.4.3 Freeze-drying (---) pressure and (—) temperature profile

Appendix C4:

Dimensionless Henry's volatility coefficient to determine $C_G^e(0)$

Table C.4.1 Partition coefficient K^{ac} UNIFAC (Dortmund)

Ethanol %(v/v)	Ethyl acetate	Isoamyl acetate	Isoamyl alcohol
0	7.46E-03	1.58E-02	5.56E-04
0.05	6.73E-03	1.26E-02	4.73E-04
0.1	6.06E-03	9.97E-03	4.00E-04
0.15	5.45E-03	7.85E-03	3.37E-04
0.2	4.89E-03	6.14E-03	2.83E-04
0.25	4.38E-03	4.78E-03	2.37E-04
0.5	2.48E-03	1.24E-03	9.24E-05
0.75	1.43E-03	2.88E-04	3.45E-05
1			

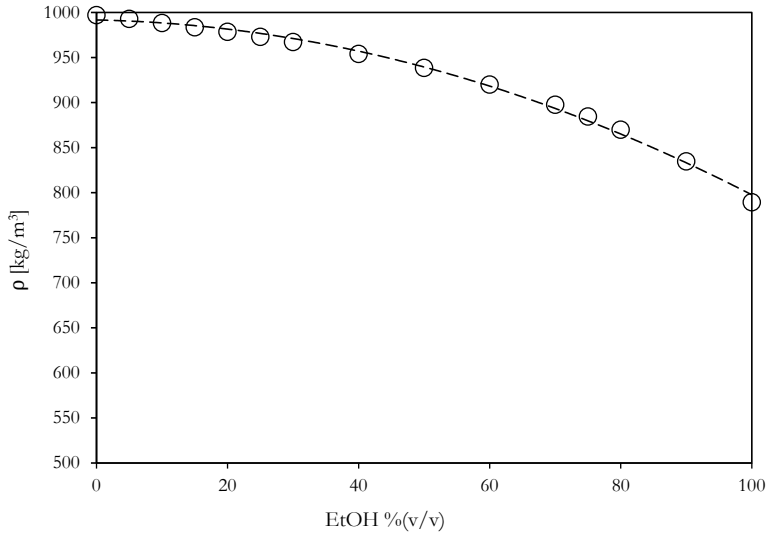

Figure C.4.1 density of solution containing 0.5 mL ethyl acetate, isoamyl acetate and isoamyl alcohol in different water-ethanol concentrations

The concentration profile of flavours in the effluent gas.

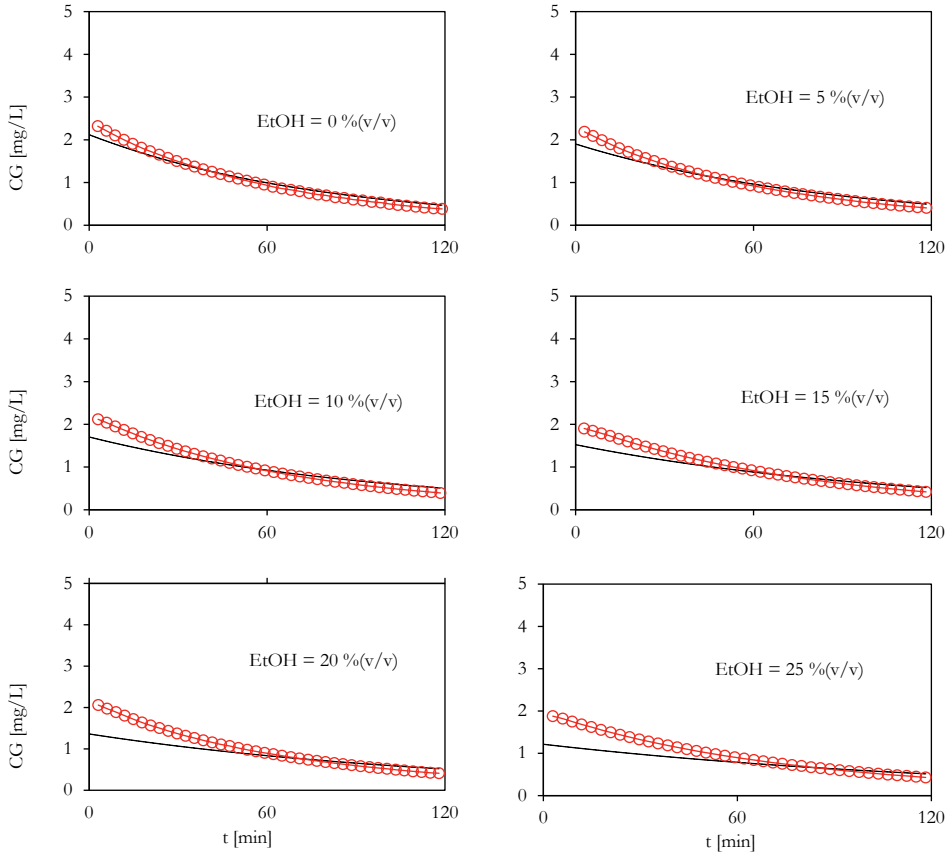

Figure C.4.2 Concentration of flavours in effluent gas a) □ ethyl acetate; markers denote experimental values, (--) predicted by UNIFAC; with a gas flow rate of 2000 mL/ min; right-hand side values are ethanol volume fractions

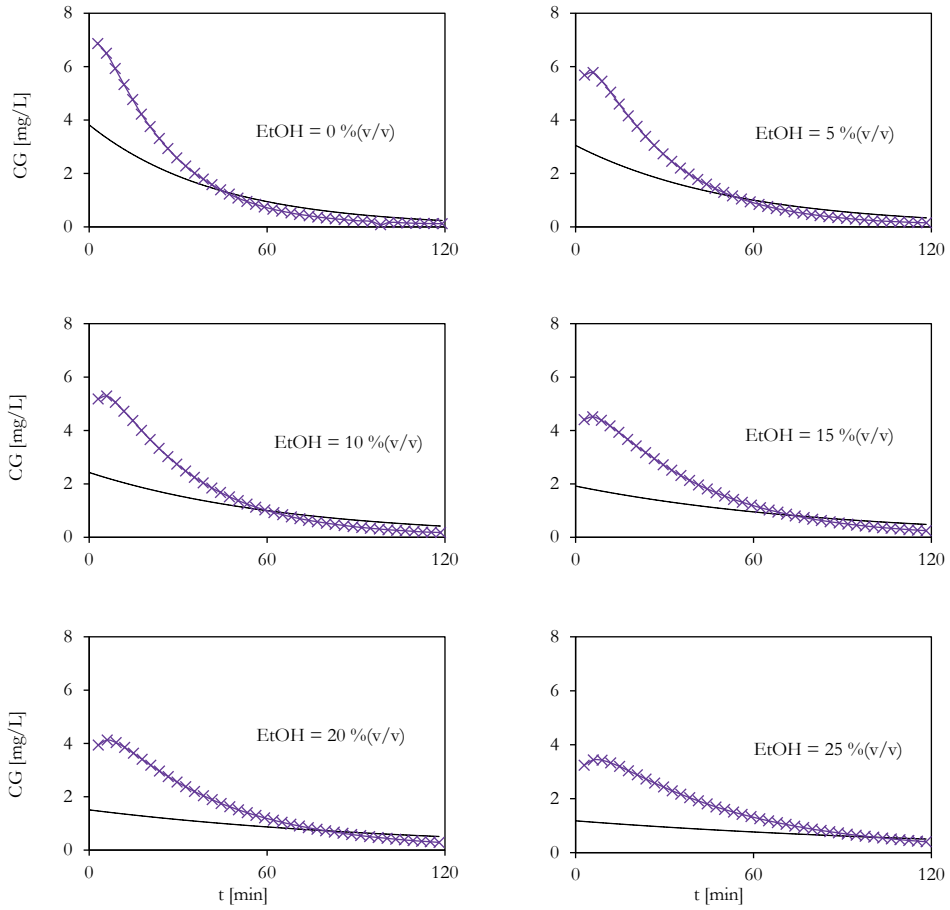

Figure C.4.3 Concentration of flavours in effluent gas, × isoamyl alcohol; markers denote experimental values, (--) predicted by UNIFAC with a gas flow rate of 2000 mL/min; right-hand side values are ethanol volume fractions

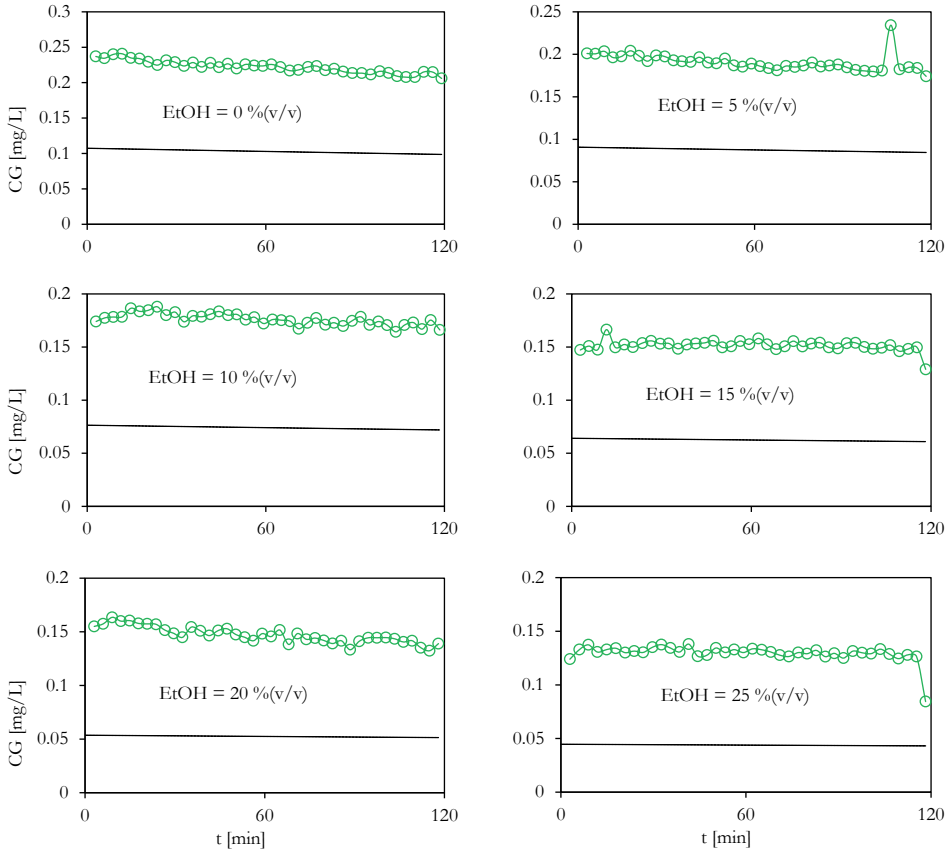

Figure C.4.4 Concentration of flavours in effluent gas, ○ isoamyl alcohol; markers denote experimental values, (--) predicted by UNIFAC with a gas flow rate of 2000 mL/min; right-hand side values are ethanol volume fractions

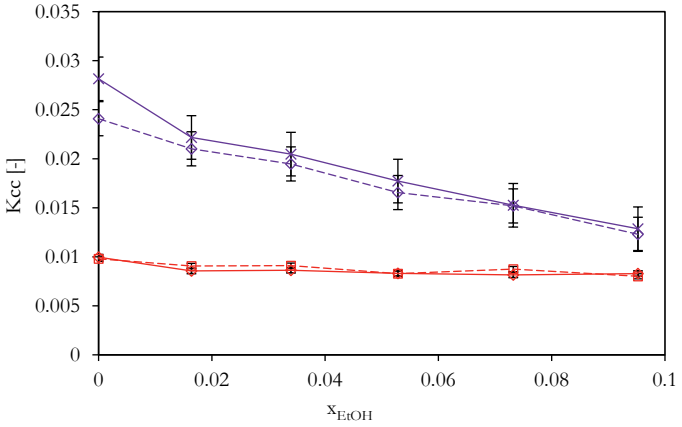

Figure C.4.5. The effect of CO_2 gas flow rate on HLC of □ ethyl acetate, × isoamyl acetate; (—) 3000 mL/min at average temperature of 294.80 with standard error of 0.043, (--) 2000 mL/min at average temperature of 294.89with standard error of 0.045

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Chapter V

Selective Separation of Flavour-active Compounds from Strip Gas using Frictional Diffusion

Attaining constant flavour composition in products that are produced batch-wise, such as beer, is not trivial given the inherent variability in fermentation. CO_2 stripping is feasible but unselective. Condensation of the flavour is possible but energy-intensive. We here propose the use of frictional diffusion (also called FricDiff), which is based on differences in diffusion rates in a sweep or carrier gas such as CO_2 through an inert porous medium. Application of a slight counter-flow of the sweep gas can be used to adapt the selectivity between different flavours. It is shown that from a difference in the diffusion rate of 25%, a selectivity of more than 10 can be obtained between ethyl acetate and isoamyl acetate, albeit at the cost of the flavour flux through the porous barrier.

The manuscript is submitted as:
A.Ammari, K. Schroen and R. Boom, 2020. Parametric Study of Multicomponent Separation of Flavour-active Compounds from CO_2 using the FricDiff Method. Sep. Purif. Technol.

5.1 Introduction:

Flavours are an important element in foods, but their profile may vary, due to variation in the production process, or raw materials [1]. An example is the brewing of beer. The fermentation process is generally operated as a batch process, and slight variation in the fermentation or the exact composition of the raw materials, such as the malt, may give rise to variations in the flavour profile. To avoid the beer to vary in quality to the consumer, the flavour of the beer may be adapted by selectively removing some of the flavours, while retaining others.

Volatile flavours can be controlled through various recovery, separation or removal processes [2]. Vacuum distillation that is known to protect nutrients, is a classical method of volatile separation; however, the selectivity is toward lighter compounds such as ethyl acetate and ethanol. This implies that a second step separation step is needed to process the effluent vapour and obtain the desired fraction and return the resulting fraction to the beer.

Some membrane separation techniques such as reverse osmosis [3] have been used to selectively remove the ethanol whereas, nanofiltration has been described to separate flavours next to ethanol [4]. Using these two methods would also require a recycling loop as described in the previous section for vacuum distillation. Pervaporation allows more selective removal of flavours, depending on the membrane, but is relatively intensive in energy, and the separation is mostly dependent on the properties of the membrane; hence it does not leave much flexibility for adaptation of the separation to mitigate batch to batch variation [5], [6].

From the above, it is clear that there is no single step separation technique that can be used to target flavour compounds specifically. Here we propose to start with stripping the beer, with for example CO_2, which is a naturally occurring component in the beer itself is an attractive primary stage. This will remove the flavours in proportion to their volatility. The actual composition can be changed by selectively removing them from the strip gas. Since compression and cooling processes are highly energy-intensive, recovery of compounds directly from the gas phase is favourable. Alternatively, the condensate can be treated as reported by Saffarionpour and co-workers [7] using adsorption, for example with active carbon or zeolites, to selectively remove the flavours. While this does allow flexibility in terms of separation, it is a semi-batch process, in which the columns regularly need to be regenerated, which complicates process operation.

For correcting dynamic variations, as opposed to structural deviations in flavour profile, a flexible process is necessary, which can be quickly adapted to changes in fresh beer quality, without costing too much energy or other auxiliaries. Geboers et al. [8] proposed the frictional diffusion (FricDiff) process principle for azeotrope breakage. Different from existing methods, it has the

possibility to adapt the selectivity between different components, and therefore it may also be of value for the selective, adjustable removal of flavours from a strip gas.

As can be seen in figure 5.1, frictional diffusion relies on differences in the diffusion rate between the flavours. By simultaneously imposing a small convective flow of the strip gas against the flavour diffusion, selective flavour removal can be achieved. Thus, any change in the flavour profile of the raw material can be mitigated by the adaptation of the pressure over the barrier.

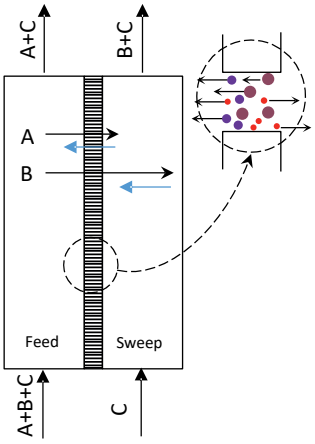
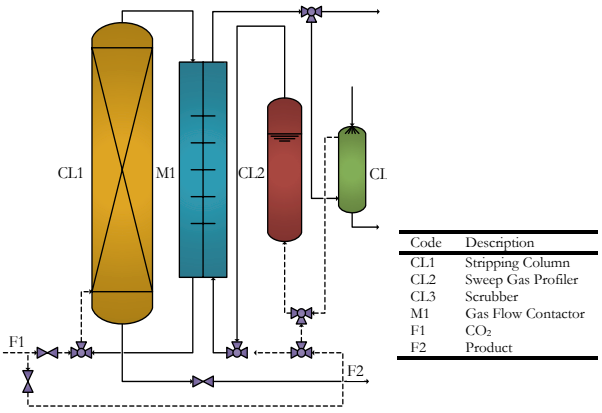


Figure 5.1: The principle of frictional diffusion. The strip gas D coming from the beer containing flavours A and B, is contacted to a porous barrier. The same gas C is also flowing over the other side of the barrier. The flavour components A and B diffuse through the gas that is present in the pores of the barrier. Depending on their rates of intermolecular and Knudsen diffusion, they will diffuse at different rates. A slight difference in pressure over the barrier changes the selectivity between the two flavour molecules.

We here present the feasibility of the frictional diffusion principle for dynamic adaptation of flavour removal, adopting the Maxwell-Stefan approach that Geboers and Kerkhoff introduced. We will show the possibility of having selective removal of flavour, show how this can be adapted through imposing a counter flux of the strip gas, and how different system parameters may influence the results.

Figure 5.2 illustrates the overall system that we envision the frictional diffusion module will be part of. CL1 is the stripping column from which our feed solution stems, and that contains CO_2 and flavours. This gas is next contacted in M1 with a secondary gas phase in our case carbon dioxide through a porous barrier. Based on the concentration gradient between the feed side and pure carbon dioxide diffusion of various components takes place. Components with low diffusivity can be retained in the feed by applying elevated sweep gas pressure. It is also possible to tune the driving force for separation of a certain component by enriching the sweep gas with that component. The process is expected to further contain a sweep gas profiler (CL2) and a scrubber (CL3).



Code	Description
CL1	Stripping Column
CL2	Sweep Gas Profiler
CL3	Scrubber
M1	Gas Flow Contactor
F1	CO_2
F2	Product

Figure 5.2 Schematic representation of the proposed location for FricDiff Dash lines are CO_2)

Since CO_2 is a naturally occurring gas in fermentation, it is our sweep gas of choice, also to avoid waste. In this paper, we focus on the gas contactor only, in which the sweep gas can either be pure or can be profiled by adding ethanol and/or water. The effects that can be created in this way will be evaluated using the FricDiff approach that is discussed next.

5.2 Theory

4.3 The Frictional diffusion concepts

Frictional diffusion was introduced by Geboers *et al.* [8] initially as an alternative technique for azeotrope mixture separation. Within this approach, a feed mixture and a sweep gas are separated by a nonselective porous layer (barrier). Components will diffuse through the barrier with different velocities, depending on the diffusivities. Pressure can be imposed over the barrier to influence the permeation rates, which will induce flow. This may lead to suppression of the more slowly diffusing components, while faster diffusion components may still be able to reach the other side of the membrane. The detailed concept is presented in earlier publications [9]–[13].

We assume a flat sheet membrane made of an inert material (more properties will be detailed later) with negligible pressure drop or differences in concentrations along its length, due to relatively fast crossflow on both sides. Axial concentration gradients at the sweep side and the feed side are also assumed to be small and have not been considered in this study. The motion of the gases inside the pores of the barrier can be described with [8]

$$\nabla p_i = RT\frac{\tau^2}{\varepsilon}\left[-\sum_{j=1}^{n}\frac{\left(p_j N_i - p_i N_j\right)}{p_t Đ_{ij}} - f_{im}N_i\right] \tag{5.1}$$

Here, p_i is the partial pressure of component i, N_i the molar flux, p_t the total pressure, τ the tortuosity of the pores inside the barrier, here taken 1.3 a typical value found in FricDiff investigations [9], [10], [12], [13], and ϵ the porosity of the barrier, chosen at 0.5 which is a very acceptable value for membrane porosity [14]; R and T are the gas constant and the temperature, respectively. The thickness of the barrier L is 0.5 mm. ∇p is the local partial pressure gradient. The term $f_{im}N_i$ represents the friction between the diffusing component i and the pore walls in the barrier, through viscous friction and Knudsen interaction (collisions between molecules of i and the barrier pore walls). For the wall-friction coefficients f_{im} Kerkhof and Geboers, [15] proposed

$$f_{im} = \left(D_i^K + \frac{p_i r_p^2}{8\kappa_i} \right)^{-1} \tag{5.2}$$

In which r_p is the radius of a pore which is assumed to be cylindrical, p_i is the partial pressure of component i, and κ_i is the fractional viscosity of component i. The Knudsen diffusivity may be approximated under the assumption of complete diffusive reflection at the wall and the absence of any molecule-molecule interaction [16] by:

$$D_i^K = 0.89\, r_p \left(\frac{8}{\pi} \frac{RT}{M_i} \right)^{1/2} \tag{5.3}$$

with M_i the molecular weight of component i. The fractional viscosity κ_i is defined with

$$\kappa_i = \frac{x_i \eta_i^0}{\sum_{j=1}^{n} x_j \xi_{ij}} \tag{5.4}$$

with η_i^0 the viscosity of the pure gas i, and ξ_{ij} the Wilke [17] parameter, given by

$$\xi_{ij} = \frac{\left[1 + \left(\frac{\eta_i^0}{\eta_j^0} \right)^{0.5} \left(\frac{M_j}{M_i} \right)^{0.5} \right]^2}{\left[8 \left(1 + \frac{M_i}{M_j} \right) \right]^{0.5}} \tag{5.5}$$

The viscosities of the pure components, η_i^0, are calculated using the DIPPR method:

$$\eta_{G_i} = \left[\frac{B_{1i}T^{B_{3i}}}{1+\frac{B_{3i}}{T}}\right] \quad \text{for} \quad T_{min} > T > T_{max} \tag{5.6}$$

in which B_1, B_2, B_3 are dependent on the component i (see Appendix A Table A3). The binary Maxwell-Stefan diffusivities $Đ_{ij}$ can be described using the following correlation:[18]

$$Đ_{ij} = \frac{3.16\cdot 10^{-8}\,T^{1.75}}{p_t\left(v_i^{1/3}+v_j^{1/3}\right)^2}\left(\frac{1}{M_i}+\frac{1}{M_j}\right)^{\frac{1}{2}} \tag{5.7}$$

in which v_i is the molar diffusion volume of component i (see appendix table A.5.1). The Maxwell-Stefan diffusion coefficients obey the reciprocal relations $Đ_{ij} = Đ_{ji}$. To evaluate the use of frictional diffusion, the following definition of the selectivity between components *i* and *j* is used:

$$\alpha_{i,j} = \frac{N_i/x_i}{N_j/x_j} \tag{5.8}$$

5.3 Results and discussions

5.3.1 A simplified system with CO_2 and two flavours

Substituting equation 5.2 in 5.1, we assume that the flavour components i are dilute and that we have only carrier gas c ($p_1 \ll p_c$), we can separate the fluxes of the several flavours, since they will only have interaction with the sweep gas. Thus, for each flavour we obtain

$$\frac{dp_i}{dx} = RT\frac{\tau^2}{\varepsilon}\left[\frac{(p_iN_c - p_cN_i)}{p_tĐ_{ij}} - \frac{N_i}{D_i^K + \frac{p_i r_p^2}{8\kappa_i}}\right] \tag{5.9}$$

Since these flavours are dilute, $p_c \approx p_t$, and we get

$$\frac{dp_i}{dx} = RT\frac{\tau^2}{\varepsilon}\left[\frac{p_iN_c}{p_tĐ_{ij}} - \frac{N_i}{Đ_{ij}} - \frac{N_i}{D_i^K + \frac{p_i r_p^2}{8\kappa_i}}\right] \tag{5.10}$$

Here, we should bear in mind that N_c is either zero (no pressure difference), or negative, in case we want to reduce the flavour diffusion to the sweep side by imposing a counter-flux against the direction of diffusion of the flavours. Thus, we find that

$$\frac{dp_i}{dx} = \left(\frac{RT}{p_t Đ_{ic}}\frac{\tau^2}{\varepsilon}\cdot N_c\right)\cdot p_i - \left(RT\frac{\tau^2}{\varepsilon}\cdot N_i\right)\cdot\left(\frac{1}{Đ_{ic}} + \frac{1}{D_i^K + \frac{p_i r_p^2}{8\kappa_i}}\right) \tag{5.11}$$

Assuming a tubular geometry, with a moderate gas flow rate of $1m/s$, the Biot number can be estimated through

$$Bi = \frac{hL\tau^2}{D_{ic}\epsilon} \tag{5.12}$$

and is found to be 4.13, confirming our assumption that mass transfer is limited by internal mass transfer. Hence, we will assume that the partial pressures at the entrance of the barrier pores at the feed side are equal to the partial pressures in the feed and that the partial pressures at the end of the pores at the sweep side are equal to the partial pressures in the sweep phase. We assume that the partial pressures in the sweep phase are negligibly small.

Equation 5.9 is integrated using a fourth-order Runge-Kutta algorithm with 100 steps over the barrier (smaller steps did not change the results), in which the flavour flux is varied until the partial pressure of the flavour at the sweep side is exactly zero, using a nonlinear minimization procedure with its convergence tolerance set at 10^{-15}. Typical concentration profiles for ethyl acetate and isoamyl acetate through the barrier are shown in figure 5.3; figure 5.3a shows the normalized partial pressure profiles of ethyl acetate with different counter-fluxes of the strip gas; figure 5.3b shows the different partial pressure profiles through the barrier for ethyl acetate and isoamyl acetate, at one particular counter-flux.

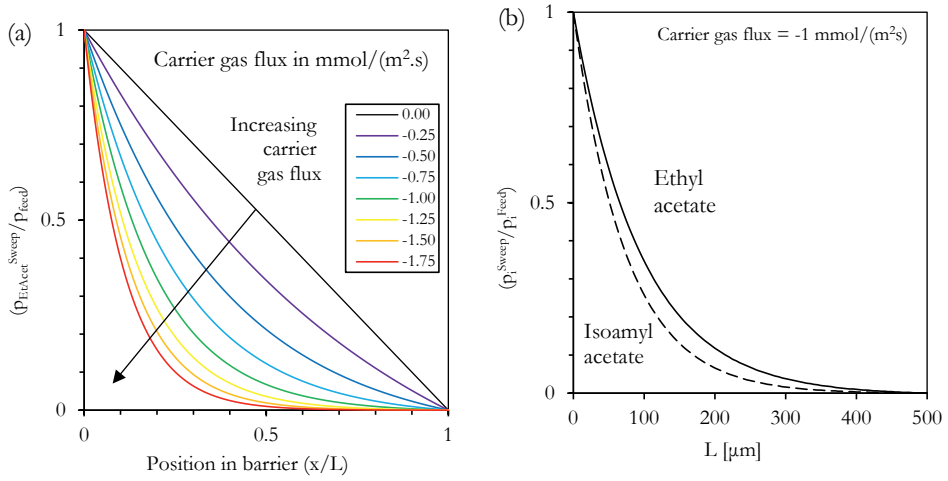


Figure 5.3. Normalized partial pressure profiles of flavours. Left-hand graph: partial pressure profiles of ethyl acetate with increasing counter-flux of CO_2 through the barrier. Right-hand graph: partial pressure profiles of ethyl acetate (–) and isoamyl acetate (--) through the barrier, with a sweep-to-feed flux of the carrier gas (CO_2) of 1 mol/(m²s). The slight difference in the diffusion coefficient of the two flavours causes a stronger drag on isoamyl acetate than on ethyl acetate; hence its overall flux through the carrier is reduced disproportionally, giving an unexpectedly large selectivity.

Figure 5.3 shows that at zero counter-flux, the concentration profile is completely straight, which is logical given that the barrier was assumed to be homogeneous. At a non-zero counter-flux of the strip gas, the partial pressure profiles become non-linear, and reduce the flux of the flavours towards the sweep gas side. Faster diffusion components such as ethyl acetate are less hindered by the counter-flow, but the profile of isoamyl acetate, which has a somewhat lower mutual diffusion coefficient with CO_2, is reduced markedly stronger.

By changing the sweep-to-feed flux of the carrier gas, we can, therefore, change the ratio of the two flavour fluxes. A zero-carrier gas flux gives unbiased diffusion of the flavours through the stagnant carrier gas inside the barrier pores, resulting in a selectivity of 1.282, which is very close to the ratio of the two flavour-CO_2 mutual diffusion coefficients, which is 1.287.

An increase in the sweep-to-feed carrier gas flux affects the slower diffusing components disproportionally strong relative to faster diffusing molecules. Therefore, imposing counter-flux increases this selectivity. Figure 5.4a shows that the selectivity between ethyl acetate and isoamyl acetate can become better than 10, even though their diffusion coefficients are only 29% different. Figure 5.4b confirms that this is because of the difference in the intermolecular diffusion coefficient with CO_2. If a barrier would be used with smaller pores, then the Knudsen diffusion becomes more important. Knudsen diffusion takes place between the flavours and the barrier pore walls, which are stagnant. This is in contrast to the intermolecular diffusion between

the flavours and the strip gas CO_2: this CO_2 gas can flow, and this flow can compensate the intermolecular diffusion between flavours and CO_2. For Knudsen diffusion, there is however no influence of any flow of the strip gas. Therefore, a barrier with pores that are smaller than around 0.5 μm, will show a reduced effect of the counter flow of CO_2.

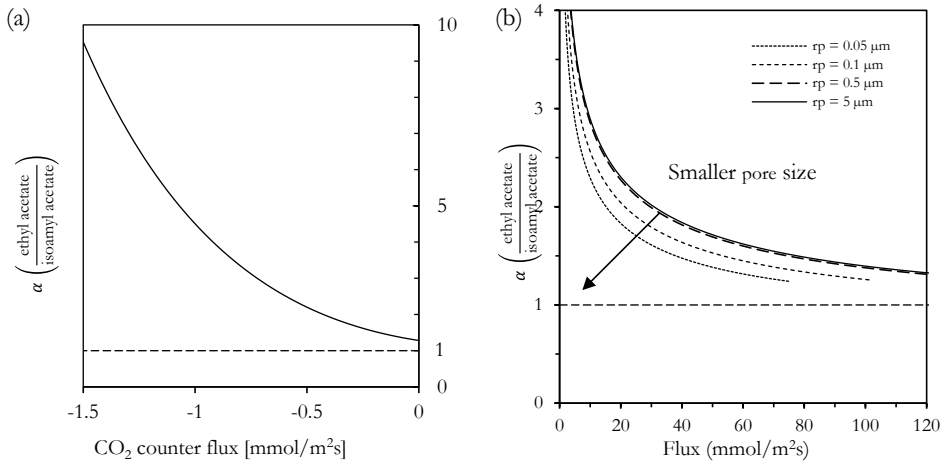


Figure 5.4 Left-hand graph: Selectivity between ethyl acetate and isoamyl acetate as a function of the sweep-to-feed carrier gas (CO_2) flux; which are negative because the carrier gas flows from sweep to feed, while the flavours diffuse from feed to sweep phase. Right-hand graph: Influence of the pore size of the barrier on the selectivity and flavour fluxes obtained. At smaller pore size, Knudsen diffusion starts to become more important' at larger pore size, intermolecular diffusion rates dominate (calculated with -1 mmol/m²s CO_2 counter flux).

The fact that we can alter the separation selectivity between the two flavours by changing the sweep-to-feed counter-flux of the carrier gas makes it fundamentally different from other separation processes. For example, a membrane-based vapour permeation or pervaporation process will have an intrinsic selectivity based on the permeability of the components, which are properties of the membrane material. An adsorption process, such as a molecular sieve, will exhibit selectivity based on the surface adsorption affinities of the components, which, once more, are material properties in this case of the adsorbents. In frictional diffusion, the separation is created by the process conditions, especially the pressure of the strip/sweep gas over the membrane, to create the counter-flux of the strip/sweep gas. The typical pressures needed to achieve these counter-fluxes are quite moderate, as is shown in figure 5.5.

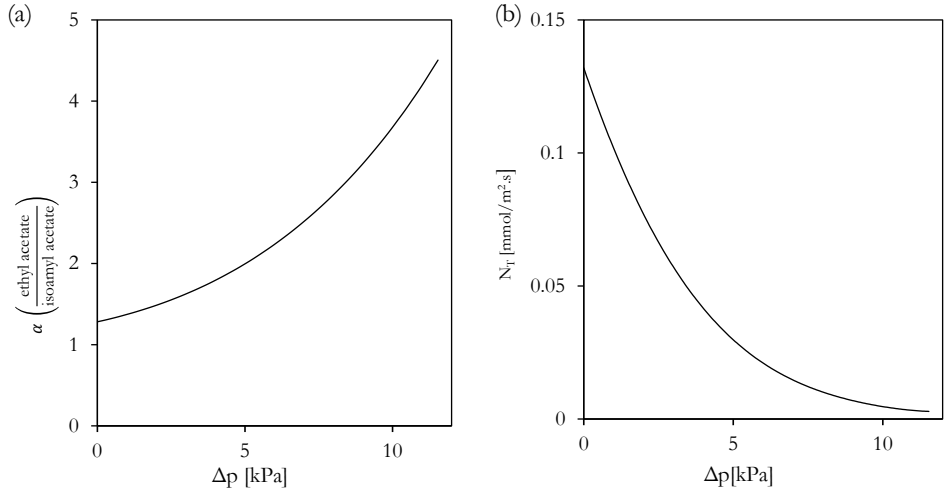


Figure 5.5 Selectivities (left) and fluxes in mmol/(m²s) (right), as a function of the applied pressure over the barrier. With a pressure drop of only 6 kPa, one can already obtain a substantially elevated selectivity and still a reasonable flux.

While the pressures needed to impose relevant counter-fluxes of the strip/sweep gas, in this case, CO_2, the specific requirements of the process will dictate what compromise is needed between the selectivity and the flux of the flavours through the barrier. A larger selectivity will imply a lower flux, and hence a larger barrier surface area will be required. Since there are no large pressure differences in the process, and the barrier is only contacted with gases on both sides, one may choose for modules that have a very high surface-to-volume ratio, for example using hollow fibres, which may have a surface area – to volume ratio between 7 000 and 13 000 m^2/m^3.[19]

We here assumed a barrier that is 50 μm thick. Fluxes can be improved by using a thinner barrier, for example by using a porous top layer on a more open supportive membrane; however, the carrier counter-flux will also be proportionally larger. The carrier flux is an important parameter for system design, as the system will feed some sweep gas (CO_2) from the sweep side towards the strip side. This may not be a problem, as some of the CO_2 could leave the system as it will dissolve in the beer that is being stripped. If this is not sufficient, one could allow the volume of the feed side strip gas phase to slowly expand (during batch treatment) or one could remove the CO_2 using a small bleed stream. This bleed stream could be recycled again, by condensation of the flavours or by using a selective membrane process, which would make the CO_2 available again for the sweep side. Since this bleed stream is quite small, this will not significantly impact the overall energy consumption of the process.

5.3.2 Full system

We can now take the full system into account, using the carrier gas that was contacted with beer. The beer was assumed to have 4 g/L ethanol, 50 mg/L ethyl acetate, 100 mg/L isoamyl alcohol, and 10 mg/L isoamyl acetate. Using Wilson's model to estimate the activity coefficients at 4.78, 90.38, 1245 and 3998, the partial vapour pressures in the carrier gas after having equilibrated with the beer, would be 2339, 44.2, 8.98, 7.13 and 3.27 Pa, for water vapour, ethanol, ethyl acetate, isoamyl alcohol and isoamyl acetate, respectively. Calculating the fluxes with the full equation 5.1, using the same procedure by integrating the set of differential equation using 4th order Runge-Kutta, and then varying the fluxes until the concentrations at the strip side matched the one in the strip phase, shows that also in such a complex system one can use the CO_2 counter-flux to adjust the selectivities between the different flavours (see figure 5.6a). Application of a larger counter-flux of course again results in lower overall flavour fluxes through the barrier; hence a larger barrier surface area would be needed (figure 5.6b).

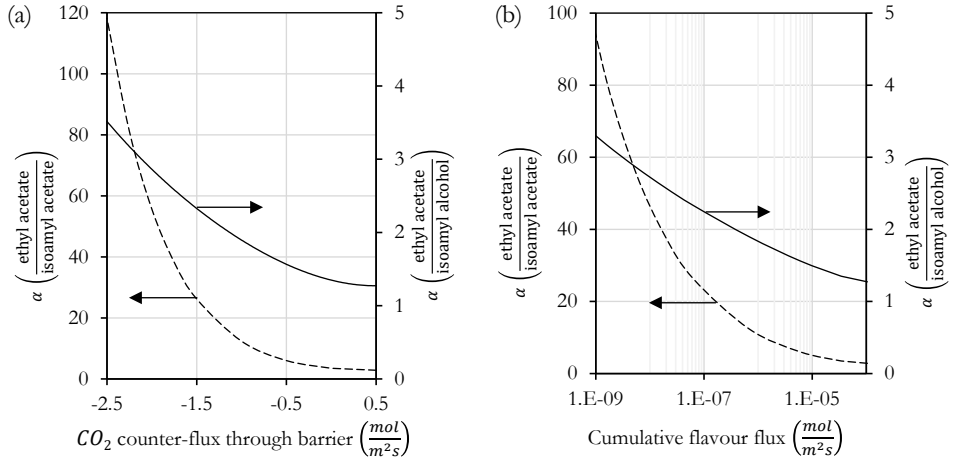


Figure 5.6 Selectivities of ethyl acetate over isoamyl alcohol and isoamyl acetate versus the imposed counter-flux of carbon dioxide through the barrier (left-hand graph), and versus the total flux of all three flavours combined (right-hand graph; both in mol/ (m^2s)). One can see quite similar behaviour as in the simplified case.

We could, of course, change the thickness of the barrier as shown earlier. There is however another possibility, which is by operating a reduced CO_2 pressure. Figure 5.7 shows that by doing this, one lowers the friction between the different gases, which increases the diffusive velocity of the diffusing components. At very low pressures, one approaches the fluxes obtained based on pure Knudsen diffusion, in which the fluxes are determined by the molecular weights (figure 5.7a). Interestingly, reducing the CO_2 pressure hardly influences the selectivities of the flavours. Please note that in figure 5.7b, the scales are strongly enlarged; the selectivity between

ethyl acetate and isoamyl alcohol changes just 1.6%, and that between ethyl acetate and isoamyl acetate only 0.5%. This gives us the possibility to improve the fluxes without much change of the selectivities.

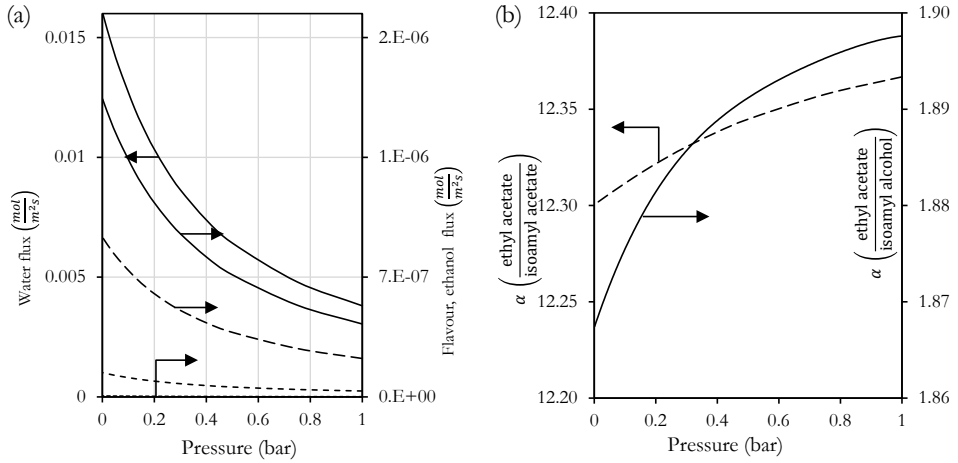


Figure 5.7: The fluxes can be increased strongly by operating at reduced pressure. This decreases the friction between the gases, and thus increases the diffusive velocities. The fluxes at zero pressure are solely determined by Knudsen diffusive rates. All values were calculated using a CO_2 counter-flux of –0.1 mol/(m^2s)

Figure 5.8 shows that when using pure CO_2 as strip phase, also water and ethanol vapour are transferred to the strip side. This can be easily adjusted by allowing a certain vapour pressure of water and ethanol at the strip side as well. Figures 5.8b and c show that by imposing on the strip side a fraction of the vapour pressure of water and ethanol on the feed side, one can effectively stop water and ethanol vapour from being transferred. At the same time, the fluxes of the flavours are hardly affected. This implies that by adjusting the composition of the strip gas, one can select only those components that one would wish to transfer to the strip gas.

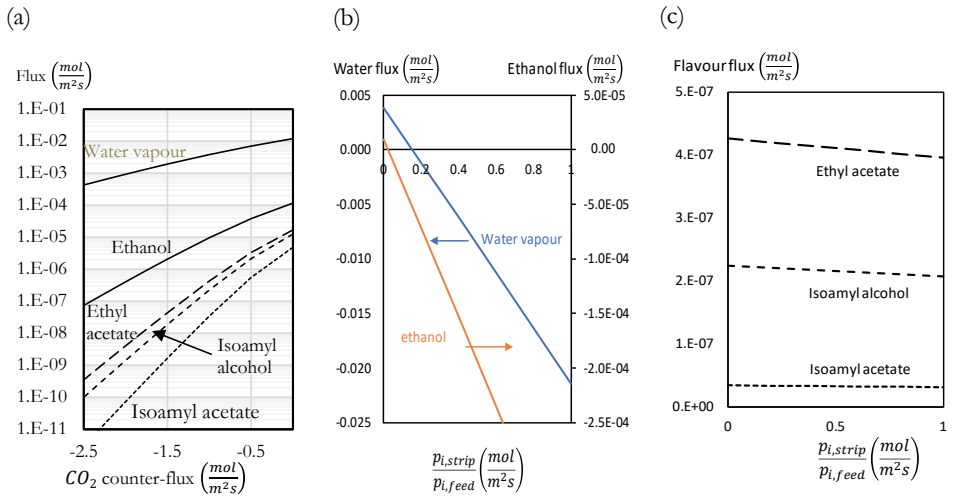


Figure 5.8: The left-hand graph shows the fluxes as a function of the CO_2 counter-flux. One can see that by far the largest fluxes are water and ethanol vapour. The middle graph shows that if the vapour pressures of water and ethanol are enlarged from 0 to 100% of their vapour pressure on the feed side, their fluxes can become zero or negative. Careful adjustment of these vapour pressures, therefore, can stop these components from moving through the barrier. The right-hand graph shows that this hardly affects the fluxes of the flavours (or their selectivities).

5.4 Conclusion

We showed at frictional diffusion (FricDiff) may be a suitable technique that allows the creation of a strip process that can be dynamically adapted to varying requirements on flavour removal. The strip gas is contacted with a porous, inert barrier that is on the other side in contact with the same gas but without flavours. Different diffusion rates of the flavours through the gas-filled pores of the barrier yield a separation between the flavours. By imposing a small positive pressure over the barrier, a small counter-flux of the sweep/strip gas is created, and both the fluxes of the flavours and the selectivity between these changes.

It is shown that the selectivity rises disproportionally with the counter-flux, but that the flavour fluxes go down. The pressure needed over the barrier is below 0.15 bar, which means that the selectivity can be quickly adapted to the exact needs of the moment. The absolute pressure (i.e.., not the difference) can be used to increase all fluxes. It is shown that all fluxes rise strongly when reducing the overall pressure of the carrier gas.

Water and ethanol are volatile as well and therefore will be present in the carrier gas after contacting it with beer. Their fluxes can be quite large, but can be completely countered by allowing a certain partial vapour of these two components in the strip side as well. It was shown that this will hardly influence the fluxes of the flavour components.

Appendix A5

Table A.5.1 Gas Phase Diffusion Coefficient (eq. 5.1) and diffusion volumes

	v*	Water	Ethanol	Ethyl acetate	Isoamyl acetate	Isoamyl alcohol	CO_2
Water	1.27E-05	-	1.59E-05	1.14E-05	1.05E-05	8.81E-05	2.19E-05
Ethanol	5.04E-05	1.59E-05	-	5.58E-06	5.21E-06	4.34E-06	1.10E-05
Ethyl acetate	9.28E-05	1.14E-05	5.58E-06	-	3.58E-06	2.93E-06	7.85E-06
Isoamyl acetate	1.12E-04	1.05E-05	5.21E-06	3.58E-06	-	2.76E-06	7.28E-06
Isoamyl alcohol	1.54E-04	8.81E-06	4.34E-06	2.93E-06	2.76E-06	-	6.10E-06
CO_2	2.69E-05	2.19E-05	1.10E-05	7.85E-06	7.28E-06	6.10E-06	-

*Diffusion volumes are calculated using Lightfoot (1973)

Table A.5.2 typical concentration of major volatiles in beer [21]

Ethyl Acetate	Ethanol	Isoamyl Acetate	Isoamyl Alcohol
[mg/L]	*[g/L]*	*[mg/L]*	*[mg/L]*
15~44	36.6~39.9	~4	62~112

Table A.5.3. Parameters used in vapour viscosity DIPPR method (taken from AspenPlus® database.)

Component	Water	Ethanol	Ethyl acetate	Isoamyl Acetate	Isoamyl alcohol	CO_2
B1 [Pa.s]	1.71E-08	1.06E-07	3.21E-06	8.93E-08	8.90E-08	2.14E-6
B2 [-]	1.11	0.81	0.36	0.789	0.80	0.46
B3 [K]	0	52.7	667	89.73	77.65	290
T_{min}[K]	273.16	200	189.6	194.65	155.95	194.67
T_{max} [K]	1073.15	1000	1000	1000	1000	1500

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Chapter VI

General discussion

The findings of the previous chapters were compiled into general conclusions on the use of stripping and stripping combined with frictional diffusion, for selective adjustment of flavour profiles in beer. These general conclusions were concretised into the conceptual design for two situations; one for the selective removal of flavours that diffuse relatively fast in a gas phase, and one for the selective removal of flavours that diffuse relatively slowly. In both cases, frictional diffusion could be used, and in both cases, the total surface area that is needed for the contactor is feasible. The selectivity can be strongly improved by application of a counter-pressure over the barrier, which however does require a larger surface area of the barrier in both cases. The typical pressures needed do not exceed 15 kPa and are generally lower. The overall conclusion is that the combination of primary stripping of the beer, using frictional diffusion to achieve selectivity, and unselective adsorption to a hydrophobic resin, results in feasible, selective processes that can be used to flexibly adapt flavour profiles in beer, using the pressure drop over the barrier as an easily adapted process parameter.

6.1 Introduction

This thesis aimed to assess the selective removal of flavours from beer using a closed-loop stripping process combined with the regeneration of the stripping gas through using frictional diffusion (FricDiff). While chapters III and IV centred around the stripping process (equilibrium and kinetic aspects), chapter V discussed on the regeneration step, carried out with frictional diffusion. While beer typically carries a multitude of flavours, we chose to concentrate on the separation of several model flavours; however, we feel that their properties are sufficiently representative for the other flavours, to conclude. An integrated two-stage separation process was designed, comprising of a stripping step with CO_2 as a closed-loop carrier gas, with an in-line separation step, in which the frictional diffusion concept was applied. This principle is not energy-intensive, and combines a relatively simple process configuration, with flexibility in the separation characteristics.

6.2 Findings

We will first summarize the main conclusions that were made in the earlier chapters of this thesis.

Chapter II reviewed experimental and predictive methods for assessing flavour-matrix interactions in aqueous systems. For a typical composition in liquid foods (water, proteins, polysaccharides, oil droplets) flavours are primarily influenced by the presence of oil that may serve as a reservoir but will also delay the release of flavours. The affinity of flavours to proteins is less, but important especially in foods that do not any substantial amount of oils or fats. Third, there is also interaction with polysaccharides, especially starch, which may form complexes with flavour components.

While a range of adequate methods is available to measure both the equilibrium interactions and the release dynamics, the amount of experimental data that is available is not large, and generally only for diluted systems. Besides, the application of thermodynamic models is limited by the availability of the parameters for these models.

In chapter III, the influence on the presence of ethanol on the release of flavour was investigated. Using an approach based on Margules' equation and comparison with experimental values based on the phase ratio variation method, it was found that the presence of ethanol at concentrations that are relevant for beer, slightly reduces the equilibrium release of flavours (up to ~ 40%).

Chapter IV then focused on the first stage of the envisaged process, stripping the beer with carbon dioxide, using a packed column. Experiments showed that while the transfer of ethyl acetate and isoamyl acetate was limited by the liquid side transfer velocity, the transfer of isoamyl alcohol was limited by the gas side transfer velocity. This indicates that the overall profile of flavours that is stripped depends on the process conditions, and can therefore also be influenced by this.

Chapter V assessed the second stage of the process, in which the flavours are separated from the stripping gas; in this case by a system based on the frictional diffusion (FricDiff) principle. While the fundamental separation through the porous barrier is based on the rates of (gas) diffusion of the flavours through the pores of the barrier, the application of a slight pressure difference over the barrier induces a convective counter-flow that reduces the overall transfer rate, but greatly increases the separation selectivity between flavours. This would allow the adjustment of the separation characteristics by simply adjusting the pressure difference over the membrane, yielding a very flexible process.

6.3 Effect of Ethanol and matrix

As mentioned in the introduction (chapter I), we considered two techniques namely stripping and vacuum evaporation. During vacuum distillation, evaporating ethanol in the vapour phase may influence the secondary separation stage, in which the flavour components are separated. Condensation within the pores of the porous barrier used in a frictional diffusion module potentially would slow down and change the diffusive and advective transfer of flavour compounds; therefore, stripping was our primary process of choice. To design a stripping column properly, we derived reliable partition coefficients of all compound(s) in the full system in chapter III. Since the flavours are quite dilute, the most important interactions are between the flavours, water, ethanol and the carbohydrates and proteins present in beer.

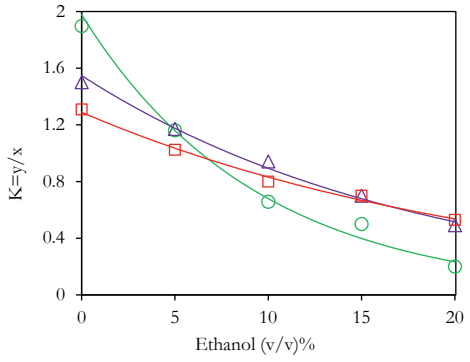

Figure 6.1 The effect of ethanol volume on partition coefficient (mol/L in vapour/mole/L in liquid) of the flavour compounds at 100 [mbar] □ *ethyl acetate,* △ *isoamyl acetate and* ○ *isoamyl alcohol*

Fig. 6.1 shows that reasonable agreement was found between the experiments and the estimated values of the partition coefficients of the flavours (ethyl acetate, isoamyl acetate and isoamyl alcohol), as a function of the ethanol concentration.

Besides ethanol, also other components, such as proteins and carbohydrates are expected to influence the partitioning of flavours. It is known that proteins have interaction with many if not

most flavours (see e.g. [1]). Also, carbohydrates may influence the release of flavours, either by interaction or by a change in viscosity and hence mass transfer. The overall concentration of these components is around 40 g/L. Lager beer dry matter has 35 g/L of carbohydrates mainly with DP>6, and 5 g/L proteins or peptides. The minerals concentration is minimal at around 0.1 g/L. In chapter II, we thus discussed that dry matter hardly influences flavour retention.

The effects of salts were not well investigated until now, therefore figure 6.1 shows some measurements, carried out by equilibrating 750 mL solution with CO_2 gas. One can see some effects that may have influenced the activity of other components and thus their partitioning behaviour. Esters are affected more than alcohols; and long-chain esters are more affected than their short-chain counterparts, as also found for other systems in chapter II.

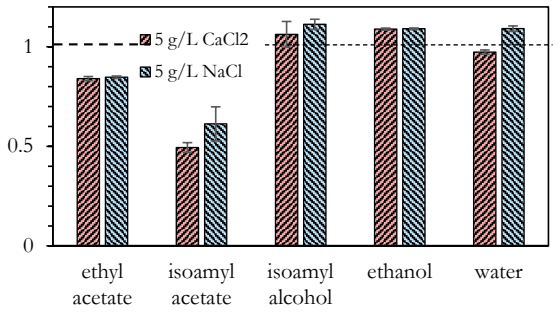

Figure 6.2 Effect of 5 g/L $CaCl_2$ (blue) or NaCl (orange) on the relative gas concentration of ethyl acetate, isoamyl acetate, isoamyl alcohol ethanol and water for a 1-litre stripping column with 750 mL feed and CO_2 as stripping gas at 3000 mL/min flow.

6.4 Conceptual process design

We will now investigate the conceptual design of a process to adapt the flavour composition using the processes that were investigated in this thesis. For this, we will assume a stripping column using CO_2, which is regenerated using a frictional diffusion (FricDiff) module.

The stripping unit will be adapted from chapter IV, assuming the use of a packed column with a Salzer® Mellapak M750Y packing having 746 m^2/m^3 specific area, or similar. The second stage is a FricDiff module, used to regenerate the CO_2 gas that carries the flavours (and other components) to the FricDiff module, which brings it into contact with the secondary stripping gas.

The stripping gas that takes up the flavours from the feed carrier gas, may either be discarded or used elsewhere, as it is still very dilute in the flavours or maybe regenerated using hydrophobic adsorption media, such as active carbon or hydrophobic resins such as Amberlite XAD16N or Sepabeads SP20S [2]. These resins will be unselective when far from saturation, so the FricDiff system may be used to regulate the overall selectivity between the flavours, using the counter-

pressure over the porous barrier as a process parameter. As there will be some counter-pressure over the FricDiff module, a small supplementation of CO_2 has to be done to the secondary gas recycle. This implies that there will be a small supply of CO_2 through the FricDiff barrier, towards the beer. We assume that this CO_2 is taken up by the beer, as beers are often carbonated in practice.

Parameters in the process are the counter-pressure over the porous barrier in the FricDiff module, which will influence the selectivity of the flavours, to adjust the flavour profile, and the concentrations of both water and ethanol, which will influence the fluxes of water and ethanol vapours through the FricDiff module, in his way avoiding any change in the water and ethanol content of the beer. Other parameters may be used, such as the structure and thickness of the porous barrier, and the temperature.

We will here assume a beer that has the following flavour composition:

	Concentration in beer
Ethanol	4 g/L
Ethyl acetate	100 g/L
Isoamyl alcohol	100 mg/L
Isoamyl acetate	10 g/L

6.4.1 Case 1: reduction of the concentration of fast-diffusing flavours

We will first consider the reduction of the concentration of fast diffusing flavours. To be concrete, we will reduce the ethyl acetate concentration by 10%, i.e., to 45 mg/L. We assume that water and ethanol will not be adsorbed on the adsorption module, due to their relative hydrophilicity. This implies that they will accumulate in the secondary sweep gas and their fluxes through the FricDiff module will become zero. We also assume that the adsorption module adsorbs any flavour that is present in the secondary sweep gas; i.e., that it is completely unselective. Figure 6.3 shows a schematic process outline. We use the mass transfer coefficients that were found in chapter IV, and the diffusion and partition coefficients that were estimated in chapters II and III. We further assume that the flow in the FricDiff module is maintained using a crossflow system, implying that we can retain the crossflow velocity required to have limitation by the diffusion rates inside the porous barrier.

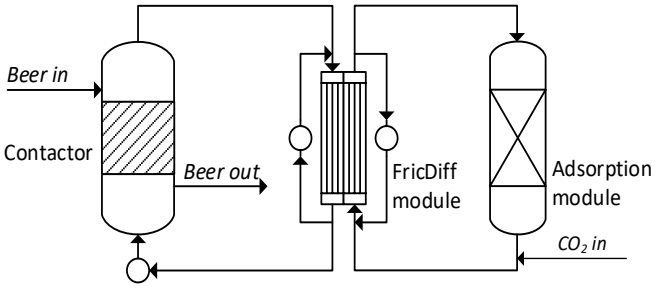

Figure 6.3. Process configuration using an adsorption module to regenerate the secondary sweep gas. This configuration will be selective for removing the fast diffusing flavours.

Figure 6.4 shows the results of calculations using the model that was presented and discussed in chapter V. The calculations show that one can indeed selectively remove the fast diffusing component, ethyl acetate, from the beer. The counter-pressure may be used to limit the loss of the other flavours. In this case, the loss of isoamyl acetate can be reduced to just a few per cent, while still removing 10% of the ethyl acetate. This counter-pressure will result in a lower overall flux of the flavours through the porous barrier, so more barrier surface area is required: from about 1 m2 without any counter-pressure, to 100 – 200 m^2 with a counter-pressure of -15 kPa. However, even with significant counter-pressures, the surface areas necessary are not excessive.

One should consider that the barrier is contacted with gas on both sides, while the pressure difference over the barrier is quite limited. This makes the system very suited for the employment of hollow fibre modules, which can have typically 1000 m^2/m^3 surface area. This means that the FricDiff module can be quite compact.

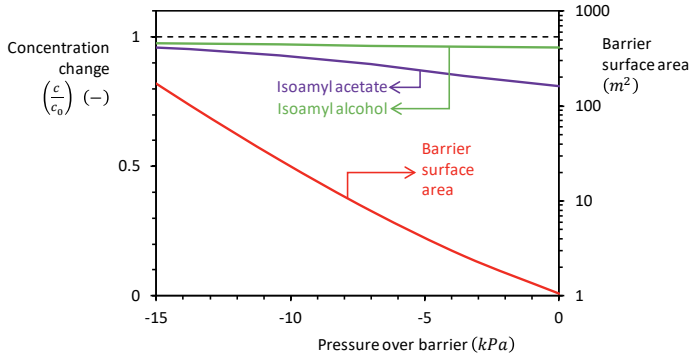

Figure 6.4. Relative changes in isoamyl alcohol (purple) and isoamyl acetate (green) concentration, and required barrier surface area needed (red), to reduce the ethyl acetate concentration by 10% in 1 m^3/h beer.

6.4.2 Case 2: Reduction of the concentration of slow-diffusing flavours

The above case is relatively straightforward, in that it aims to separate the flavour that diffuses fastest. The FricDiff process is most selective to these flavours. The system should be different when one would want to reduce the concentration of the *slowest* diffusing species. Isoamyl acetate is the model component for these flavours.

For achieving selective removal of slow-diffusing species, the system needs to be reconfigured. This stream has to be re-introduced to the beer since the flavour that should be retained passes most quickly through the FricDiff module. Instead, the primary stripping gas that is depleted of this component, should be discarded (or brought into contact with a second adsorption module, if one would like to retain this flavour). This should be done such, that the least possible flavour is lost.

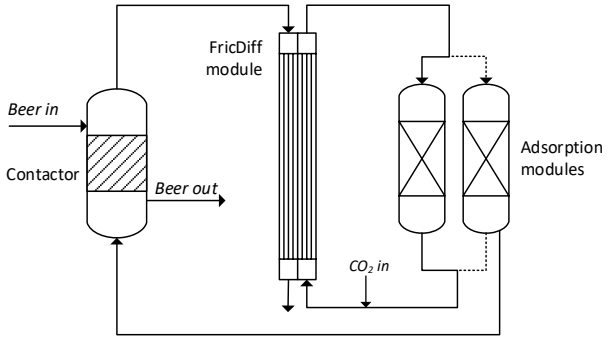

Figure 6.5. Process configuration using adsorption to regenerate the secondary sweep gas. This configuration will be selective for removing the more slowly diffusing flavours.

We here assume a counter-current contactor, that exchanges the flavours over the barrier; once more in the form of one or more hollow fibre modules. We simulate the system here as operating in complete counter-current mode with plug flow at both sides; we assume that still the same flow conditions can be maintained as assumed earlier. The system is operated such that the overall removal of isoamyl acetate is 10% of the initial amount in the beer, evaluated with the criterion

$$\Phi_f \frac{p_{iaa}}{p_T} = 0.10\Phi_b x_{iaa} \qquad 6.1$$

with Φ_f and Φ_b being the total molar flows of primary strip phase and beer, respectively, p_T the pressure of the primary strip phase, and p_{iaa} and x_{iaa} the partial pressure in the primary strip phase and the molar fraction in the incoming beer of isoamyl acetate, respectively.

We have two system parameters, the counter-pressure over the FricDiff porous barrier, and the total flow of primary stripping gas used (Φ_f). Figure 6.6 shows that the system can yield very good selectivity for the slow-diffusing flavours, while not needing excessive surface areas, taking into account the large surface-to-volume ratio of gas-to-gas contactors. Obviously, at larger counter-pressures over the barrier, fluxes are reduced and hence more surface area is needed.

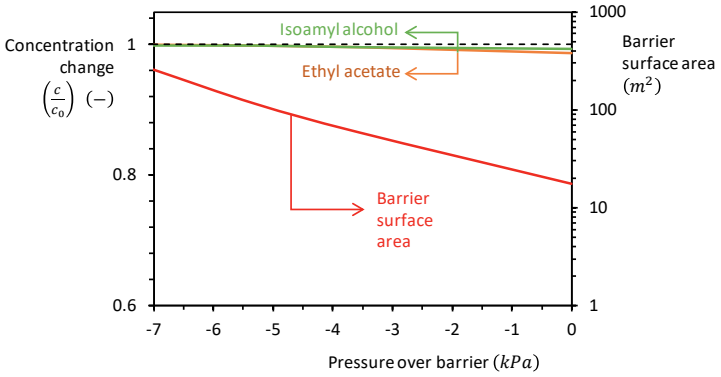

Figure 6.6. Relative changes in isoamyl alcohol (purple) and ethyl acetate (green) concentration, and required barrier surface area needed (red), to reduce the isoamyl acetate concentration by 10% in 1 m^3/h beer.

Next to the counter-pressure over the barrier, leading to a counter-flux of the carrier gas against the flavour fluxes, the second process parameter is the flow of the primary stripping gas, which takes up the flavours from the beer and brings it to the contactor. Using one primary stripping gas flow of 1 mol/s (for 1 m3/h beer), we obtain figure 6.6, which shows that while somewhat more surface area is needed to achieve the separation, we can get even better retention of the faster-diffusing flavours, ethyl acetate and isoamyl alcohol, while reducing the concentration of the isoamyl acetate by 10%. Here, there is hardly any difference in the behaviour of these flavours, so only one line can be seen in the graph. At larger stripping flow, the selectivity of the system increases somewhat, but one also needs a larger surface area of the barrier. Given that even at small flows of the primary stripping gas one can already get very good separation, a smaller flow would be most suited.

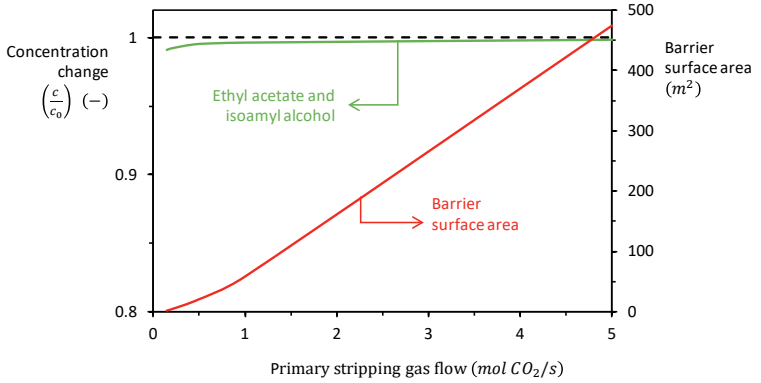

Figure 6.7. Relative changes in isoamyl alcohol and ethyl acetate concentrations (green – lines overlap), and required barrier surface area needed (red), to reduce the isoamyl acetate concentration by 10% in 1 m^3/h beer; as a function of the applied flow of the primary stripping gas (CO_2).

6.4.3 Conclusion on process configurations

The frictional diffusion system is not suitable to isolate one flavour at a time; instead, we conclude that the frictional diffusion concept is useful to adjust a flavour *profile*, not just for selectively removing the faster-diffusing components, but also for removing the slower-diffusing components. While one does need a different process configuration to switch from one to the other mode, one can use the counter-pressure over the barrier as a control to very quickly adapt the separation characteristics to varying compositions of the incoming beer, such that the outgoing beer has a constant flavour profile.

The process configurations evaluated here can be improved and other configurations are possible. Therefore, it is eminently possible that further improvements can be made. The configurations here have been merely used to demonstrate the feasibility of the use of frictional diffusion combined with stripping.

6.5 Outlook

Our overall conclusion is that while the process investigated here is not suited for the selective removal of one particular flavour component, it is possible to use frictional diffusion as a selective process that selectively adapts the overall flavour profile, and which can complement unselective adsorption of flavours. The overall system design, both for the removal of fast-diffusing flavours, and for removal of slow-diffusing flavours, is feasible with realistic barrier surface areas, and low counter-pressures needed.

The conceptual design carried out here is only schematic; further design should include non-ideal plug flow, pressure gradients along with the barrier modules, should analyse the overall resource use and the amount of CO_2 carrier phase that is needed. However, our first conceptual design shows that frictional diffusion may be a valuable tool that can adjust the flavour profile in beer, which can be adapted in-line, and without any changes in configuration, simply by adapting the counter-pressure over the barrier.

This thesis has contributed to the development of separation methods that can be used to adapt flavour profiles, offering fast adaptation by changing the system parameters. This included an overview of all methods currently available in the literature, a thorough study on the reliability of the estimation of the activities of the components in a system like beer, estimations on the mass transfer rates, plus the conceptual evaluation of the overall process.

Further studies should compare the approach taken in this thesis, to chromatographic methods as were proposed for example by Saffarionpour et al.[3], and to other methods, such as stripping with subsequent condensation and distillation of the flavours. Besides, while for beer the interaction with other components than ethanol was found insignificant, this is probably not the case for other foods.

References

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Summary

Volatile organic compounds (VOC) present at low concentrations may have a tremendous effect on the flavour profile of e.g. fermented beverages such as wine and beer. Controlling the flavour profile requires a detailed understanding of the physiochemical interactions of these components with the food matrices in which they occur. This thesis tries to answer the question of whether it is possible to separate any of the major volatile flavours in lager beers, especially isoamyl acetate. The proposed technique to do so had to meet a series of criteria. It had to be mild to protect biological ingredients such as proteins from being damaged, be able to handle high throughput (~100 to 500 m3/hr), satisfy food-grade conditions and must be compatible with current flavour stripping processes. To design such a process, more fundamental knowledge was needed, especially regarding the thermodynamics of solutions and kinetics of separation. These two topics are therefore addressed throughout the thesis.

In chapter II we start with a critical review of the current knowledge on flavour-matrix interactions in aqueous systems. We found that the fundamental data needed to design flavour separation processes for beer have neither been investigated experimentally nor through predictive modelling. The main focus in most papers was on the sensory aspects of flavour retention and release and directly linked to food design, and not to flavour design. Along with providing the first results from our work, we discussed and challenged the experimental techniques and data interpretation methods that are currently common practice, and recommended techniques to avoid pitfalls.

Based on our observations in chapter 2, we quantified Henry's Law Constant (HLC) in chapter III for the three major flavour compounds in beer (ethyl acetate, isoamyl acetate and isoamyl alcohol) in a model system containing ethanol concentrations below 25 %(v/v). We used the static headspace analysis method and showed that a major effect on flavour retention takes place at ethanol concentrations between 15 and 20 %(v/v) and higher. We also modelled this behaviour using Henry coefficients for aqueous binary, and ternary systems using the Wohl expansion for excess Gibbs free energy coupled with the one-parameter Margules equation. The first approach was not complex enough to cover the behaviour of the components, but based on the second model, we could. Wohl's expansion parameter for ethanol-water can be interpreted as solvent-solvent interaction. Furthermore, we quantified HLCs based on Van 't Hoff parameters between 30 to 60°C.

In chapter IV, we used a stripping column with structural packing to observe the effect of beer dry matter on flavour behaviour. We observed that the major components are carbohydrates and small proteins that in general enhance migration of esters from the aqueous body of the beer.

However, there was a slight retention of isoamyl alcohol that was due to changes in mass transfer resistance. The effect of gas flow rate on the partition coefficient of the compounds was minor, but it almost doubled the mass transfer coefficient of volatile flavour compounds. For isoamyl alcohol, the mass transfer resistance was found to be in both phases whereas for ester groups and ethanol the major resistance is in the gas phase which explains the difference in behaviour.

In chapter V we examined the possibility of using frictional diffusion (FricDiff) for separation of volatile compounds from a model gas mixture as it may exit a stripping column operating with carbon dioxide. We showed that a flat sheet FricDiff module can separate isoamyl acetate from the gas feed and that the presence of water or ethanol on the sweep side creates additional friction on flavour compounds and thus enhances separation but not enough to retain them completely. This may be further improved by adding flavours to the sweep gas, or alternatively, the thickness of the membrane and the pore size would need to be adjusted, which in turn would theoretically also improve the selectivity of the process in absence of wall friction.

In the general discussion (chapter VI), we bring all the findings presented earlier together and wrap up with recommendations for process design.

About the Author

Ali Ammari was born in Khoy, Western Azerbaijan of Iran. After graduation from the Islamic Azad University of Gachsaran in chemical engineering (oil refinement industries), he joined the catalytic reforming unit of Tehran oil refinery and was involved in many process simulation and designs for various companies active in oil and gas sector. Later on, he joined Sasol polymer company as a maintenance planner for C_2-cracker unit. After acquiring hands-on experience in energy/material production processes, the wave toward sustainable energy processes brought him back behind the study desk. He moved to Stockholm and received his Master's degree in chemical engineering from the Royal Institute of Technology (KTH) (Energy processes) in 2013.

As a freelance engineer, he moved to Vienna where he joined a team of researchers at the Austrian Institute of Technology (AIT) investigating two-phase microfluidic processes for innovative absorber design. After this, Ali went on to work as a PhD candidate at Wageningen University in the laboratory of Food Process Engineering to apply his classical engineering experience in the area of food science. This thesis is entitled "Separation Kinetic and Phase Behaviour of Volatile Flavour Active Compounds in Aqueous Food Streams", of which the result is described here.

Overview of Completed Training Activities

Discipline-specific activities

Numerical Methods for Chemical Engineers (the Netherlands, 2014)

MATLAB Fundamentals (the Netherlands, 2014)

Advanced Course on Thermodynamic Models (the Netherlands, 2015)

Sustainability Analysis in Food and Biobased Production (the Netherlands, 2014)

Int. School on Modelling and Simulation in Food and Bio Processes (Italy, 2016)

Molecular Affinity Separation (the Netherlands, 2014)

Han-sur-Lesse Winterschool (Belgium, 2017)

The 2nd International Conference on Chemical and Biochemical Engineering (ICCBE17) (Spain, 2017) †

19th International Conference on Chemical and Food Engineering (ICCFE 2017) (Bangkok) (Thailand, 2017) †

† Oral presentation in a conference

General courses

Project and Time Management (P&TM) (the Netherlands, 2014)

Stress Identification & Management (SI & M) (Netherlands, 2014)

Reviewing a Scientific Paper (RCP) (the Netherlands, 2014)

Training WUR council (the Netherlands, 2015-2016)

The Essentials of Scientific Writing and Presenting (ESWP) (the Netherlands, 2014)

Writing Grant Proposals (WGP) (the Netherlands, 2017)

Competence Assessment (COA) (the Netherlands, 2017)

WGS PhD Workshop Carousel (the Netherlands, 2017)

Optional activities

PhD Trip (Brazil and Chile, 2014)

PhD Trip (Germany and Switzerland, 2016)

The research described in this thesis was supported financially
by the Institute for Sustainable Process Technology (ISPT)