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Diethylacetal Synthesis in Simulated Moving Bed Reactor
Diethylacetal Synthesis in Simulated Moving Bed Reactor

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by

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To my parents and brother
There are those who look at things the way they are, and ask why...
I dream of things that never were, and ask why not?

Robert F. Kennedy
Resumo

Este trabalho consiste numa determinação da cinética de reação da síntese do dictilacetal a partir de etanol e acetaldeído, catalisada por resinas de permuta iônica e na obtenção das isômericas de adsorção dos compostos na resina, com vista ao desenvolvimento de um novo processo de produção de dictilacetal, basado na tecnologia de reatores de leito móvel simulado, SMBR.

O dictilacetal é usado directamente na indústria de perfumaria, farmacêutica e alimentar e também como solvante e intermediário na síntese de compostos químicos. Recentemente, o dictilacetal foi considerado um aditivo para o diesel. A informação existente na literatura relativa a dados termodinâmicos e de reação é escassa e as poucas patentes que mencionam a produção de dictilacetal referem-se à produção numa escala laboratorial em processos descontínuos. Apresenta-se uma pesquisa bibliográfica relativa às aplicações do dictilacetal e o estado de arte dos processos de produção de compostos oxigenados.

Construiu-se uma instalação experimental com um reactor fechado, equipado com um sistema automático de amostragem e aquisição de dados com vista à obtenção de dados termodinâmicos e de cinética da reação. Apresentam-se os dados experimentais relativos à reação de síntese de dictilacetal em fase líquida, catalisada pela resina Amberlyst 18. Determinou-se a constante de equilíbrio da reação expressa em actividades, na gama de temperaturas 20 a 60°C, à pressão de 6 atm. A conversão de equilíbrio, a 20°C, é aproximadamente 60%. Os resultados cinéticos experimentais são descritos através de um modelo matemático de um reactor fechado, que inclui difusão no filme e nos poros e utiliza uma lei cinética com dois parâmetros baseada no modelo de Langmuir-Hinshelwood e expressa em actividades.

A reação de acetalização é reversível e o produto final obtido é uma mistura de etanol, acetaldeído, dictilacetal e água. O subsistema dictilacetal- etanol- água apresenta três azeotropos binários e um azeotropo ternário formando os processos de separação por destilação economicamente desfavoráveis quando comparados com os processos adsorptivos. Por este motivo, realizaram-se estudos experimentais de produção de dictilacetal num reactor adsorptivo de leito fixo. As isômericas multicomponente do equilíbrio de adsorção foram obtidas através de experiências de adsorção dinâmica de misturas binárias não-reactivas realizadas em coluna. O desempenho do reactor cromatográfico adsorptivo foi previsto através de um modelo matemático, que inclui dispersão axial e resistência à transferência de massa no filme e na partícula.

No caso de reações limitadas pelo equilíbrio químico, onde há formação de mais do que um produto de reação, a conversão pode ser aumentada através da utilização de reatores multifuncionais que permitem a separação dos produtos à medida que eles são obtidos. Como a resina usada na síntese do dictilacetal pode actuar simultaneamente como catalisador e como adsorvente seletivo, o processo de reação por leito móvel simulado (SMBR) é adequado ao sistema em estudo. Nesse sentido, efectuou-se a produção e separação simultânea de dictilacetal numa unidade SMBR piloto, modelo Lacosep 12-26 (Novasep, França) existente no LSRF. Analisou-se a influência dos parâmetros de operação para determinar a região de separação, para uma determinada pureza de dictilacetal. Os dados experimentais de SMBR obtidos são previstos pelo modelo TMBR desenvolvido e indicam que o reagente limitante atinge conversões de 98-100%, acima da conversão de equilíbrio (60%).
Abstract

This work deals with the measurement of reaction kinetics of diethylacetal synthesis from ethanol and acetaldehyde catalyzed by ion exchange resins and adsorption equilibrium of the species on the resin in order to develop a novel process for diethylacetal production based on the Simulated Moving Bed Reactor technology, SMBR.

Diethylacetal is used in perfume, pharmaceutical and food industry and also as solvent and intermediate for the synthesis of various chemicals. Recently, acetal was considered as additive to diesel fuel. There is scarce information in the available literature concerning thermodynamics and reaction data; only few patents mention the diethylacetal production and at a laboratory scale in batch processes. Therefore, a literature survey on diethylacetal applications and the state of the art of production process aspects and patented processes for oxygenates production is initially presented.

A batch reactor experimental set-up, with automatic sampling system and data acquisition was designed and built to measure thermodynamic and reaction kinetics data. Experimental results for the liquid-phase reaction of acetal production catalyzed by the macroporous sulphonic resin Amberlyst 18 are presented. The reaction equilibrium constant based on activities is evaluated, in the range of 20-60°C, at 6 atm. The equilibrium conversion is about 60%, at 20°C. A mathematical model of the batch reactor, which include film and pore diffusion mechanisms and uses a two-parameter rate model based on a Langmuir-Hinshelwood expression using activities describes the experimental kinetic results.

Acetalization is a reversible reaction and therefore the product is a mixture that contains ethanol, acetaldehyde, diethylacetal and water. The subsystem acetal-ethanol-water exhibits three binary azeotropes and one ternary azeotrope; thus the conventional manufacturing processes based on energy-intensive distillation steps are economically disadvantageous when compared with the adsorption based technologies. For that reason, experimental studies for the diethylacetal production in a fixed bed adsorptive reactor are carried out. Dynamic adsorption experiments of binary non-reactive mixtures were performed in order to obtain multicomponent adsorption equilibrium isotherms. The behaviour of the chromatographic reactor was predicted with the obtained reaction kinetic and adsorption data through a mathematical model of the adsorptive reactor, which also included axial dispersion, external and internal mass-transfer resistances.

In reactions limited by chemical equilibrium where more than one product is formed, conversion can be enhanced in a hybrid apparatus or multifunctional reactor where the products are separated as they are formed. Since the resin used in acetal synthesis can act both as a catalyst and a selective adsorbent, the use of the simulated moving bed reactor (SMBR) is a feasible process. Therefore, the diethylacetal production and separation is performed in a SMBR pilot unit Licosep 12:26 (Novasep, France), available at LSRE. The influence of some operating parameters are analysed in order to determine the separation region for the desired purity of diethylacetal. The TMBR process model reasonably predicted the experimental data obtained. SMBR data show that the conversion of the limiting reactant can reach 98-100%, well above the thermodynamic equilibrium value.
Résumé

Le présent travail concerne la mesure de la cinétique de la réaction de synthèse du diéthylacétal à partir de la mélange éthanol et acétaldéhyde, catalysée par une résine acide, et de l'équilibre d'adsorption des espèces dans la résine en vue du développement de la technologie du réacteur de lit mobile simulé (SMBR) pour la production de diéthylacétal.

Diéthylacétal est utilisé en parfumerie, industries pharmaceutique et alimentaire, et aussi comme solvent et intermédiaire pour la synthèse des produits chimiques. Il a été considéré récemment comme additif du diesel. Une révision bibliographique concernant les aspects de production d'oxigénés et brevets et patents.

Une installation avec un réacteur fermé équipé avec un système automatique pour données la échantillonnage et aquisition a été construite. Les résultats expérimentaux pour la réaction en phase liquide de production de diéthylacétal catalysée par la résine Amberlyst 18 sont présentés. La constante d'équilibre est calculée dans la gamme de température 20-60 °C, à 6 atm. La conversion d'équilibre est d'environ 60% à 20 °C. Les résultats cinétique sont décrits par un modèle du réacteur fermé avec transport de matière dans le film et dans les pores, qui utilise une vitesse de réaction décrite par un modèle à deux paramètres basé sur l'expression de Langmuir-Hinshelwood, en termes d'activités.

La réaction de acetalisation est réversible et donc le produit est un mélange de éthanol, acétaldéhyde, diéthylacétal et eau. Le subsystème diéthylacétal-éthanol-eau présente trois azéotropes binaires et un azéotrope ternaire ; en conséquence la séparation par distillation peut être remplacée par technologiques d'adsorption. Une étude de production du diéthylacétal en réacteur adsorptive en lit fixe a été réalisé. Des expériences dynamiques en colonne pour les binaires non-réactives ont été mises en vue de l'obtention des isothermes d'équilibre d'adsorption. La performance du réacteur chromatographique a été prévue à partir des données cinétique, et d'adsorption mesurés au laboratoire.

La technologie du réacteur à lit mobile simulé a été développée une fois que pour les réactions reversibles on peut déplacer l'équilibre si un produit est enlevé par adsorption. Les expériences ont été conduits dans une unité pilote Licosep 12-26 (Novasep, France), disponible au LSRE. Des données expérimentales obtenues ont confirmé qui une conversion du réactif limitant (acétaldéhyde) de 98-100% est possible.
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1. Introduction

1.1 Relevance and Motivation

The main purpose of this thesis is to study the diethylacetal synthesis, focusing on the thermodynamic and kinetic aspects, and adsorption on acid ion exchange resins to support the development of a new technology (Simulated Moving Bed Reactor).

Diethylacetal (herein called acetal) is an important raw material for fragrances and pharmaceutical products and is used in the flavoring of spirit drinks. In perfumery, acetal is used for the design of synthetic perfumes to increase the resistance to oxidation and therefore the lifetime of perfumes. Acetal also finds widespread use as intermediate for the synthesis of various industrial chemicals, especially alkyl vinyl ethers and polyacetal resins. In the last years, the development of gasolines and fuels that are more environmentally acceptable has been studied intensively. Acetals have been under consideration as oxygenated additives to diesel fuel because they drastically reduce the emission of particles and NOx. It has been reported recently that diethylacetal is an attractive additive to diesel oil by keeping or improving the cetane number and helping in the combustion of the final products, without decreasing the ignition quality. Diethylacetal is also used as an additive of ethanol fuel to decrease the auto ignition temperature.

Acetal is produced by a reversible liquid phase reaction between acetaldehyde and ethanol, in acid medium. These processes are of particular interest to the Latin American countries, because bioethanol and acetaldehyde are subproducts of the cane sugar industry and have been studied in the framework of a CYTED Project IV.9: "Production of Oxygenated Additives to Diesel From Ethanol", to obtain high-added value products from ethanol.
In reactions limited by chemical equilibrium where more than one product is formed, conversion can be enhanced in a hybrid apparatus where the products are separated as they are formed. Since the resin used in acetal synthesis can act both as a catalyst and a selective adsorbent, the use of a chromatographic reactor-separator is a feasible process, in particular the simulated moving bed reactor (SMBR).

1.2 Objectives and Outline

The main goal of this thesis is to obtain thermodynamic, reaction kinetics and adsorption data in view of the application to a simulated moving bed reactor for the synthesis of diethylacetal. The scope of the thesis comprises:

Experimental data for reaction (equilibrium and kinetic) and mass transfer in a batch reactor, adsorption in fixed bed adsorptive reactor has been focused on the production of diethylacetal. Therefore, this work also aims to draw attention to a possibly attractive economic process for diethylacetal synthesis: the Simulated Moving Bed Reactor (SMBR).

The thesis comprises 6 chapters dealing with different aspects of diethylacetal production. For chapters 2 throughout 5, there are separate sections for introduction, conclusions and references. A literature review section is also included, where pertinent.

In Chapter 2, a literature survey on diethylacetal applications, mainly in perfumery and flavouring and as additive to diesel fuel is presented. The state of the art of production process aspects as patented process for oxygenates production; the use of ethanol, a renewable resource, and acetaldehyde as reactants; the advantages of heterogeneous catalyst, such as ion exchange resins (acid type) or zeolites; the methods used to displace equilibrium towards acetal formation are addressed. An overview in some reactive separations as reactive distillation, chromatographic reactors and membrane reactors applied to the production of oxygenates is reviewed in order to improve the overall efficiency of the process of diethylacetal synthesis.

Chapter 3 starts by a detailed description of the experimental set-up for the thermodynamic and reaction kinetics acquisition data. Experimental results for the liquid-phase reaction of acetal production from ethanol and acetaldehyde catalyzed by the macroporous sulphonic resin Amberlyst 18 are presented. The reaction equilibrium constant based on activities using activity coefficients calculated from the UNIFAC method is evaluated. A two-parameter model based
on a Langmuir-Hinshelwood rate expression using activities was proposed to describe the experimental kinetic results. A mathematical model including film and pore diffusion was developed in order to verify the existence of limitations due to mass transfer and to obtain the true kinetic constant.

In Chapter 4, experimental results for the diethylacetal production in a fixed bed adsorptive reactor are shown. Dynamic adsorption experiments of binary non-reactive mixtures were performed in order to obtain multicomponent adsorption equilibrium isotherms of Langmuir type. The reaction kinetics and adsorption data were used in the mathematical model of the adsorptive reactor, which also included axial dispersion, external and internal mass-transfer resistances.

The performance of a SMBR pilot unit for the production of diethylacetal was tested. The experimental and simulated results are presented in Chapter 5. The influence of feed composition, mass transfer, switching time and length section on the SMBR performance is studied. The criteria evaluated were the raffinate and extract purities, productivity, solvent consumption and acetaldehyde conversion. The concept of separation region is used in order to find the operating conditions of existing SMBR equipment applied to the production of diethylacetal.

Finally, the general conclusions drawn from this work and the suggestions for future work are presented in Chapter 6.
2. State-of-the art on Diethylacetal: Applications and Production Processes

In this chapter a literature survey on applications of diethylacetal (perfumes and flavours; additives to fuel) and production processes (patents, renewable resources, catalysts and new technologies) are addressed.

2.1 Applications

Acetals are oxygenated organic compounds produced by the reaction, in acid medium, between an alcohol (R₁–OH) and an aldehyde (R₂–CHO) and they are represented by the following structure R₂–CH–(O–R₁)₂, wherein R₁ and R₂ each independently represent an alkyl group. Acetals are used in perfumes to imparting fruity odour, in the flavouring of food (Kohlpaintner et al, 1999) and in the aroma of alcoholic beverage, such as spirit drinks (Kelly et al, 1999). Acetals are also used as starting materials for agricultural chemicals (Iwasaki et al, 1996) and intermediates for pharmaceuticals products, such as vitamins (Hoffmann-LaRoche, 1958), analgesics and antifungal (Iwai and Fujigaski, 2002).

Acetaldehyde diethylacetal (herein called acetal or 1,1-diethoxyethane) is used as solvent, specially for cellulose and its derivatives (Johnson, 1966), plasticizers, fuel for internal combustion engines and blenders (Mallet, 1948). Acetal also finds widespread use as intermediate for the synthesis of various industrial chemicals where it is necessary to protect the carboxylic group of aldehydes and ketones, especially alkyl vinyl ethers (Handlin et al, 2001)
and synthetic perfumes. It is a minor component of acetal resin (Merten and Wagner, 1961), used as adhesives (Aizawa et al, 1994). The main area of polyacetal resins consumption in Western Europe are the automotive sector (39 %), domestic, household and office equipment (14.7 %), and in electrical engineering industry (10.8 %) (Sextro, 1999). The annual consumption of polyacetals in USA, Japan and Europe was estimated in 388000 ton, but the polyacetal resins are expensive and are being replaced by other cheaper polymers (polypropylene, polystyrene).

In the last years, the development of gasolines and fuels that are more environmentally acceptable has been studied intensively. Reduction of pollutants in exhaust emissions of diesel engines represents a challenge to modern society. Acetals have been under consideration as oxygenated additives to diesel fuel because they reduce drastically the emission of particles and NOx (Thüner et al, 1999). The NOx emissions can be reduced by decreasing the combustion temperature. One way to achieve this lower combustion temperature is to add water to the fuel. However, by adding water, phase separation will occur in most fuel systems, especially at lower temperatures, for example below 0 °C. Some patents address the problem of water in the fuel composition by including in the fuel polyethers and/or acetals with or without methanol or ethanol. It is known that alcohol-containing fuels provide relatively low emissions of carbon, carbon oxide and nitrogen oxide (Golubkov and Golubkov, 2002).

### 2.1.1 Perfumes and flavours

Since early antiquity, resins from animal and plant sources have been used extensively for perfumery and flavour purposes. One of the most important steps in the history of natural fragrance materials was the industrialisation of essential oils production. With the industrial synthesis of vanillin (1874) and coumarin (1878), a new branch of the chemical industry was founded (Bauer et al, 1999). The number of synthetically produced fragrance and flavour chemicals has since expanded continuously. Modern perfumery began at the end of the 19th century when the first synthetic fragrance substances became available. The importance of perfumery has increased greatly since then. It includes not only the manufacture of fine products (perfume and eau de cologne), but also the use of perfumes in cosmetic, toiletries,
soaps, and house or industrial products. Worldwide consumption of perfume oils for all applications in 1984 was estimated at ca. 1.8×10⁶ EUR, see Figure 2.1 (Sturm and Peters, 1999).

![Pie chart](image)

**Figure 2.1** Applicational distribution of perfume oils (Sturm and Peters, 1999).

Aliphatic aldehydes are among the most important components used in perfumery. Acetals derived from aliphatic aldehydes have odour characteristics that resemble those of the aldehydes but are less pronounced. In spite of the aroma of acetals being weaker and slightly different than the correspondent aldehyde, they are used as stabilizers in the industry of perfumes. These acetals are used for the design of synthetic perfumes to increase the resistance to oxidation and therefore the lifetime of perfumes. Because of their stability toward alkali, acetals are used as soap perfume oils (Kohlpaintner et al., 1999).

Diethylacetal is an important fragrance and a raw material for fragrances and pharmaceutical products. Elimination of alcohol from acetal easily gives, for example, vinyl ether that is a reactive building block for pharmaceutical and fragrance synthesis (Kaufhold and El-Chabawi, 1996). It is a high impact chemical used to top note fruit flavours (apple, peach) and spirits (whiskey) and contributes with a significant strong, sweet, fruity odour to the typical aroma of Sherry Wines (Medina, 2002). Diethylacetal is referred as a basic fragrance in perfume and aromatic compositions, by the Scientific Committee on Cosmetic Products and Non-Food Products (SCCNFP) and by the European Flavour and Fragrance Association (EFFA) (SCCNFP, 2000).
Acetals are used to prepare aqueous liquids since they are extraordinary suitable as solubility promoters in micro-emulsions and liquid-crystalline phases. Applications of micro-emulsions and liquid-crystalline phases are also known as formulations for crop protection, cosmetics and pharmacy, as new type of solvents and in emulsion polymerization. Particularly suitable are acetals having a total of from 5 to 15 carbon atoms (Miller et al, 2002). Diethylacetal appears in the composition of many cosmetically acceptable aqueous medium (compatible with keratinous materials such as the skin or hair), such as shampoos (Perron et al, 2002) and conditioners, styling gels and mousses (Garnier and Samain, 2002), for example.

2.1.2 Additives to fuel

In recent years there has been a considerable increase in research and development in the area of environmentally acceptable alternative fuels as well as the use of alternative feedstocks as building blocks for applied chemicals and petrochemicals (Table 2.1). Conventional process industries are also faced with restricted emission control requirements. This trend is going to intensify for the next several decades because of the dwindling supply of petroleum reserves, emphasis on environmentally safe chemical technologies, fierce competitiveness in the global petrochemical market.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Environmental Problems</th>
<th>Availability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasoline (with catalyst)</td>
<td>CO₂, ozone among others</td>
<td>worldwide</td>
</tr>
<tr>
<td>Diesel fuel</td>
<td>CO₂, particle NOₓ, ozone</td>
<td>worldwide</td>
</tr>
<tr>
<td>LPG</td>
<td>CO₂, among others</td>
<td>some countries</td>
</tr>
<tr>
<td>Methanol</td>
<td>fossil</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>formaldehyde</td>
<td></td>
</tr>
<tr>
<td></td>
<td>formaldehyde</td>
<td></td>
</tr>
<tr>
<td>Ethanol (biomass)</td>
<td>acetaldehyde</td>
<td>Brazil</td>
</tr>
<tr>
<td>Vegetable oils</td>
<td>Particle, among others</td>
<td>Possible locally to some extent</td>
</tr>
</tbody>
</table>

However the utilization of alternative fuels requires a separate fuel distribution infrastructure and vehicle fuel systems need to be modified for these fuel properties. In contrast, blending oxygenates in existing gasoline fuel provides energy equivalent higher than conventional
gasoline. Its distribution cost is minor as compared with alternative fuels, and the automotive fuel system modification is not needed. In essence, the high octane and environmental benefits make oxygenates more attractive (Lee, 1997).

2.1.2.1 Oxygenated additives to gasolines

At the end of the 1950s, petroleum refinery seems to have reached a satisfactory technological level representing a good energy/economy balance. However, great increase in energy consumption and deterioration of the environment led to the recognition during the 1960s that energy production and automotive transportation were major causes of air-quality deterioration. By the 1970s it became clear that petroleum refining had to meet a new goal: energy, economy and environment together. Whereas this objective was recognized broadly, in the USA there was a succession of legislative acts and technical interventions (Table 2.2). Since 1970, the US Environmental Protection Agency (EPA) has had the responsibility for setting and ensuring National Ambient Quality Standards (NAAQS) (Ancillotti and Fattore, 1998).

The most publicized environmental measure adopted in the 1970s was the progressive phasing-out of lead additives in motor fuels and the introduction of severe emission limits for 1975 that could be met only by the application of catalytic converters for the oxidation of CO and HC in automobile exhaust.

By 1978 even NOx emissions had to be reduced drastically. This requirement brought about the development of the three-way catalytic converter, allowing a simultaneous reduction of CO, HC and NOx.

The complete removal of lead additives from gasoline was necessary for the technical operability of catalytic converters because the catalysts are intolerant of lead that causes rapid deactivation. An important technical consequence of the reduction of lead concentration in gasoline was a notable drop in gasoline octane number which could not be tolerated by millions of automobiles designed for high-octane-number fuel. The immediate solution for the problem was to raise octane number with increasing concentrations of butanes and aromatics in gasoline (Ancillotti and Fattore, 1998). A second and more innovative solution was the use of a new class of high-octane oxygenated components, called oxygenates.
Oxygenates are liquid organic compounds that are blended into gasoline to increase its oxygen content. During combustion, the additional oxygen in the gasoline reduces the output of carbon monoxide and limits emissions of ozone-forming materials. Oxygenates began to be added to gasoline and to play an increasingly important role in gasoline formulation, as octane booster replacing alkyl lead, from 1973. During the oil crises of the early 1970s, oxygenates originating from sources partially alternative to crude oil, played also a role as volume extenders.

Table 2.2 Legislative and technical interventions on US fuel market (Ancillotti and Fattore, 1998).

<table>
<thead>
<tr>
<th>Year</th>
<th>Event</th>
</tr>
</thead>
<tbody>
<tr>
<td>1955</td>
<td>First Congress law on clean air (Public Law 159)</td>
</tr>
<tr>
<td>1970</td>
<td>The Clean Air Act (CAA)</td>
</tr>
<tr>
<td>1975</td>
<td>Catalytic converters installed on new cars, lead phase down</td>
</tr>
<tr>
<td>1978</td>
<td>EPA grants waiver for ethanol blending (up to 10 vol%) 'gasohol'</td>
</tr>
<tr>
<td></td>
<td>Ethanol blended into gasoline for the first time</td>
</tr>
<tr>
<td>1979</td>
<td>EPA grants waiver for MTBE blending up to 7 vol%</td>
</tr>
<tr>
<td>1980</td>
<td>Federal income tax credit established for ethanol blending</td>
</tr>
<tr>
<td>1981</td>
<td>EPA defines 'sub-sym' to gasoline, fuel containing 2 wt.% oxygen</td>
</tr>
<tr>
<td></td>
<td>(11 vol.% MTBE)</td>
</tr>
<tr>
<td>1985</td>
<td>EPA sets the allowed lead to 0.5 gpg. Lead banking and trading begin</td>
</tr>
<tr>
<td></td>
<td>(first environmental credit trading programs)</td>
</tr>
<tr>
<td>1987</td>
<td>Colorado oxygenated fuels program for carbon monoxide control begins</td>
</tr>
<tr>
<td></td>
<td>(first in the nation)</td>
</tr>
<tr>
<td>1988</td>
<td>EPA grants 'sub-sym.' waiver for MTBE blending (up to 15 vol%)</td>
</tr>
<tr>
<td>1989</td>
<td>EPA grants 'sub-sym.' waiver for oxygenate blending (up to 2.7 wt.% oxygen)</td>
</tr>
<tr>
<td></td>
<td>Federal Phase 1 Reid Vapor Pressure (RVP) takes effect</td>
</tr>
<tr>
<td></td>
<td>ARCO Products introduces EC-1, the first gasoline designed for</td>
</tr>
<tr>
<td></td>
<td>emission reduction</td>
</tr>
<tr>
<td>1990</td>
<td>Clean Air Act Amendments of 1990 introduce the federal oxy-fuel and</td>
</tr>
<tr>
<td></td>
<td>reformulated gasolines (RFG) program (Tier 1 standards)</td>
</tr>
<tr>
<td></td>
<td>Internal Revenue Service (IRS) extends to ETBE the federal income</td>
</tr>
<tr>
<td></td>
<td>tax credit for ethanol blending</td>
</tr>
<tr>
<td>1991</td>
<td>ARCO introduces EC-X reformulated gasoline</td>
</tr>
<tr>
<td>1992</td>
<td>Federal oxy-fuel program begins</td>
</tr>
<tr>
<td></td>
<td>Federal Phase 2 RVP standards take effect</td>
</tr>
<tr>
<td>1993</td>
<td>EPA regulations controlling the sulfur content of diesel fuel</td>
</tr>
<tr>
<td></td>
<td>extended to 0.05 wt.% take effect</td>
</tr>
<tr>
<td>1995</td>
<td>Federal RFG program begins</td>
</tr>
<tr>
<td>1999</td>
<td>National LEV program begins</td>
</tr>
<tr>
<td>2004</td>
<td>Federal Tier 2 standards begins</td>
</tr>
</tbody>
</table>

The oxygenated market was dominated by Methyl tert-Butyl Ether (MTBE), due to its octane blending value, relatively low volatility, complete miscibility with gasoline, low susceptibility to phase separation in the storage and distribution system and low tendency to undergo peroxidation. MTBE manufacture had a high commercial growth (Lee, 1997). However, the unleaded gasoline/catalytic converter solution did not completely solve the car emission abatement. At the end of 1980s, the public concern in the US about the winter high CO concentration and summer ozone levels brought to consideration a deep change in gasoline and diesel fuel composition (reformulation) as an essential mean to low road pollution.
In 1990, the Clean Air Act Amendments (CAAA) approved two new programs called the oxygenated fuel program and the reformulated gasoline program (RFG). For the first time the US government regulated the composition and quality of motor fuels as a matter of environmental and health policy. Specifications for gasoline and diesel fuel were enforced by CAAA and the two new fuels, oxygenated gasoline and RFG, require certain oxygen content. The CAAA gave to oxygenates the new role of clean air additives, advancing that of octane suppliers. Oxygenated additives as aliphatic alcohols and ethers, in specific volumes and combinations, have similar octane values as conventional gasoline and therefore they were able to provide the oxygen that gasoline needed under the oxygenated fuel program. It was in this context that MTBE and others ethers were considered oxygenates.

The use of MTBE in reformulated gasolines has resulted in contamination of water resources across U.S.A., and the introduction of ethers ethers (ETBE, TAME, DIPE and IPTBE) as oxygenated fuels are being considered. Ethers like MTBE and ETBE have advantages over lighter alcohols (e.g., methanol, ethanol, etc.), especially with lower Reid vapour pressures and lower vaporization latent heats, etc. (Table 2.3).

| Table 2.3 Oxygenates for reformulated gasoline (Ancillotti and Fattore, 1998). |
|-----------------|-----------------|-----------------|-----------------|-----------------|
|                  | Blending Octane | Reid Vapour     | Boiling Point   | Oxygen          |
|                  | (R+M)/2         | Pressure (psi)  | (°C)            | (wt.%)          |
| Ethers           |                 |                 |                 |                 |
| MTBE             | 109             | 8.10            | 55              | 18.2            |
| TAME             | 104             | 3.5             | 86              | 15.7            |
| ETBE             | 110             | 3.5             | 72              | 15.7            |
| TAAE             | 105             | 0.2             | 101             | 13.8            |
| DIPE             | 105             | 4.5             | 68              | 15.7            |
| Alcohols         |                 |                 |                 |                 |
| Methanol         | 116             | 50-60           | 65              | 49.9            |
| Ethanol          | 113             | 17-22           | 78              | 34.7            |
| TBA              | 101             | 10-15           | 83              | 21.6            |

In Europe unleaded gasoline had been introduced in the mid-1980s, but at a different pace in the different countries. It pre-empted the sales of catalyst equipped cars, but legislated that all new cars must be capable to operate on the Europremium unleaded petrol even if they are run on leaded gasoline. Some countries like Germany, Switzerland, Austria and the Scandinavian countries achieved an early introduction by encouraging sales of unleaded petrol and low-
emission catalyst equipped vehicles by using tax concessions. By 1995, when the results from the European Auto/Oil Program were evaluated, Austria, Sweden and Finland were totally unleaded whereas the share of unleaded petrol was only 22% in Spain. Another important market difference was that compared to the US, diesel fuel played a more important role in the market. As the main concern in Europe regarding air quality is on ozone, NOx, and particulate emissions, diesel vehicles (passenger cars as well as heavy duty diesel engines) were included in the study. European Union legislative acts and technical interventions are presented on Table 2.4.

<table>
<thead>
<tr>
<th>Year</th>
<th>European Directive 70/220/EEC: First vehicle emissions requirements</th>
</tr>
</thead>
<tbody>
<tr>
<td>1991</td>
<td>European Directive 93/59/EC: Euro 1 limits (3-way catalysts)</td>
</tr>
</tbody>
</table>

The Auto/Oils Programs conducted in the U.S., Europe and Japan are the scientific basis for exhaust emission legislation and fuel quality regulations these countries. Figure 2.2 shows the evolution of emissions legislation.
2.1.2.2 Oxygenated additives to diesel

Diesel engines are more efficient than gasoline engines, but they emit 10-20 times more particulate matter (PM) than gasoline engines, do the environmental and health effects of diesel engine emissions continue to be a significant concern (Table 2.5). It is known that addition of oxygenates to diesel from petroleum lowers particulate matter emissions. Just adding oxygenated compounds to diesel fuel involves problems relatively to availability, toxicity, cost, solubility and biodegradability.

Table 2.5 Emissions from conventional Light Duty vehicles made between 1981-84 under typical urban driving conditions (Economopoulos, 1993).

<table>
<thead>
<tr>
<th></th>
<th>PM gr/km</th>
<th>SO₂ gr/km</th>
<th>NOₓ gr/km</th>
<th>CO gr/km</th>
<th>VOC gr/km</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diesel oil ¹</td>
<td>0.3</td>
<td>0.35</td>
<td>0.63</td>
<td>1.1</td>
<td>1.5</td>
</tr>
<tr>
<td>Gasoline ²</td>
<td>0.04</td>
<td>1.6</td>
<td>23.4</td>
<td>2.8</td>
<td></td>
</tr>
<tr>
<td>LPG</td>
<td>0.00</td>
<td>1.2</td>
<td>3.3</td>
<td>1.4</td>
<td></td>
</tr>
</tbody>
</table>

¹ Assumed Sulphur content in Diesel oil of 0.3 weight %
² Evaporative VOC emissions from the vehicle itself, as well as from the gasoline distribution system, are not included.

The SO₂ emissions from diesel powered cars are directly related to the sulfur content of the fuel. The quality of the diesel as expressed through the cetane number (related to the ignition quality), the distillation range, and the aromatic content, considerably affects the emissions of all major pollutants. It is believed that cetane numbers below 50 tend to increase all pollutants. A rough quantitative idea about the impact of cetane number on the emission rates is given in the table below, but it should be stressed, that the data from the different sources vary widely:

Table 2.6 Impact of cetane number on the emission rates (Economopoulos, 1993).

<table>
<thead>
<tr>
<th></th>
<th>Change in Cetane Number from 52 to 47.5</th>
<th>Change in Cetane Number from 52 to 44.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>+ 19.0 %</td>
<td>+ 31.5 %</td>
</tr>
<tr>
<td>VOC</td>
<td>+ 38.0 %</td>
<td>+ 63.0 %</td>
</tr>
<tr>
<td>NOₓ</td>
<td>+ 5.5 %</td>
<td>+ 9.0 %</td>
</tr>
<tr>
<td>Smoke</td>
<td>+ 23.0 %</td>
<td>+ 38.0 %</td>
</tr>
</tbody>
</table>
For diesel the year 2000 EC specification was constrained by increasing minimum cetane number to 51 (from 49), reducing the maximum density to 845 (from 860), reducing maximum 95% point of the distillation (T95%) to 360°C (from 370), reducing maximum sulphur content to 350 ppm (from 500) and introducing a polycyclic aromatics limit of 11%. For the year 2005 a further reduction to 50 ppm sulphur was imposed (Table 2.7).

Reduction of diesel engine emissions has traditionally been achieved through a combination of fuel system, combustion chamber and engine control modification. Another method of reformulating diesel fuel to reduce emissions is to incorporate oxygen in the fuel. Oxygenation of diesel fuel offers the possibility of reducing particulate matter emissions significantly, even for the current fleet of diesel vehicles. For instance, the replacement in motor fuel of 15% of the diesel by the alcohol provides cleaner exhaust and provides acceptable power without modification of the existing diesel engines (Golubkov, 2001). However, the problem of using the most widely available and inexpensive alcohols (methanol and ethanol) as a part of motor fuel is that these components are immiscible with diesel.

<table>
<thead>
<tr>
<th></th>
<th>Euro 2 Pre-2000</th>
<th>Euro 3 2000</th>
<th>Euro 4 2005</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cetane Number (min)</td>
<td>49</td>
<td>51</td>
<td></td>
</tr>
<tr>
<td>Sulfur, ppm (max)</td>
<td>500</td>
<td>350</td>
<td>50</td>
</tr>
<tr>
<td>Density (kg/m³)</td>
<td>820 - 860</td>
<td>820 - 845</td>
<td></td>
</tr>
<tr>
<td>Polyaromatics, % (max)</td>
<td>—</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>T95%, °C (max)</td>
<td>370</td>
<td>360</td>
<td></td>
</tr>
</tbody>
</table>

Acetals having a high degree of purity were considered good blenders for fuel since they allow liquid mixture to remain homogeneous when the temperature is low (Lloyd et al, 1958). Diethylacetal (98.5% purity) has a blending power equal to about 145% that of substantially pure paraaldehyde (Maletra, 1948).

In 1980, the Daimler Benz company patented a diesel fuel composition constituted by 50% in volume of diethylacetal and 50% of diesel, with acceptable cetane number (see Table 2.8) and cleaner exhaust emissions (Boennhoff, 1980).
Diethylacetal is used as additive of dialkoxyalkanes used as diesel fuel for enhancement of ignition performance (Boennhoff, 1983) and it is also an additive of ethanol fuel to decrease the auto ignition temperature. It has been reported recently that diethylacetal is an attractive additive to diesel oil by keeping or improving the cetane number and helping in the combustion of the final products, without decreasing the ignition quality (Capeletti et al., 2000; Balzano and Laborde, 2000).

In spite of the restrictive emissions legislation in European Countries and U.S.A., modern society is concerned with the damage to the global balance of carbon dioxide in the atmosphere, which is linked to the intensive burning of petroleum, coal and fossil gas. The damage to the carbon dioxide balance in the atmosphere causes global climate warming and has a negative effect on the nature of Earth. Because of this, the development of alternative motor fuel obtained for renewable plant resources is of real significance. But the existing global inventory of vehicles and machinery with diesel engines does not allow the complete elimination of diesel oil as a motor fuel. Therefore the research and development of additives to diesel in order to decrease the emissions is still necessary, but should obey to the following physical and chemical properties (Golubkov and Golubkov, 2002):

- density at 20 °C not less than 0.775 g/cm³;
- the cloud temperature is not higher than 0 °C at atmospheric pressure;
- stable a atmospheric pressure from cloud temperature of 0 °C to initial boiling point of 50 °C;
- amounts of liquid evaporated by boiling at atmospheric pressure not less than 98 % of the total volume of the motor fuel composition distills at temperature no higher than 400 °C, suitable no higher than 370 °C and preferably no higher than 280 °C;
- heat of combustion on oxidation by oxygen of not less than 39 MJ/kg;
- self-ignition temperature from 150 °C to 300 °C;
- ability to accommodate at least 1 % of water by volume.
Diethylacetal is proposed as one of the oxygenated components to be added to diesel fuel, resulting in cleaner exhaust emissions and do not adversely affect engine performance, see Table 2.9, (Golubkov, 2001; Golubkov and Golubkov, 2002).

Table 2.9  Fuel compositions and emissions impact (Golubkov, 2001).

<table>
<thead>
<tr>
<th>Composition 5</th>
<th>Composition 8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol 1.5%</td>
<td>Ethanol 10%</td>
</tr>
<tr>
<td>Ethanol 3%</td>
<td>Diethylacetal 2.5%</td>
</tr>
<tr>
<td>Formaldehyde dimethylacetal 3%</td>
<td>Dibuty1 ether 5%</td>
</tr>
<tr>
<td>Diethylacetal 3%</td>
<td>Butyl butyrate 3.5%</td>
</tr>
<tr>
<td>Methyl acetate 1%</td>
<td>Di-isooctyl ether 6.5%</td>
</tr>
<tr>
<td>Ethyl formate 1%</td>
<td>Methyltetrahydrofuran 5%</td>
</tr>
<tr>
<td>Methyl ether 5%</td>
<td>Isoamyl acetate 2%</td>
</tr>
<tr>
<td>Ethyl n-octate 5%</td>
<td>Amyl nitrate 0.5%</td>
</tr>
<tr>
<td>Tert-butyl peroxyacetate 0.5%</td>
<td>Hydrocarbon liquid 65%</td>
</tr>
<tr>
<td>Hydrocarbon liquid 75%</td>
<td></td>
</tr>
</tbody>
</table>

Density at 20°C (g/cm³)                           0.821 0.811
Temperature limits of evaporation of the liquid by boiling up to 285 °C 95.75 % 96.5 %
Heat of combustion (MJ/kg)                        40.4 40.4
Emissions reduction (%) 2

| CO (g/km)      | 0 %       | 16.9 %     |
| HC+NO₂ (g/km) | 12.2 %    | 8.8 %      |
| PM (g/km)      | 11.4 %    | 20.5 %     |

Thermal stability

Motor fuel composition 5 is a homogeneous liquid stable at atmospheric pressure over the range of -33 °C (cloud temperature) to 52.5 °C (initial boiling temperature)

Motor fuel composition 8 is a homogeneous liquid stable at atmospheric pressure over the range of -40 °C (cloud temperature) to 78 °C (initial boiling temperature)

1 hydrocarbon liquid (Mk1 diesel fuel SS 15 54 35)
2 compared to 100% Mk1 diesel fuel (SS 15 54 35)

2.2 Synthesis of diethylacetal

The primary process for the preparation of acetals is the reaction of an aldehyde with an alcohol, accordingly to:

\[ 2 \text{Alcohol + Aldehyde} \rightarrow \text{Acetal} + \text{Water} \]
The lower acetics have boiling points distinctly higher than those of the corresponding aldehydes. Some physical data of lower acetics and respective reactants are presented in Table 2.10.

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>Methanol</th>
<th>Ethanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formaldehyde</td>
<td>Formaldehyde dimethylacetal</td>
<td>Formaldehyde diethylacetal</td>
</tr>
<tr>
<td>CH₂O</td>
<td>(methylal)</td>
<td>(ethylal)</td>
</tr>
<tr>
<td>M₀ = 30.03</td>
<td>CH₂(OC₂H₅)₂</td>
<td>CH₂(OC₂H₅CH₃)₂</td>
</tr>
<tr>
<td>Tₘ = -19 °C</td>
<td>M₀ = 76.09</td>
<td>M₀ = 104.15</td>
</tr>
<tr>
<td></td>
<td>Tₘ = 45.5 °C</td>
<td>Tₘ = 89 °C</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>Acetaldehyde dimethylacetal</td>
<td>Acetaldehyde diethylacetal</td>
</tr>
<tr>
<td>CH₃CHO</td>
<td>(1,1-dimethoxyethane)</td>
<td>(1,1-dioxyethane)</td>
</tr>
<tr>
<td>M₀ = 44.05</td>
<td>CH₃CH(OC₂H₅)₂</td>
<td>CH₃CH(OC₂H₅CH₃)₂</td>
</tr>
<tr>
<td>Tₘ = 20.8 °C</td>
<td>M₀ = 90.12</td>
<td>M₀ = 118.18</td>
</tr>
<tr>
<td></td>
<td>Tₘ = 64.5 °C</td>
<td>Tₘ = 103.2 °C</td>
</tr>
<tr>
<td>Propionaldehyde</td>
<td>Propionaldehyde dimethylacetal</td>
<td>Propionaldehyde diethylacetal</td>
</tr>
<tr>
<td>CH₃CH₂CHO</td>
<td>(1,1-dimethoxypropane)</td>
<td>(1,1-dioxypropane)</td>
</tr>
<tr>
<td>M₀ = 58.08</td>
<td>CH₃CH₂CH(OC₂H₅)₂</td>
<td>CH₃CH₂CH(OC₂H₅CH₃)₂</td>
</tr>
<tr>
<td>Tₘ = 49 °C</td>
<td>M₀ = 101.15</td>
<td>M₀ = 132.21</td>
</tr>
<tr>
<td></td>
<td>Tₘ = 85 °C</td>
<td>Tₘ = 124 °C</td>
</tr>
<tr>
<td>Butyraldehyde</td>
<td>Butyraldehyde dimethylacetal</td>
<td>Butyraldehyde diethylacetal</td>
</tr>
<tr>
<td>CH₃CH₂CH₂CHO</td>
<td>(1,1-dimethoxybutan)</td>
<td>(1,1-dimethoxybutane)</td>
</tr>
<tr>
<td>M₀ = 72.11</td>
<td>CH₃CH₂CH₂CH(OC₂H₅)₂</td>
<td>CH₃CH₂CH₂CH(OC₂H₅CH₃)₂</td>
</tr>
<tr>
<td>Tₘ = 75 °C</td>
<td>M₀ = 118.18</td>
<td>M₀ = 146.22</td>
</tr>
<tr>
<td></td>
<td>Tₘ = 112 °C</td>
<td>Tₘ = 145 °C</td>
</tr>
</tbody>
</table>

Most known methods of diethylacetal production involve the reaction of acetaldehyde and ethanol in acid medium (Bramwyche et al., 1950; Petersen, 1977), however acetaldehyde could be replaced by vinyl ether, acetylene or ethylene (Kohlpaintner et al., 1999). The advantage of using ethanol and acetaldehyde as reactants is that ethanol is produced from renewable sources (mainly, from sugarcane industry) and acetaldehyde could be produced from oxidation or dehydrogenation of ethanol.
Traditionally, the reaction is catalyzed by mineral or carboxylic acids (Morrison and Boyd, 1983). The disadvantage of using soluble catalyst is that they must be neutralized after reaction. Therefore, heterogeneous catalysts as ion exchange resins (acid type) or zeolites are used, which have the advantage of being easily separated from reaction product and having a long lifetime. Resins are of particularly interest since they act like catalyst for the acetalization reaction and as a selective adsorbent to the species involved in the process (Mazzotti et al., 1996; Mazzoti et al., 1997).

The synthesis of acetals is a reversible reaction. In order to obtain acceptable acetal yields, the equilibrium must be displaced in the direction of acetal synthesis. Several methods are used to displace equilibrium towards acetal formation, such as:

1. to use a large excess of one of the reactants, in general the alcohol, which then requires elimination of that excess in a step of purification of the desired product;

2. to eliminate water by azeotropic distillation between a solvent and water – the solvent and water must be partially miscible and the boiling points of the different constituents in the reaction medium must be compatible with that azeotrope;

3. to use reactive separations (as reactive distillation, simulated moving bed reactor, pervaporation reactor, etc.) in order to remove the products from the reaction medium.

At the present, the process of acetals production (diethylacetal, dimethylacetal or others) consists on a reaction followed by separation, usually consecutive distillations to separate the mixture (Kaufhold and El-Chabawi, 1996), (Martin and Raynolds, 1988).

In reactions limited by chemical equilibrium where more than one product is formed, conversion can be enhanced in multifunctional reactor where the products are separated as they are formed. Novel reactor configurations and choice of operating conditions can be used to maximise the conversion of reactants and improve selectivity of desired product, thereby reducing the costs associated with the separation step. Recently, reactive separations as reactive distillation, chromatographic reactors and membrane reactors have been intensively applied to esterifications processes, mainly to the production of oxygenates to fuel.
2.2.1 Patented Processes Overview

There are a great number of patents related to acetals production, any technology was performed at industrial scale. A summary of the patented is presented in Table 2.11.

<table>
<thead>
<tr>
<th>Process</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porocel Corp. (1948) (Heinemann and Darby, 1948)</td>
<td>Continuous process at room temperature: the reactant mixture is percolated through a bed of agglomerate adsorbent (catalyst). The reactive mixture is then separated by fractional distillation. Acetals yields of 50% are reported.</td>
</tr>
<tr>
<td>Bozel-Maletra (1948) (Maletra, 1948) (Maletra, 1948)</td>
<td>First method that uses catalyst neutral ammonium salts instead of strong acids, in order to avoid corrosive products. The acetal is obtained by reacting the aldehyde and the alcohol of ammonium chloride, and then separating the acetal formed from the reactive mixture by a series of extractions with a solvent (water) until the desired purity. It is reported a purity of 98.5% of diethylacetal.</td>
</tr>
<tr>
<td>Distillers Co. (1950) (Bramwych et al., 1950)</td>
<td>Diethylacetal is produced by reacting acetaldehyde with ethanol in the presence of a strong acid (sulphuric acid) and in the presence of an inert diluent (kerosene, benzene, n-hexane, carbon tetrachloride), substantially immiscible with water. The organic phase is then separated from the aqueous phase and the diethylacetal is recovered from the diluent by distillation. The yield of acetal increases from 55% (without solvent) to 76-83% (depending of the solvent used).</td>
</tr>
<tr>
<td>Dow Chemical (1954) (Frevel and Hedlund, 1950)</td>
<td>Production of acetals by carrying out the reaction in vapour phase in the absence of catalyst, cooling the effluent vapours to condense liquid product and separating the acetal from the condensed liquid.</td>
</tr>
<tr>
<td>British Celanese (1964) (Beesley and Dale, 1967)</td>
<td>Production of diethylacetal and ethyl vinyl ether by reacting ethanol and ethylene, catalyzed by a mixture constituted by a palladium (II) salt and a metal salt, in the presence of molecular oxygen. Acetaldehyde is a secondary product.</td>
</tr>
<tr>
<td>Degussa (1986) (Andrade et al., 1986)</td>
<td>Preparation of acetals through the conversion of aldehydes with alcohols in a liquid phase in the presence of a solid acid catalyst (zeolites or ion exchange resins). The reactive mixture is then filtered in order to recover the catalyst. To separate the acetal is realized a liquid-liquid extraction using water and an organic solvent (hydrocarbons). The acetal is taken up with the organic solvent and the unconverted reactants remains in the aqueous phase.</td>
</tr>
<tr>
<td>Showa Denko (1994) (Azawa et al., 1994)</td>
<td>A process to produce high purity dimethylacetal comprises three steps. The dimethylacetal is produced by reactive distillation, using methanol in large excess and sulphuric acid as catalyst. The azeotrope constituted by methanol and acetal is obtained from the top and water is discharged from the bottom. Acetal is then separated from methanol by azeotropic distillation, using n-hexane as azeotrope former. Finally the n-hexane is recovered by water extraction and recycled to the process. The acetaldehyde conversion was 100% and the acetal yield was 100%.</td>
</tr>
<tr>
<td>Huels Aktieng. (1996) (Kaufhold and El-Chabawi, 1996)</td>
<td>A process for preparing diethylacetal involving the reaction between acetaldehyde and ethanol in the presence of sulphuric acid and in the presence of an entrainer (hexane). The mixture constituted by hexane, ethanol/water and acetaldehyde is distilled from the reactor and then condensed and separated into phases by means of a water separator. The entrainer phase is directly recirculated. The acetaldehyde presented in the aqueous phase is separated off and recovered by distillation. The acetal formed is obtained from the bottom product of the reactor. Acetals yields of 74% and acetaldehyde conversion of 80% are reported.</td>
</tr>
<tr>
<td>Hoffmann-La Roche (2001) (Boesch and Heragujuella, 2001)</td>
<td>Production of acetals by reacting aldehyde and alcohol in the presence of solid acid (Amberlyst A15) and removing water from the reaction product by pervaporation.</td>
</tr>
</tbody>
</table>
The reaction is usually catalyzed by a strong acid, as sulphuric acid. The use of solid acid catalysts, as zeolites and ion exchange resins, are also mentioned. In order to overcome equilibrium limitations excess of one reactant is commonly applied. Another technique is the use of a solvent (n-hexane, kerosene, benzene), substantially immiscible with water in order to extract the acetal. Distillation is the most used separation technology, few patents mention liquid-liquid extraction and pervaporation as alternative. Based on the SRI Consulting (http://sric-db-server.sric.sri.com) information there are three producing companies of diethylacetal in Europe and one in Middle East.

2.2.2 Renewable Resources

Renewable resources were for centuries virtually the only energy carriers and raw materials for chemical products, although in the 19th and 20th centuries they were driven back, first by coal and latter by petroleum. Over the last 50 years, advances in petroleum processing and industrial organic chemistry have enable petroleum to become a primary source of energy and the major feedstock for industrial organic chemicals. In fact, over 90% (by tonnage) of all organic chemicals are derived from petroleum (Embree et al, 2001).

After the oil crises of the 1970s, there is a growing interest in reducing dependence on petroleum and returning to use of renewable resources to meet at least some of the demand for fuel and organic chemicals. The most obvious reason to reduce dependence on petroleum feedstocks is that petroleum is a finite resource. Although projections vary, most estimates indicate that over the next 10-40 years petroleum will become considerably less abundant and more expensive than in today (Kendall, 2001), (Riley, 1999). Moreover, petroleum resources are also available to certain geographic regions in the world (i.e. the Middle East).

In addition, many countries have biomass resources that could be converted into renewable feedstocks for fuel, chemicals and materials. In fact, in some cases these ‘resources’ are nuisance wastes that pose a disposal problem, and a there are growing concernsments to convert that subproducts into high added value products. The use of renewable resources has been encouraged on USA and European levels with the aid of subsidies and tax reliefs, and their political importance has been emphasized. Examples of current efforts to reduce the dependence on oil imports and create additional markets for agricultural wastes and biomass are the production of oxygenated fuels. Namely, one advantage of ETBE relatively to MTBE
is that it can be made from bioethanol (a renewable oxygenate). A schematic oxygenate production pattern is shown in Figure 2.3.

![Diagram of oxygenated production pattern](image)

**Figure 2.3. Oxygenated production pattern, adapted from (Ancillotti and Fattore, 1998).**

The synthesis of diethylacetal using ethanol and acetaldehyde as reactants seems to be of great interest, mainly to the Latin American countries, because molasses as a waste material from cane sugar industry is important for fermentation ethanol production. In USA, the production
of ethanol is based on corn. The capacities and annual production figures for already installed plants producing synthetic and fermentation ethanol in the world are listed in Table 2.12. In 1977, 158000 m³ of ethanol was used as a raw material for chemical manufacturing in the CE. In these countries, ca. 55% of the ethanol was derived from fermentation (Kosaric et al, 1999). Bioethanol producers in the industrialized nations import some of their raw materials in the form of molasses from the sugar producing industries of developing countries.

In some countries, such as Brazil and India, the production of a variety of chemicals products is based on bioethanol, such as acetaldehyde. Acetaldehyde could be produced from dehydrogenation of ethanol. In Western Europe about 15% of acetaldehyde production is by ethanol oxidation, being the most used process based in ethylene oxidation.

<table>
<thead>
<tr>
<th>Developed countries</th>
<th>Synthesis Production (10⁶ L/a)</th>
<th>Fermentation Production (10⁶ L/a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Australia, New Zeland</td>
<td>-</td>
<td>40</td>
</tr>
<tr>
<td>Eastern Europe</td>
<td>-</td>
<td>165</td>
</tr>
<tr>
<td>Western Europe</td>
<td>610</td>
<td>974</td>
</tr>
<tr>
<td>Israel, Japan, South Africa</td>
<td>69</td>
<td>138</td>
</tr>
<tr>
<td>North America</td>
<td>880</td>
<td>2153</td>
</tr>
<tr>
<td>Soviet Union</td>
<td>55</td>
<td>128</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>1614</strong></td>
<td><strong>3598</strong></td>
</tr>
<tr>
<td>Developing countries</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Africa</td>
<td>-</td>
<td>155</td>
</tr>
<tr>
<td>Asia</td>
<td>62</td>
<td>691</td>
</tr>
<tr>
<td>Asia (centrally planned economies)</td>
<td>605</td>
<td></td>
</tr>
<tr>
<td>Central America</td>
<td>-</td>
<td>290</td>
</tr>
<tr>
<td>South America</td>
<td>-</td>
<td>1156</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>667</strong></td>
<td><strong>2297</strong></td>
</tr>
<tr>
<td><strong>Total worldwide</strong></td>
<td><strong>2282</strong></td>
<td><strong>5895</strong></td>
</tr>
</tbody>
</table>

2.2.3 Acid Catalysis

The selection of catalysts for the synthesis of diethylacetal was, considering the nature of the reaction, oriented to acid substrates. Most of all the industrial applications to oxygenates
synthesis have adopted acidic ion exchange resins as catalysts. Less attention was given to inorganic acids that seem not offering, as a whole, convincing performances to substitute the resins in industrial applications. The first synthesis of ethers (MTBE, ETBE), esters, acetals and ketals were done on inorganic catalysts as mineral acids, such as sulphuric acid. But these catalysts presented low selectivity, favouring the formation of dehydrated by-products. Moreover, the use of soluble inorganic acids makes the separation and purification of the desired product a rather complex operation. Solid catalysts as alumino silicates (like montmorillonites and bentonites), and zeolites (Y, mordenite, ZSM, ferrierites) were demonstrated to be good catalysts, but catalytic activity and/or selectivity of these catalysts resulted always lower compared to macroreticular acid resins.


The catalytic behaviour of several catalysts for diethylacetal synthesis is presented in Figure 2.4 and the properties of the tested catalysts are presented in Table 2.13. A coarse ranking of performances can be established to be A15 > montmorillonites > mordenite, zeolitic and amorphous FCC catalysts.
Ion exchange resins have functional groups tied to insoluble molecules; those groups contain hydrogen and hydroxyl ions and are able to catalyze many reactions normally carried out in homogeneous systems. The structure of these heterogeneous catalysts obtained by polymerization can be of gel-type resins (continuous microporous matrix) or macroreticular-type resins. Macroreticular resins have macropores which allow a significant increase in the reaction rate between nonpolar molecules or compounds with a high molecular weight. Ion exchange resins conventionally used to catalyze etherification and esterification reactions can be used, examples of such ion exchange resins are Dowex 50 (Dow Chemical), Amberlite IR120, Amberlyst A15 and A36 (Rohm & Haas), Lewatit (Bayer), as shown in Table 2.14.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Description</th>
<th>Surface area (m²/g)</th>
<th>Pore volume (ml/g)</th>
<th>Acidity (meq/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A15</td>
<td>Polystyrene-polydivinilbenzene sulfonic resin, Rohm and Haas</td>
<td>45</td>
<td>0.360</td>
<td>4.7³</td>
</tr>
<tr>
<td>K10</td>
<td>Acid treated montmorillonite, Aldrich</td>
<td>345</td>
<td>0.564</td>
<td>0.273</td>
</tr>
<tr>
<td>M</td>
<td>Mordenite, Norton</td>
<td>436</td>
<td>0.210</td>
<td>0.649</td>
</tr>
<tr>
<td>MAA</td>
<td>Acid treated montmorillonite, natural</td>
<td>235</td>
<td>0.262</td>
<td>0.640</td>
</tr>
<tr>
<td>R</td>
<td>Zeolite FCC catalyst, Fresh BR1160, Engelhard UCS: 24.72Å</td>
<td>342</td>
<td>0.259</td>
<td>0.540</td>
</tr>
<tr>
<td>S</td>
<td>Zeolite FCC catalyst, Isoplus 1000, Engelhard UCS: 24.40Å</td>
<td>336</td>
<td>n.a.</td>
<td>0.474</td>
</tr>
<tr>
<td>T</td>
<td>Amorphous FCC catalyst, HA-HPV, Ketjen 25% Al₂O₃</td>
<td>454</td>
<td>0.688</td>
<td>0.382</td>
</tr>
<tr>
<td>U</td>
<td>Amorphous FCC catalyst, LA-LPV, Ketjen 12% Al₂O₃</td>
<td>559</td>
<td>0.642</td>
<td>0.350</td>
</tr>
<tr>
<td>W</td>
<td>Equilibrium zeolitic FCC catalyst, BR1160, Engelhard UCS: 24.31Å</td>
<td>175</td>
<td>0.213</td>
<td>0.065</td>
</tr>
<tr>
<td>X</td>
<td>Equilibrium zeolitic FCC catalyst, Octavision, FCC S.A. UCS: 24.24Å</td>
<td>151</td>
<td>0.120</td>
<td>0.160</td>
</tr>
</tbody>
</table>

Table 2.13: Properties of the catalysts tested for diethylacetal synthesis (Capeletti et al., 2000).
### 2.2.4 Equilibrium Displacement

Similar to etherification and esterification reactions, the acetalization has a limited conversion by the nature of the equilibrium reaction. In order to increase the acetal yield, therefore, it would be necessary to take some manipulation, for example using one of the reactants in large excess or removing one product from the reaction system. The use of a large excess of one of the reactants, implies another step of separation in order to recover and recycle the exceeding reactant.

<table>
<thead>
<tr>
<th>Resin</th>
<th>Product</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amberlyst A15</td>
<td>MTBE</td>
<td>(Oktar et al., 1999), (Rehfinger and Hoffmann, 1990), (Zhang and Datta, 1995), (Ali and Bhatia, 1990)</td>
</tr>
<tr>
<td></td>
<td>ETBE</td>
<td>(Zhang et al., 1997)</td>
</tr>
<tr>
<td></td>
<td>TAME</td>
<td>(Syed et al., 2000)</td>
</tr>
<tr>
<td></td>
<td>Acetic acid</td>
<td>(Sircar and Rao, 1999)</td>
</tr>
<tr>
<td></td>
<td>Methyl acetate</td>
<td>(Pöpken et al., 2000)</td>
</tr>
<tr>
<td></td>
<td>Ethyl acetate</td>
<td>(Mazzoti et al., 1997)</td>
</tr>
<tr>
<td></td>
<td>β-phenyl acetate</td>
<td>(Kawase et al., 1996)</td>
</tr>
<tr>
<td>Amberlyst A16</td>
<td>TAME</td>
<td>(Kiviranta-Pääkkönen et al., 1998)</td>
</tr>
<tr>
<td></td>
<td>TAEE</td>
<td>(Linnekoski et al., 1998)</td>
</tr>
<tr>
<td>Amberlyst A18</td>
<td>MTBE</td>
<td>(Caetano et al., 1994), (Quinta-Ferreira et al., 1996)</td>
</tr>
<tr>
<td></td>
<td>ETBE</td>
<td>(Prior, 2001)</td>
</tr>
<tr>
<td>Amberlyst A31</td>
<td>Bisphenol A</td>
<td>(Kawase et al., 1999)</td>
</tr>
<tr>
<td>Lewatit SPC 118</td>
<td>TAME</td>
<td>(Oost and Hoffmann, 1996)</td>
</tr>
<tr>
<td>Bayer K2631</td>
<td>MTBE</td>
<td>(Fite et al., 1998)</td>
</tr>
<tr>
<td></td>
<td>ETBE</td>
<td>(Vila et al., 1993)</td>
</tr>
<tr>
<td>ZSM-5</td>
<td>IPTBE</td>
<td>(Calderón et al., 1997)</td>
</tr>
<tr>
<td></td>
<td>ETBE</td>
<td>(Oudshoorn et al., 1999)</td>
</tr>
</tbody>
</table>
When synthesising from acetaldehyde and ethanol, the best diethylacetal yield is obtained when the water formed is the eliminated as the reaction advances. A number of methods can be used to eliminate the water: distillation of an azeotrope between a solvent and water – the solvent and the water must be at least partially miscible and the boiling points of the different constituents in the reaction medium must be compatible with that azeotrope; or the water can be captured by adsorption on a dehydrating solid which may be a molecular sieve or any other compound which can adsorb water without interfering in the reaction of acetal formation. Again, the use of a solvent to form an azeotrope with water leads to an additional separation step.

The conventional manufacturing processes use energy-intensive distillation steps, which are often rendered difficult by the formation of azeotropes. The subsystem acetal-ethanol-water exhibits three binary azeotropes and one ternary azeotrope, as shown in Figure 2.5. The complexity of the vapour-liquid and liquid-liquid equilibrium makes the design and the synthesis of separation sequences a difficult task.

![Diagram of azeotropes](image)

**Figure 2.5** Azeotropes for the ternary system acetal-ethanol-water, and boiling points for pure species and azeotropic mixtures at 1.8 atm (Cristófoli et al, 1999).
Innovative reactor configurations and choice of operating conditions of reactants and improve selectivity of desired product, thereby reducing the cost associated with the separation step. In recent years there has been considerable academic and industrial interest in the area of reactive separation units which combine reaction and separation of species in as a single step in a process. Reactive separations offer the following advantages:

- increase conversion of reactants beyond thermodynamic limit;
- improved selectivities and yields of desired products;
- reduced requirements for external energy supply or cooling capacity;
- reduced capital costs by process intensification.

### 2.2.5 Reactive Separations

Reaction and separation are traditionally viewed as separate steps in a chemical process. This paradigm is still main stream in the chemical industry. However, the combination of reaction and separation in a single unit has arisen considerably interest in the chemical engineering research and industry. The term multifunctional reactor is often used to embrace reactive separations technology, which promises reduction in capital costs, increased conversion and reduced by-product formation; a variety of separation principles and concepts can be incorporated into the reactor, see Figure 2.6.

The advantages of coupling chemical reaction and separation have been exploited since 1921 (Backaus, 1921) for methyl acetate production with reactive distillation processes and have been applied in the petrochemical industry. In this case, the multifunctional reactor is a distillation column filled with catalytically active packing. In the column, chemicals are converted on the catalyst while reaction products are continuously separated by fractioning (thus overcoming equilibrium limitations). The advantages of catalytic distillation units, besides the continuous removal of reaction products and higher yields due the equilibrium shift, consist mainly of reduced energy requirements and lower capital investments (Stankiewicz and Moulijn, 2000).
One example with a success story of reactive distillation technology is the methyl acetate production. Conventional process use one or more liquid-phase reactors with large excess of one reactant in order to achieve high conversions of the other. A typical flowsheet of a conventional process is shown in Figure 2.7 in which the reaction section is followed by eight distillation columns, one liquid-liquid extractor and a decanter. This process requires a large capital investment, high energy costs and a large inventory of solvents. In the reactive distillation process for methyl acetate, the entire process is carried out in a single unit (see Figure 2.7) and represents one-fifth of the capital investment of the conventional process and consumes only one-fifth of the energy (Krishna, 2002).
Figure 2.7 Task-integrated methyl acetate column is much simpler than the conventional plant (Stankiewicz and Mouljin, 2000).

2.2.5.1 Reactive Distillation (RD)

The design and operation issues for reactive distillation systems are considerably more complex than those involved for either conventional reactor or conventional distillation columns. Some of the advantages of RD can be illustrated by a simple example. Consider the reversible reaction: \( A + B \rightleftharpoons C + D \) where the components A, C, D and B have increasing boiling points. The conventional process for consist of a reactor followed by a sequence of distillation columns, as shown in Figure 2.8a. The alternative RD column, Figure 2.8b, consist in a reactive section in the middle with non-reactive rectifying and stripping sections at the top and bottom. In the reactive section the products are separated as they are formed, driving the equilibrium towards products formation and preventing any undesired side reactions. For a properly RD column, ideally 100% conversion and 100% yield can be achieved.
Reactive distillation technology is being widely applied for oxygenates production as MTBE (Sneesby et al., 1998) and (Sundmacher et al., 1999), ETBE (Oudshoorn et al., 1999) or TAME (Oost and Hoffmann, 1996). For these examples, the benefits of RD are several:

- improved conversion of reactant approaching 100%, reducing recycle costs;
- improved selectivity by removing one of the products from the reaction medium;
- avoidance of azeotropes;
- significant capital savings and heat integration benefits.

However, there are constraints and difficulties in RD implementation, mainly volatility constraints. In order to maintain high concentrations of reactants and low concentrations of products in the reaction zone, the reactants and products must have suitable volatility. Also, it is necessary that both products have different boiling points to ensure the separation. Because of these, the production of diethylacetal using RD technology doesn’t seem feasible, since acetal and water have similar boiling points. However, acetalization of formaldehyde with methanol in RD columns was studied (Kolah et al., 1996).
2.2.5.2 Pervaporation Membrane Reactor

The application of membrane reactors to esterifications reactions has been studied as alternative technology to RD. In recent years the potential use of pervaporation technology for the separation of organic component from an organic mixture (specially azotropic or close boiling mixtures) has attracted significant attention in the research community. The combination of pervaporation with a chemical reactor has been found to be an interesting alternative to conventional process for condensation reactions, since equilibrium could be shifted by continuously removing water through a selective membrane (Lipnizki et al, 1999).

Typical condensation reactions included:

\[ \text{Esterification: } R^-\text{COOH} + H_2O \rightarrow R^-\text{COOR} + H_2O \]

\[ \text{Acetalization: } R^-\text{CHO} + 2 H_2O \rightarrow R^-\text{CH}-(OR)\text{2} + H_2O \]

\[ \text{Ketalization: } R^-\text{CO} + 2 HO-R \rightarrow R^-\text{C}(OR)\text{2} + H_2O \]

Condensation reactions are normally equilibrium-limited, the removal of co-product water allows reduction of production costs because of (Wynn, 2001):

- Higher yield - lower reagent consumption
- Faster reaction - greater reactor throughput
- Purer products - less effort for product purification.

The use of a pervaporation membrane reactor can be found in a recent European patent for the acetic acid esterification reaction with ethanol (Pearce, 1986). The membrane reactor described in the patent consists of two half-cells with a flat membrane disk (commercial PVA or Nafion) placed in the middle, as shown in Figure 2.9. For an ethanol to acetic acid ratio of 2, liquid hourly space velocities in the range of 2-5 and at temperature of 90 °C, complete conversion of the acetic acid was reported.
The esterification of carboxylic acid with ethanol to produce ethyl carboxylate using a pervaporation reactor membrane was carried out in a tubular reactor in the liquid phase (Zhu et al, 1996); see Figure 2.10. In the construction used the walls of the tube were made of a ceramic support that was impregnated with polyetherimide, which is selective to water permeation, see Figure 2.11. The obtained conversion was higher than the conventional tubular reactor and beyond thermodynamics equilibrium conversion.

For comparison with RD technology, it should be noticed that even though conversion above equilibrium is achieved in a pervaporation membrane reactor, the conversion does not reach 100%; this means that the product contains the ester, along with water and unreacted...
carboxylic acid and alcohol. In order to obtain pure ester, an additional distillation step is required (Krishna, 2002).

Figure 2.11 Special model houses ceramic membranes (Wynn, 2001).

2.2.5.3 Simulated Moving Bed Reactor (SMBR)

Among the continuous chromatography processes, the Simulated Moving Bed (SMB) technology has provided one of the most convenient solutions for numerous applications in pharmaceutical and fine chemical industries (food, cosmetics, etc.).

Besides classical separation applications, the SMB technology has been also proposed for hybrid processes, where chromatographic separation and chemical reaction take place in the same unit. The SMB can be used as a unit operation to carry out separations and reactions, as shown in Figure 2.12. In fact, in reactions limited by chemical equilibrium where more than one product is formed, conversion can be enhanced in a hybrid apparatus where the products are separated as they are formed. In the 60's the integration of chemical or biochemical reactions in chromatographic separation processes has been patented (Broughton and Gerhold, 1961).

Recently, with reference to esterification reactions, it has been shown that cation exchange resins can act both as selective adsorbent and heterogeneous catalyst. Esterification reactions are reversible and may be catalyzed by acid sites promoted by sulphonic groups present in cross linked polystyrene-based resins. Moreover, the resin may selectively adsorb the chemical species involved and enhance the separation of reaction products. As a result reactions may be
driven to complete conversion and no catalyst has to be removed from the products. This property from a class of ion-exchange resins has motivated the study of the esterification of acetic acid by ethanol on a simulated moving bed reactor (Mazzotti et al, 1996), the esterification of acetic acid by β-phenethyl alcohol (Kawase et al, 1996) and the production of bisphenol A (Kawase et al, 1999)

![Diagram of a Simulated Moving Bed Reactor (SMBR)](image)

*Figure 2.12  Scheme of a Simulated Moving Bed Reactor (SMBR).*

Although the SMBR technology allows 100% of conversion with 99.9% of recovery of the desired product (P), a further step is necessary to separate the product from the raffinate mixture.

### 2.3 Conclusions

This chapter was focused on some aspects of oxygenates production, mainly the use of a heterogeneous catalyst, the equilibrium limitations and the use of a reactive separation to overcome the thermodynamic equilibrium conversion.
In this thesis, the use of acid ion exchange resins Amberlyst 18 and 15, to catalyse the reaction between ethanol and acetaldehyde for the synthesis of diethylacetal and the separation of acetal from the reaction mixture in a Simulated Moving Bed Reactor will be addressed.

2.4 References


K. Boennhoff, "1,1-Diethoxyethane as Diesel Fuel", DE2911411 (1980).


3. Thermodynamic, Kinetics and Mass Transfer Studies in a Batch Reactor

In this chapter a detailed description of the experimental set-up for the thermodynamic and reaction kinetics acquisition data is made. Experimental results for the liquid-phase reaction of acetal production from ethanol and acetaldehyde by the macroporous sulphonic resin Amberlyst 18 are presented. The reaction equilibrium constant based on activities using activity coefficients calculated from the UNIFAC method was evaluated. A two-parameter model based on a Langmuir-Hinshelwood rate expression using activities was proposed to describe the experimental kinetic results and it was compared with the kinetic rate law expressed in terms of molar fractions. A mathematical model including film and pore diffusion was developed in order to verify the existence of limitations due to mass transfer and to obtain the true kinetic constant. The dependence of the effectiveness factor with the Thiele modulus and temperature was studied using the infinite bath approach.

3.1 Introduction

Acetal formation is basically an acid catalyzed reaction between acetaldehyde and ethanol, accordingly to the reaction:

\[ 2 \text{Ethanol (A)} + \text{Acetaldehyde (B)} \leftrightarrow \text{Acetal (C)} + \text{Water (D)} \]
The synthesis of diethylacetal for homogeneous catalysis is constituted by three steps (Morrison and Boyd, 1983). The reaction between a molecule of acetaldehyde and a molecule of ethanol typically leads to the formation of a hemi-acetal, which reacts further with another molecule of ethanol to yield the acetal, thereby liberating a molecule of water:

\[ A + B \rightleftharpoons I_1 \]

\[ I_1 + H^+ \rightleftharpoons I_2 + D \]

\[ I_2 + A \rightleftharpoons C + H^+ \]

where \( I_1 \) and \( I_2 \) are intermediate species.

Unless the water of reaction is removed continuously, or a large excess of ethanol is taken initially, the reaction does not go to completion. The hemi-acetal formation is reported to be quite fast in comparison with the acetal formation. Therefore, the reaction of water formation is the limiting step.

Several mineral acids have been employed as homogeneous catalysts in acetals synthesis: sulphuric acid, nitric acid and hydrochloric acid. Instead of highly polluting and corrosive mineral acids, the use of solid catalysts, such as zeolites and ion exchange resins in alkylation, isomerization, esterification, acylation, has been studied intensively in the last years. Particularly relevant applications based in reactions between olefins and alcohols catalyzed by acid resins, are those that involve the production of oxygenated compounds (see Table 3.1).

For the acetalization, the extension of the mechanism to heterogeneous catalytic reactions has been proposed for the reaction between n-octanal and methanol (Yadav and Pujari, 1999). It was also considered a three step reaction mechanism:

- the reaction between the adsorbed aldehyde and methanol to give the hemi-acetal;
- the reaction of water formation, that was considered the limiting step;
- the reaction of acetal formation.
<table>
<thead>
<tr>
<th>Source</th>
<th>Experimental apparatus</th>
<th>Product</th>
<th>Catalyst</th>
<th>Kinetic model</th>
<th>Expression of the components</th>
<th>Activation energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Rchfinger and Hoffmann, 1990)</td>
<td>CSTR</td>
<td>MTBE</td>
<td>A15</td>
<td>Langmuir-Hinshelwood</td>
<td>activities</td>
<td>92.4</td>
</tr>
<tr>
<td>(Caetano et al, 1994)</td>
<td>CSTR</td>
<td>MTBE</td>
<td>A18</td>
<td>Langmuir-Hinshelwood</td>
<td>concentrations</td>
<td>130.2</td>
</tr>
<tr>
<td>(Zhang and Datta, 1995)</td>
<td>Upflow integral reactor, continuous</td>
<td>MTBE</td>
<td>A15</td>
<td>Langmuir-Hinshelwood</td>
<td>Molar fractions</td>
<td>85.4</td>
</tr>
<tr>
<td>(Fite et al, 1994)</td>
<td>Differential tube reactor</td>
<td>ETBE</td>
<td>Lewatit K2631</td>
<td>Eley-Rideal</td>
<td>activities</td>
<td>79.3</td>
</tr>
<tr>
<td>(Oost and Hoffmann, 1996)</td>
<td>Continuous flow recycle reactor</td>
<td>TAME</td>
<td>Lewatit SPC 118</td>
<td>Adsorption based kinetic model</td>
<td>activities</td>
<td>89.5</td>
</tr>
<tr>
<td>(Mazzotti et al, 1997)</td>
<td>CSTR</td>
<td>Ethyl Acetate</td>
<td>A15</td>
<td>Equilibrium between liquid and resin using Flory-Huggins theory</td>
<td>activities</td>
<td>15.8</td>
</tr>
<tr>
<td>(Fite et al, 1998)</td>
<td>Continuous upflow packed-bed reactor</td>
<td>MTBE</td>
<td>Bayer K2631</td>
<td>Introduction of an empirical correction</td>
<td>activities</td>
<td>79.49</td>
</tr>
<tr>
<td>(Pöpken et al, 2000)</td>
<td>CSTR</td>
<td>Methyl Acetate</td>
<td>A15</td>
<td>Adsorption based kinetic model</td>
<td>activities</td>
<td>60.47</td>
</tr>
</tbody>
</table>
In this chapter, the liquid phase reaction of ethanol and acetaldehyde catalyzed by sulfonic acid ion exchange resin as catalyst (Amberlyst 18) reactor in the temperature range 288-333 K at 0.6 MPa was studied. Due to the lack of thermodynamic and kinetic data our efforts were directed to the design of a laboratory scale experimental set-up (Figure 3.1) in order to:

- obtain thermodynamic data for the synthesis of diethylacetal;
- study the effect of temperature, initial molar ratio of reactants and pressure on reaction kinetics;
- suggest a reaction mechanism and a rate equation with experimentally measured kinetic parameters.
- study the internal mass transfer effects on kinetics.

Figure 3.1   Experimental set-up.
3.2 Experimental Set-up

The reaction kinetics was studied in an automated set-up to acquire and to analyse the data in real time. The scheme of the installation set-up is shown in Figure 3.2 and it is constituted by three sections: reaction, sampling/analysis and data acquisition.

![Experimental set-up for kinetic studies](image)

**Figure 3.2** Experimental set-up for kinetic studies. BR-batch reactor; M-motor; TT-temperature sensor; P1-pressure sensor; PM-manometer; BV-blow-off valve; V1-sampling valve; V2-injection valve; NV-needle valve; GC-gas chromatograph; TB-thermostatic bath.

3.2.1 Reaction section

The experiments were carried out in a glass jacketed 1 dm³ autoclave - model Buchi BEP280 (Büchi, Switzerland), operating in a batch mode, mechanically stirred. The stirrer is fed by a 3-phase motor with adjustable velocity between 0 to 2900 rpm (Planetroll, German), with 0.33 kW of power. The reactor cover allows internal water circulation and it has four holes to connect measurement sensors and sampling lines. The reactor is equipped with pressure
sensors (pressure transducer Lucas P1231-0005-15 BAR A and manometer), a temperature sensor (thermocouple K type, Omega, TJ36-CAIN-116(G)-12) and with a blow-off valve. The temperature was controlled by thermostatic bath, model RE104 (Lauda, Germany), with 4 litres of capacity and temperature range from -10°C to 120 °C. There is a line for helium admission in order to pressurize the reactor and another line with a 5 μm filter for sampling the reaction mixture in the liquid phase by means of a three-way valve (Valco, USA). There is also a small basket (Figure 3.3) made from stainless steel net (10 μm mesh) where the catalyst is kept during the experience, in order to avoid abrasion with the stirrer. The basket is placed at the top of the stirrer shaft, and falls down in the reactant solution at the beginning of the agitation (time zero). In the final of the experiment, the reactor is depressurized manually through a needle valve.

![The basket used to keep the catalyst.](image)

3.2.2 Sampling/analysis section

The sampling line is connected directly to a three-way valve that together with a sampling valve (Valco, USA) controls the sampling, analysis and line cleaning, as shown in Figure 3.4. During the experiment, there are periodic cycles for the sampling and the line cleaning. The cycle is constituted by two steps:
1st step: at time zero, the reactor line is open and the pressurized liquid flows in the tube (1/16") until it fills the loop. This step takes 1 minute, in order to ensure that the loop is completely full. At the end of the tube there is a needle valve to guarantee that all line is pressurized, avoiding vaporization of liquid inside. The total amount of liquid that leaves the reactor is about 1 ml.

2nd step: initially, the reactor is closed and the loop inside the sampling line switches on the position, the liquid sample is then carried with helium to the injector where it is vaporized and then is separated in the column; simultaneously, the sampling line is cleaned by means of vacuum. The line is completely cleaned after 7.5 min from the beginning and at this time the gas chromatograph is ready to start a new analysis.

![Diagram of the process](image)

**Figure 3.4** Valves scheme for sampling, analysis and line cleaning control.

### 3.2.3 Data acquisition section

The computer used was a Pentium II 233 MHz, 64 Mb of RAM and 6 Gb of hard disk connected to a data acquisition board Advantech, model PCL-818HG. This board has the
following features: 16 single-ended and 8 differential analog inputs, switch selectable; 12-bit A/D, up to 100 KHz sampling rate with MA transfer and different gain for each channel; one 12-bit analog output channel; 16 digital inputs and 16 digital outputs, TTL/DTL compatible. The PCL-818HG package includes a special wiring board (PCLD-8115) with a DB-37 connector and CJC circuits, which allows directed reading from thermocouple. The signals measured (pressure, temperature and the thermal conductivity detector) are saved in a file.

The computer is also connected to the PCLD-885 Power Relay Output Board (Advantech), which is equipped with 16 electromechanical SPST relay outputs, driven via a 16 bit digital output port. These relays can be used for general purpose switching control applications, such as setting up test configurations or power ON/OFF switching. This board is used to send the signal to the motor in the beginning of the experiment, to the gas chromatograph to start the samples analysis and to command the valves V1 and V2.

3.2.4 Analytical methods

The samples were analysed on a gas chromatograph (Chrompack 9100, Netherlands) and the compounds were separated in a fused silica capillary column (Chrompack CP-Wax 57 CB), 25 m x 0.53 mm ID, df=22.0 µm using a thermal conductivity detector (TCD 903 A) for peak detection.

The operating conditions used for sample analysis are presented in Table 3.2. The column temperature was programmed with a 2 min initial hold at 50 °C, followed by a 40 °C/min ramp up to 100 °C and held for 1 min. The carrier gas used was Helium N50. At these conditions the retention time for acetaldehyde, acetal, ethanol and water are 1.0, 2.1, 2.6 and 3.4 minutes, respectively.

<table>
<thead>
<tr>
<th>Table 3.2 Operating conditions used in gas chromatography.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Injector temperature</td>
</tr>
<tr>
<td>Detector temperature</td>
</tr>
<tr>
<td>Column pressure drop</td>
</tr>
<tr>
<td>Column flowrate at 50 °C</td>
</tr>
<tr>
<td>Make-up flowrate</td>
</tr>
<tr>
<td>Reference flowrate</td>
</tr>
</tbody>
</table>
The calibration curves were obtained for each component by injecting several volumes of pure component, at a certain temperature (see Appendix B). The response factor, \( f_i \), was defined as:

\[
  n_i = f_i A_i
\]  

(3.1)

where \( n_i \) is the number of moles of component \( i \) (\( \mu \text{mol} \)) and \( A_i \) is the peak area of component \( i \) (u.a.). The values obtained are presented in Table 3.3. The points for the calibration curves were obtained by calculating the average area of at least 3 analysis for each sample. The criteria of reproducibility, based on peak area was:

\[
  R.C. \,(\%) = \frac{\sigma_A}{A} \times 100 \leq 5\%
\]  

(3.2)

<table>
<thead>
<tr>
<th>Component</th>
<th>Retention time (min)</th>
<th>Response factor (( \mu \text{mol}/\text{u.a.} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetaldehyde</td>
<td>1.00</td>
<td>7.0876</td>
</tr>
<tr>
<td>Acetal</td>
<td>2.07</td>
<td>3.1997</td>
</tr>
<tr>
<td>Ethanol</td>
<td>2.63</td>
<td>6.5547</td>
</tr>
<tr>
<td>Water</td>
<td>3.38</td>
<td>13.054</td>
</tr>
</tbody>
</table>

For the determination of species concentration in mixtures, the molar fraction of each species was first calculated, according to:

\[
  x_i = \frac{f_i A_i}{\sum_j f_j A_j}
\]  

(3.3)

The concentration was then evaluated using the liquid molar volumes:

\[
  C_i = \frac{x_i}{\sum_n x_n V_{ml,n}}
\]  

(3.4)

With this procedure, the results were not affected if occurred some changes in operating condition (different injection volume, change in helium flowrate) since all peak areas would be affected in the same way. The calibration curves were determined every time that some changes occurred (change of helium bottle, maintenance, flowrate adjustments, etc) and verified
at the beginning of each experiment by analysing a standard sample. It was also verified the good agreement between manual and automatic injection.

### 3.2.5 Chemicals

The chemicals used were ethanol (> 99.9 % pure), acetaldehyde (> 99.5 % pure) and acetal (> 99.0 % pure) (Sigma-Aldrich, U.K.). The water used for calibration was deionised. The use of those chemicals, mainly acetaldehyde and acetal, requires certain precautions. In Appendix C the safety data for acetaldehyde, acetal and ethanol are presented.

#### 3.2.5.1 Physical and Thermodynamic Properties

In Table 3.4 some physical and thermodynamic properties of ethanol, acetaldehyde, acetal and water, available from literature are presented.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Acetaldehyde</th>
<th>Ethanol</th>
<th>Acetal</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weigh - M (g/mol)</td>
<td>44.054</td>
<td>46.069</td>
<td>118.177</td>
<td>18.015</td>
</tr>
<tr>
<td>Melting temperature - T_f (K)</td>
<td>150.2</td>
<td>159.1</td>
<td>173.0</td>
<td>273.2</td>
</tr>
<tr>
<td>Normal boiling temperature - T_b (K)</td>
<td>294.0</td>
<td>351.4</td>
<td>375.4</td>
<td>373.2</td>
</tr>
<tr>
<td>Critical temperature - T_c (K)</td>
<td>461.0</td>
<td>513.9</td>
<td>543.0</td>
<td>647.3</td>
</tr>
<tr>
<td>Critical pressure - P_c (bar)</td>
<td>55.7</td>
<td>61.4</td>
<td>30.2 a b</td>
<td>221.2</td>
</tr>
<tr>
<td>Critical volume - V_c (cm³/mol)</td>
<td>154.0</td>
<td>167.1</td>
<td>401.5 a b</td>
<td>57.1</td>
</tr>
<tr>
<td>Acentric factor - ω</td>
<td>0.300</td>
<td>0.644</td>
<td>0.178 b</td>
<td>0.344</td>
</tr>
</tbody>
</table>

a) from (Simmrock et al, 1986)
b) calculated (Reid et al, 1987)

In Appendix D other thermodynamic data (gas phase and reaction thermochemistry data) and the correlations for pure components and mixture properties estimations are presented.
3.2.6 Catalyst

A commercial sulfonic acid ion exchange resin (Amberlyst 18, Rohm and Haas) was used as catalyst. The resin is a bead-form macro reticular polymer of styrene and divinylbenzene, with particle diameter varying between 0.2 to 1.2 mm. The ion exchange capacity is 4.5 meq H\(^+\)/g of dry resin and the inner surface area is 30 m\(^2\)/g. In Table 3.5 a comparison between Amberlyst 18 and Amberlyst 15 is presented.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Amberlyst 18</th>
<th>Amberlyst 15</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture content</td>
<td>51-54 %</td>
<td>52-57 %</td>
</tr>
<tr>
<td>Shipping weight</td>
<td>790 g/l</td>
<td>770 g/l</td>
</tr>
<tr>
<td>Particle size</td>
<td>0.2-1.2 mm</td>
<td>0.3-1.2 mm</td>
</tr>
<tr>
<td>Concentration of acid sites</td>
<td>1.8 meq/ml</td>
<td>1.7 meq/ml</td>
</tr>
<tr>
<td>Surface area</td>
<td>30 m(^2)/g</td>
<td>45 m(^2)/g</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.63 ml/g</td>
<td>---</td>
</tr>
<tr>
<td>Average pore diameter</td>
<td>43 nm</td>
<td>24 nm</td>
</tr>
</tbody>
</table>

Resin conditioning

The catalyst should be conditioned before use in order to guarantee anhydrous resin. It may be convenient to rinse off water by another solvent (ethanol). By placing water-wet Amberlyst 18 in a column and allowing 2.5 bed volumes of ethanol to percolate through the resin over a period of one hour, most of the water is removed. Finally, the resin should be vacuum-dried at 1 mm pressure and 105 °C for two to four hours. This procedure would reduce the water in the dried resin to less than 0.5 percent by weight. The procedure adopted was not exactly this; the resin was dried at atmospheric pressure and 90 °C during 24 hours. The water adsorbed on the catalyst surface decreases the reaction kinetics, because it is one of the reaction products.
Moreover, the equilibrium conversion is lower on the pre-wetted sample when compared with the catalyst dried at 100 °C (Capeletti et al., 2000), as shown in Figure 3.5.

![Figure 3.5](image)

**Figure 3.5**  Effect of water on ethanol conversion as a function of reaction time for catalyst A15 (Capeletti et al., 2000). Symbols: ■ dry resin, □ pre-wetted resin.

3.3 Thermodynamic Results

Some essential thermodynamics quantities in process design such as the enthalpy change of the reaction and equilibrium constants have not been reported yet. The reaction thermochemistry data available in literature (see Appendix D) lead to a value of reaction enthalpy of -25.45 kJ/mol, calculated from data shown in Table 3.6. The group of Gutiérrez-Ortiz obtain the equilibrium constant from the optimization of kinetic data expressed in terms of molar concentration in the temperature range of 20-35 °C (Fedrani et al., 2000). The temperature dependence of equilibrium constant was determined from the Van't Hoff equation:

\[
\ln K_{eq} = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT}
\]  

(3.5)
and the values of $\Delta H^\circ$ and $\Delta S^\circ$ were -64.19 kJ/mol and -230 J/mol.K. The value of the equilibrium constant at 4 °C obtained is 1.213 l/mol. The value of $\Delta H^\circ$ proposed by Laborde's group is of 44.9 kJ/mol, that is very different (Balzano and Laborde, 2000).

Therefore, this work was undertaken to determine experimental values of the equilibrium constant at several temperatures. Then the standard enthalpy change of acetal synthesis could be determined and compared with that estimated theoretically. It is also possible to calculate the standard enthalpy of acetal formation in liquid phase in order to compare with the value -491.4 kJ/mol calculated from the heat of combustion (Pilhaja and Heikkila, 1968).

<table>
<thead>
<tr>
<th>Properties</th>
<th>Acetaldehyde</th>
<th>Ethanol</th>
<th>Water</th>
<th>Acetal</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H^\circ$ (kJ/mol)</td>
<td>-196.4 *</td>
<td>-277.69 **</td>
<td>-285.83 **</td>
<td>-491.4</td>
</tr>
<tr>
<td>$\Delta G^\circ$ (kJ/mol)</td>
<td>-128.08</td>
<td>-174.78 **</td>
<td>-237.129 **</td>
<td></td>
</tr>
<tr>
<td>$S^\circ$ (J/mol.K)</td>
<td>117.3 *</td>
<td>160.70 **</td>
<td>69.91 **</td>
<td></td>
</tr>
</tbody>
</table>

* NIST Handbook
** Wagner et al., 1982

The experiments to measure the equilibrium constant were carried out in a temperature range 293-333 K, at 1.0 MPa, with 1.5 g of dry catalyst, reaction volume of 600 ml, and initial molar ratio of reactants $r_{A/B} = 2.2$. All the experiments lasted long enough for the reaction to reach the equilibrium. Table 3.7 shows the experimental conditions and the average equilibrium composition at each temperature.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Acetaldehyde</th>
<th>Ethanol</th>
<th>Acetal</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.1583</td>
<td>0.3862</td>
<td>0.2278</td>
<td>0.2278</td>
</tr>
<tr>
<td>30</td>
<td>0.1648</td>
<td>0.3930</td>
<td>0.2211</td>
<td>0.2211</td>
</tr>
<tr>
<td>40</td>
<td>0.1699</td>
<td>0.4029</td>
<td>0.2136</td>
<td>0.2136</td>
</tr>
<tr>
<td>60</td>
<td>0.1806</td>
<td>0.4234</td>
<td>0.1980</td>
<td>0.1980</td>
</tr>
</tbody>
</table>
The thermodynamic equilibrium constant for the liquid phase reaction considered as a non-ideal system is given by:

\[ K_{eq} = \frac{a_c}{a_A} \frac{a_B}{a_A} = \frac{x_c}{x_A} \frac{x_B}{x_B} = x_c \frac{A_B}{A_B} \frac{Y_c}{Y_B} = K_X K_Y \]  
(3.6)

The equilibrium constant was also evaluated in terms of molar fractions, if the mixture has an ideal behaviour:

\[ K_y = \frac{x_c}{x_A} \frac{x_B}{x_B} \]  
(3.7)

Some authors express the equilibrium constant as function of molar concentrations:

\[ K_C = \frac{C_c}{C_A} \frac{C_B}{C_B} \]  
(3.8)

The concentrations were determined from the liquid molar volumes, estimated with Gunn-Yamada method (see Appendix D), according to:

\[ C_i = \frac{x_i}{\sum_j x_j V_{m,i,j}} \]  
(3.9)

The concentrations obtained are shown in Table 3.8.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Ethanol</th>
<th>Acetaldehyde</th>
<th>Acetal</th>
<th>Water</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>5.677</td>
<td>2.327</td>
<td>3.348</td>
<td>3.348</td>
<td>14.700</td>
</tr>
<tr>
<td>30</td>
<td>5.725</td>
<td>2.400</td>
<td>3.221</td>
<td>3.221</td>
<td>14.567</td>
</tr>
<tr>
<td>40</td>
<td>5.816</td>
<td>2.452</td>
<td>3.083</td>
<td>3.083</td>
<td>14.435</td>
</tr>
<tr>
<td>60</td>
<td>5.995</td>
<td>2.557</td>
<td>2.803</td>
<td>2.803</td>
<td>14.159</td>
</tr>
</tbody>
</table>

The activity coefficients of compounds were computed by the UNIFAC method (Fredeslund et al., 1977). The parameters needed for its use (relative molecular volume and surface area of pure species and the interaction parameters) are presented in Table 3.9 and Table 3.10. The activity coefficients obtained are shown in Table 3.11.
### Table 3.9  Relative molecular volume and surface area of pure species parameters (Reid et al, 1987).

<table>
<thead>
<tr>
<th>molecule (i)</th>
<th>Group Identification</th>
<th>$v_k^{(i)}$</th>
<th>$R_k$</th>
<th>$Q_k$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Name</td>
<td>No. Main</td>
<td>No. sec.</td>
<td></td>
</tr>
<tr>
<td>1-ethanol</td>
<td>CH$_3$</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>CH$_2$</td>
<td>1</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>OH</td>
<td>5</td>
<td>15</td>
<td>1</td>
</tr>
<tr>
<td>2-acetaldehyde</td>
<td>CH$_3$</td>
<td>1</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>CHO</td>
<td>10</td>
<td>21</td>
<td>1</td>
</tr>
<tr>
<td>3-acetal</td>
<td>CH$_3$</td>
<td>1</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>CH</td>
<td>1</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>4-water</td>
<td>H$_2$O</td>
<td>7</td>
<td>17</td>
<td>1</td>
</tr>
</tbody>
</table>

### Table 3.10  Interaction parameters (Fredenslund et al, 1998).

<table>
<thead>
<tr>
<th>$a_{m,n}$</th>
<th>1</th>
<th>5</th>
<th>7</th>
<th>10</th>
<th>13</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>986.5</td>
<td>1318</td>
<td>677</td>
<td>251.5</td>
</tr>
<tr>
<td>5</td>
<td>156.4</td>
<td>0</td>
<td>353.5</td>
<td>-203.6</td>
<td>28.06</td>
</tr>
<tr>
<td>7</td>
<td>300</td>
<td>-229.1</td>
<td>0</td>
<td>-116</td>
<td>540.5</td>
</tr>
<tr>
<td>10</td>
<td>505.7</td>
<td>529</td>
<td>480.8</td>
<td>0</td>
<td>304.1</td>
</tr>
<tr>
<td>13</td>
<td>83.36</td>
<td>237.7</td>
<td>-314.7</td>
<td>-7.838</td>
<td>0</td>
</tr>
</tbody>
</table>

### Table 3.11  Activity coefficients for the equilibrium composition.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Ethanol</th>
<th>Acetaldehyde</th>
<th>Acetal</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>1.072</td>
<td>1.194</td>
<td>1.365</td>
<td>1.587</td>
</tr>
<tr>
<td>30</td>
<td>1.077</td>
<td>1.196</td>
<td>1.369</td>
<td>1.630</td>
</tr>
<tr>
<td>40</td>
<td>1.082</td>
<td>1.197</td>
<td>1.374</td>
<td>1.668</td>
</tr>
<tr>
<td>60</td>
<td>1.086</td>
<td>1.196</td>
<td>1.385</td>
<td>1.742</td>
</tr>
</tbody>
</table>
The equilibrium constants calculated in terms of molar fraction, concentration and activities are presented in Table 3.12.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>( K_x )</th>
<th>( K_C )</th>
<th>( K_a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>2.198</td>
<td>0.150</td>
<td>3.472</td>
</tr>
<tr>
<td>30</td>
<td>1.921</td>
<td>0.132</td>
<td>3.086</td>
</tr>
<tr>
<td>40</td>
<td>1.655</td>
<td>0.115</td>
<td>2.708</td>
</tr>
<tr>
<td>60</td>
<td>1.211</td>
<td>0.086</td>
<td>2.072</td>
</tr>
</tbody>
</table>

The pressure influence in the value of equilibrium constant was estimated by the correction factor \( K_p \) (Smith and Van Ness, 1987):

\[
K_p = \exp\left[\frac{(P-1)}{RT} \sum v_i V_{nl,i}\right]
\]  

(3.10)

where \( P \) is the pressure, \( v_i \) is the stoichiometric coefficient of component \( i \) and \( V_{nl,i} \) is the molar volume of component \( i \). By using the liquid molar volumes in Table 3.13 and the experimental conditions of the present work, it can be seen that neglecting \( K_p \) in the calculation of \( K_{eq} \) the error introduced is about 0.3 %. Therefore we can assume that \( K_{eq} \) is only a function of temperature.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>( V_A )</th>
<th>( V_B )</th>
<th>( V_C )</th>
<th>( V_D )</th>
<th>( K_p )</th>
</tr>
</thead>
<tbody>
<tr>
<td>293.15</td>
<td>58.402</td>
<td>56.639</td>
<td>142.236</td>
<td>18.054</td>
<td>0.9973</td>
</tr>
<tr>
<td>303.15</td>
<td>59.276</td>
<td>57.602</td>
<td>143.965</td>
<td>18.231</td>
<td>0.9972</td>
</tr>
<tr>
<td>313.15</td>
<td>60.187</td>
<td>58.623</td>
<td>145.752</td>
<td>18.413</td>
<td>0.9971</td>
</tr>
<tr>
<td>333.15</td>
<td>62.133</td>
<td>60.878</td>
<td>149.528</td>
<td>18.789</td>
<td>0.9969</td>
</tr>
</tbody>
</table>

The dependence on temperature can be estimated by fitting experimental values of \( \ln K_{eq} \) vs. \( 1/T \) to Van't Hoff equation, as shown in Figure 3.6.
The values of $\Delta H^\circ$ and $\Delta S^\circ$ are obtained from the slope and intercept of $\ln K_{eq}$ vs. $1/T$, respectively. The standard free energy change for the liquid phase reaction can be related to the standard enthalpy and entropy changes by:

$$\Delta G^0 = \Delta H^0 - T \Delta S^0$$  \hspace{1cm} (3.11)

The values obtained for the standard reaction properties are presented at Table 3.14.

<table>
<thead>
<tr>
<th>Properties</th>
<th>from $K_C$</th>
<th>from $K_X$</th>
<th>from $K_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H^\circ$ (kJ/mol)</td>
<td>-11.43</td>
<td>-12.20</td>
<td>-10.56</td>
</tr>
<tr>
<td>$\Delta S^\circ$ (J/mol.K)</td>
<td>-54.66</td>
<td>-34.91</td>
<td>-25.56</td>
</tr>
<tr>
<td>$\Delta G^\circ$ (kJ/mol)</td>
<td>4.86</td>
<td>-1.79</td>
<td>-2.94</td>
</tr>
</tbody>
</table>
The standard enthalpy, free Gibbs energy and entropy for acetal formation in the liquid phase were calculated by Equations 3.12, 3.13 and 3.14, based on the experimental values $\Delta H^0$, $\Delta G^0$, $\Delta S^0$ and the standard formation properties presented in Appendix D.

$$\Delta H^0 = \sum_i v_i \Delta H^0_{f,i}$$  \hspace{1cm} (3.12)

$$\Delta G^0 = \sum_i v_i \Delta G^0_{f,i}$$  \hspace{1cm} (3.13)

$$\Delta S^0 = \sum_i v_i S^0_{f,i}$$  \hspace{1cm} (3.14)

<table>
<thead>
<tr>
<th>Properties</th>
<th>from $K_C$</th>
<th>from $K_e$</th>
<th>from $K_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H^0_f$ (kJ/mol)</td>
<td>-477.4</td>
<td>-478.1</td>
<td>-476.5</td>
</tr>
<tr>
<td>$\Delta G^0_f$ (kJ/mol)</td>
<td>-235.6</td>
<td>-242.3</td>
<td>-243.5</td>
</tr>
<tr>
<td>$S^0_f$ (J/mol.K)</td>
<td>314.13</td>
<td>333.88</td>
<td>343.23</td>
</tr>
</tbody>
</table>

Comparing the experimental values of the standard heat of reaction, $\Delta H^0$, and the standard formation enthalpy for acetal, $\Delta H^0_{f,acetal}$, with the theoretical values (-25.45 kJ/mol and -491.4 kJ/mol, respectively), the errors are about 55% and 3%, respectively, as shown in Table 3.16. Possible errors could be due to the presence of adsorbed water in the resin, since the procedure adopted to dry the resin was not exactly the proposed.

<table>
<thead>
<tr>
<th>Error (%)</th>
<th>from $K_C$</th>
<th>from $K_e$</th>
<th>from $K_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>error in $\Delta H^0$</td>
<td>55.1</td>
<td>52.1</td>
<td>58.5</td>
</tr>
<tr>
<td>error in $\Delta H^0_{f,acetal}$</td>
<td>2.9</td>
<td>2.7</td>
<td>3.0</td>
</tr>
</tbody>
</table>
3.4 Kinetic Results

To quantify the influence of external mass transfer resistance preliminary experiments at different stirring speeds were run. With a stirring speed of 800 rpm, the limitation due to external resistance is eliminated, so all further experiments were done at 800 rpm.

3.4.1 Particle size

The catalyst was separated by particle size and three classes with different mean diameters were obtained: 267 μm, 477 μm and 854 μm. Figure 3.7 shows the conversion of acetaldehyde, $X$, as a function of time; there are internal diffusion limitations for the experiments with pellet diameters equal to 477 and 854 μm.

![Figure 3.7](image.png)

Figure 3.7  Effect of catalyst particle size on the conversion of acetaldehyde history: $T = 15\,^\circ\text{C}$, $P = 6\,\text{atm}$, $m_0 = 325\,\text{g}$, $r_{A/B} = 2.2$, $u_{\text{col}} = 1.5\,\text{g}$, $V = 576\,\text{ml}$

3.4.2 Initial molar ratio of reactants

Since the experiments were done without introducing an inert in the liquid phase, it was not possible to study the influence of the initial concentration of each reactant individually. So the effect of initial composition concerns the study of initial molar ratio of reactants, $r_{A/B}$. The kinetic is not very much affected by the ratio $r_{A/B}$, as shown in Figure 3.8, but the molar fraction of acetal, $x_C$, is greater for the stoichiometric ratio ($r_{A/B} = 2$).
Figure 3.8 Effect of initial ratio of reactants on the acetal molar fraction as function of time: $T = 10^\circ$C, $P = 6$ atm, $V = 570$ ml, $w_{cat} = 1.5$ g, $d_r = 477$ μm.

3.4.3 Mass of catalyst

The effect of the mass of catalyst in the acetaldehyde conversion is shown in Figure 3.9. For the same experimental conditions, an increase of 2-fold in the mass of catalyst results in an equal increase in the initial reaction rate.

Figure 3.9 Effect of the mass of catalyst in the acetaldehyde conversion as function of time: $T = 20^\circ$C, $P = 6$ atm, $r_{AB} = 2.1$, $V = 570$ ml, $d_r = 477$ μm.
3.4.4 Pressure

The total pressure of the reactor ensures that reactants and products are in the liquid phase. The VLE calculations for the system shows that the total number of moles in the vapour phase represent 1.6 % of that in the liquid phase, see Figure 3.10, and 92 % of the gas is helium. So the total pressure does not affect the reaction, as shown in Figure 3.11.

![Figure 3.10](image)

**Figure 3.10** Total number of moles in the liquid and vapour phases histories: $T = 20 \, ^\circ\text{C}$, $P = 5 \, \text{atm}$, $m_{A0} = 277 \, \text{g}$, $r_{A/B} = 2.1$, $w_{\text{cat}} = 2.6 \, \text{g}$, $V = 500 \, \text{ml.}$

![Figure 3.11](image)

**Figure 3.11** Influence of the pressure of the reactor on the acetaldehyde conversion history: $T = 10 \, ^\circ\text{C}$, $V = 571 \, \text{ml}$, $m_{A0} = 325 \, \text{g}$, $r_{A/B} = 2.2$, $w_{\text{cat}} = 1.5 \, \text{g.}$
3.4.5 Temperature

Each run was carried out at almost constant temperature. The maximum variation of 1 °C was noticed at the beginning of reaction, and then temperature decreases. The rate of reaction increased with temperature (see Figure 3.12), although the equilibrium conversion decreased due to the exothermic nature of the reaction.

![Graph showing influence of temperature on conversion of acetaldehyde](image)

*Figure 3.12 Influence of the temperature on the conversion of acetaldehyde history: P=6 atm, m_{A0}=325 g, r_{AW}=2.2, w_{ad}=1.5 g, V=570 ml, d=477 μm.*

3.5 Kinetic Model

This model is based on the following steps:

- adsorption of ethanol:
  \[ A + S \rightleftharpoons \underset{k_{s}}{\text{K}} \rightarrow AS \]  \hspace{1cm} (3.15)

- adsorption of acetaldehyde:
  \[ B + S \rightleftharpoons \underset{k_{s}}{\text{K}} \rightarrow BS \]  \hspace{1cm} (3.16)

- surface reaction between the adsorbed species of ethanol and aldehyde to give adsorbed hemi-acetal (\(1S\)):
  \[ AS + BS \rightleftharpoons 1S + S \quad K_1 = \frac{\theta_{1S}}{\theta_A \theta_S} \]  \hspace{1cm} (3.17)
surface reaction to obtain adsorbed water, DS (rate controlling step):

\[ I_2S + S \underset{k_2}{\overset{k_2}{\rightleftharpoons}} I_2S + DS \]

\[ K_2 = \frac{k_2}{k_2} = \frac{\theta_i}{\theta_0} \]  \hspace{1cm} (3.18)

surface reaction of formation of adsorbed acetal, CS:

\[ I_2S + AS \underset{k_3}{\overset{k_3}{\rightleftharpoons}} CS + S \]

\[ K_3 = \frac{\theta_i}{\theta_0} \frac{\theta_A}{\theta_A} \]  \hspace{1cm} (3.19)

desorption of acetal:

\[ CS \overset{k_{c,p}}{\longrightarrow} C + S \]  \hspace{1cm} (3.20)

desorption of water:

\[ DS \overset{k_{s,p}}{\longrightarrow} D + S \]  \hspace{1cm} (3.21)

\[ \mathfrak{R} = k_2 \theta_i \theta_0 - k_2 \theta_i \theta_D \]  \hspace{1cm} (3.22)

where \( \mathfrak{R} \) is the rate of reaction and \( \theta_0 \) is the fraction of vacant sites.

Langmuir adsorption isotherms are assumed to describe the adsorption behaviour of the compounds of the reaction mixture in the surface of the resin. The model is based on activities \( (a_i) \) and therefore the adsorption equilibria of the species \( A_i \) is given by:

\[ \theta_i = \frac{K_{s,i} a_i}{1 + \sum_{j=1}^N K_{s,j} a_j} \]  \hspace{1cm} (3.23)

where \( \theta_i \) is the fraction of sites occupied by \( A_i \) and \( K_{s,i} \) is the equilibrium adsorption constant.

Combining the above equations, the reaction rate becomes:

\[ \mathfrak{R} = k_2 \frac{a_A a_B - a_C a_D}{K_{eq} a_A} \left( 1 + \sum_{i=d}^N K_{s,i} a_i + K_{s,i} a_A a_B + K_{s,i} \frac{a_C}{a_A} \right)^2 \]  \hspace{1cm} (3.24)

In order to reduce the number of optimization parameters several rate equations derived from Equation 3.23 were tested. The best fittings were obtained by considering that the products
(acetal and water) and the intermediate $I_2$ are more adsorbed than the other species. The simplified rate equations are then:

- **Model 1** – Acetal is more adsorbed than the other species:

  $$\mathfrak{R} = k_e \frac{a_A a_B - a_C a_D}{\left(1 + K_{e,C} a_C\right)^2}$$  
  \(3.25\)

- **Model 2** – Water is more adsorbed than the other species:

  $$\mathfrak{R} = k_e \frac{a_A a_B - a_C a_D}{\left(1 + K_{s,D} a_D\right)^2}$$  
  \(3.26\)

- **Model 3** – The intermediate $I_2$ is more adsorbed than the other species:

  $$\mathfrak{R} = k_e \frac{a_A a_B - a_C a_D}{\left(1 + K_{s,I_2} a_{I_2}\right)^2}$$  
  \(3.27\)

Each kinetic model contains two parameters, the kinetic constant ($k_e$) and the adsorption parameter ($K_{e,C}$, $K_{s,D}$ or $K_{s,I_2}$).

**Parameter Estimation from Experimental Data**

The mass balance in a batch reactor for acetal, in the liquid phase, at constant temperature is:

$$\frac{d n_c}{dt} = w_{cav} \mathfrak{R}$$  
\(3.28\)

where $n_c$ is the number of moles of acetal, $t$ is the time, $w_{cav}$ is the mass of catalyst and $\mathfrak{R}$ is the reaction rate referred to the catalyst mass.

The number of moles of component $i$ ($n_i$) as a function of the conversion $X$ of the limiting reactant ($I$) is:

$$n_i = n_{i,0} \left(1 + \frac{X}{v_f} \right)$$  
\(3.29\)

where $n_{i,0}$ and $v_f$ are, respectively, the initial moles number and the stoichiometric coefficient of the limiting reactant and:
\[ r_{i,t} = \frac{n_{i,0}}{n_{i,0}} \quad (3.30) \]

\( n_{i,0} \) is the initial number of moles of component \( i \).

Introducing Equation 3.29 into Equation 3.28 we get:

\[ \frac{n_{i,0}}{w_{col}} \frac{d X}{d t} = k_i \left( a_1, a_2, a_3, a_4, T, P \right) \quad (3.31) \]

where \( k_i \) is given by Equations 3.25, 3.26 or 3.27 and the initial condition of Equation 3.31 is \( t = 0; \ X = 0 \).

The suggested reaction rate was fitted, at each temperature, to the experimentally measured rates of reaction. The estimation of model parameters was carried out with a non-linear regression subroutine d88ln (IMSL, 1991) that uses the Levenberg-Marquardt method to minimise the sum of residual squares (SRS) between the experimental and calculated rate of reaction:

\[ SRS = \sum (k_{\text{exp}} - k_{\text{theo}})^2 \quad (3.32) \]

Theoretical reaction rate (\( k_{\text{theo}} \)) is expressed by the r.h.s. of Equation 3.31 and the experimental rate of reaction (\( k_{\text{exp}} \)) is expressed by the l.h.s. The values of the optimized parameters for each model are presented in Table 3.17. Analysing the average squares for error for each model, it is possible to conclude that model 3 provides the best fitting. However, it seems that model 2, which considers that the water is more adsorbed than the others species, is more reliable in terms of physical meaning. On the other hand, the temperature dependence of kinetic and adsorption constants were fitted with the Arrhenius equation:

\[ k_i = k_{n,\text{c}} \exp \left( \frac{-E_{n,c}}{RT} \right) \quad (3.33) \]

\[ K_i = K_{n,\text{c}} \exp \left( \frac{\Delta H_i}{RT} \right) \quad (3.34) \]

It is verified that the Arrhenius equation fits well the constants for models 1 and 2, as shown in Figure 3.13 and Table 3.18.
Table 3.17  Kinetic constant, $k_c$ (mol g⁻¹min⁻¹), adsorption constant, $K_s$ (dimensionless) and the average square errors, RS, using the kinetic law expressed in terms of activities.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Model 1</th>
<th></th>
<th>Model 2</th>
<th></th>
<th>Model 3</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>0.318</td>
<td>0.588</td>
<td>$2.2 \times 10^{-5}$</td>
<td>0.321</td>
<td>$1.9 \times 10^{-5}$</td>
<td>0.344</td>
</tr>
<tr>
<td>20</td>
<td>0.394</td>
<td>0.721</td>
<td>$2.0 \times 10^{-5}$</td>
<td>0.395</td>
<td>$1.8 \times 10^{-5}$</td>
<td>0.393</td>
</tr>
<tr>
<td>26</td>
<td>0.612</td>
<td>1.022</td>
<td>$5.8 \times 10^{-5}$</td>
<td>0.614</td>
<td>$5.0 \times 10^{-5}$</td>
<td>0.562</td>
</tr>
</tbody>
</table>

Figure 3.13  Representation of experimental values of $\ln k$ as function of $1/T$ and linear fitting: a) model 1; b) model 2; c) model 3.
Table 3.18  Arrhenius parameters for the kinetic and adsorption constant with the respective correlation factors.

<table>
<thead>
<tr>
<th>Model</th>
<th>$k_{0,e}$ (mol g⁻¹min⁻¹)</th>
<th>$E_{o,e}$ (kJ mol⁻¹)</th>
<th>$R^2$</th>
<th>$K_{0,e}$ (—)</th>
<th>$\Delta H_s$ (kJ mol⁻¹)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$1.209 \times 10^8$</td>
<td>47.5</td>
<td>0.992</td>
<td>$9.737 \times 10^6$</td>
<td>40.0</td>
<td>0.998</td>
</tr>
<tr>
<td>2</td>
<td>$1.046 \times 10^8$</td>
<td>47.2</td>
<td>0.990</td>
<td>$6.373 \times 10^5$</td>
<td>33.2</td>
<td>0.986</td>
</tr>
<tr>
<td>3</td>
<td>$0.981 \times 10^8$</td>
<td>47.0</td>
<td>0.989</td>
<td>$1.056 \times 10^8$</td>
<td>36.0</td>
<td>0.977</td>
</tr>
</tbody>
</table>

Since the resin is selective to water, the model 2 was selected to describe the kinetic law. Figure 3.14, Figure 3.15 and Figure 3.16 show the comparison between experimental and simulated results (with model 2) for ethanol at 16 °C, 20 °C and 26 °C, respectively.

![Figure 3.14](image_url)  
Experimental and simulated curves of number of moles of ethanol as a function of time: $T = 16$ °C, $P = 6$ atm, $w_{ini} = 0.5$ g, $d_p = 267 \mu m$.  

Figure 3.14 Experimental and simulated curves of number of moles of ethanol as a function of time: $T = 16$ °C, $P = 6$ atm, $w_{ini} = 0.5$ g, $d_p = 267 \mu m$.  


Figure 3.15  Experimental and simulated curves of number of moles of ethanol as a function of time: $T = 20^\circ C$, $P = 6$ atm, $w_{\text{air}} = 0.5$ g, $d_p = 267 \, \mu$m.

Figure 3.16  Experimental and simulated curves of number of moles of ethanol as a function of time: $T = 26^\circ C$, $P = 6$ atm, $w_{\text{air}} = 0.5$ g, $d_p = 267 \, \mu$m.

Figure 3.17 shows the comparison between experimental and simulated number of moles as a function of time, for all species in a typical run.
In order to simplify the proposed rate law (model 2), the kinetic data were adjusted considering an ideal system ($a_i \equiv x_i$):

$$
\dot{\mathbf{R}} = k_c \frac{x_A x_B - x_C x_D}{K_{x_D} x_A} \left(1 + K_{x_D} x_D\right)^2
$$

The model parameters are presented in Table 3.19. This simplification provides also a good fitting; however, the error is slightly higher than when activities are used.

| T (°C) | $k_c$ (mol g$^{-1}$ min$^{-1}$) | $K_{x_D}$ (dimensionless) | RS
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>0.356</td>
<td>0.675</td>
<td>2.2×10$^{-5}$</td>
</tr>
<tr>
<td>20</td>
<td>0.440</td>
<td>0.824</td>
<td>2.0×10$^{-5}$</td>
</tr>
<tr>
<td>26</td>
<td>0.689</td>
<td>1.309</td>
<td>5.4×10$^{-5}$</td>
</tr>
</tbody>
</table>
The temperature dependence of kinetic and adsorption constants were fitted with the Arrhenius equation (see Figure 3.18), leading to:

\[ k_{0,c} = 1.621 \times 10^8 \text{ mol g}^{-1}\text{min}^{-1}; \quad E_{a,c} = 48.0 \text{ kJ mol}^{-1}; \quad R^2 = 0.990 \]

\[ K_{0,s} = 3.408 \times 10^8; \quad \Delta H_s = 48.2 \text{ kJ mol}^{-1}; \quad R^2 = 0.998 \]

![Figure 3.18](image)

Figure 3.18  Representation of experimental values of \( \ln k \) as function of \( 1/T \) and linear fitting.

### 3.6 Mass transfer analysis

It was shown in the previous section that the experiments with pellet diameters of 477 and 854 \( \mu \text{m} \) have limitations due to internal diffusion. However, it was not possible to ensure, that for the lower fraction (267 \( \mu \text{m} \)) the controlling step is the surface reaction. In order to verify if there are mass transfer effects in the kinetic results presented, it is necessary to develop a complete model, including the mass transfer resistances. In case of the controlling mechanism being the internal diffusion, it is necessary to re-analyse the data in order to determine the true kinetic constant.

#### 3.6.1 Mathematical Model

The model considers that the batch reactor operates in isothermal conditions. It is also considered the diffusion of the species at the bulk external film and then diffusion through the pores of the particle until reaches the solid surface, where reaction occurs.
Mass balance in the bulk fluid \((j=1, 2, 3, \text{ and } 4)\):

\[
\frac{d C_{b,j}}{dt} = -\frac{A_p}{V_{\text{liq}}} D_j \frac{\partial C_{p,j}}{\partial r} \bigg|_{r=r_p}
\]

\[
A_p = \frac{3}{r_p} V_p
\]

where \(C_{b,j}\) is the bulk concentration for species \(j\), \(C_{p,j}\) is the concentration of species \(j\) inside the particle, \(A_p\) is the external exchange area between the bulk fluid and the particles, \(V_{\text{liq}}\) is the total volume of reactant mixture, \(D_j\) is the effective diffusivity of species \(j\) inside the pores, \(r_p\) is particle radius, \(V_p\) is the total volume of the particles, \(r\) is the radial position and \(t\) is the time coordinate.

Mass balance in the intraparticle fluid \((j=1, 2, 3, \text{ and } 4)\):

\[
\varepsilon_p \frac{\partial C_{p,j}}{\partial t} = \frac{1}{r_p^2} \frac{\partial}{\partial r} \left[ D_j r_p^2 \frac{\partial C_{p,j}}{\partial r} \right] + (1 - \varepsilon_p) V_j \rho_{\text{solid}} \dot{R}_p
\]

where \(\varepsilon_p\) is the particle porosity, \(V_j\) is the stoichiometric coefficient of species \(j\), \(\rho_{\text{solid}}\) is the true density of the resin and \(\dot{R}_p\) is the reaction rate relative to the local pore concentration.

Initial condition:

\[
t=0 \quad C_{b,j} = C_{b0,j}; \quad C_{p,j} = C_{p0,j}
\]

Boundary conditions:

(symmetry condition) \(r=0\):

\[
\frac{\partial C_{p,j}}{\partial r} = 0
\]

(flow condition) \(r=r_p\):

\[
D_j \frac{\partial C_{p,j}}{\partial r} \bigg|_{r=r_p} = k_j \left( C_{b,j} - C_{p,j} \bigg|_{r=r_p} \right)
\]

Considering the following variable change \(\rho = r / r_p\), the model equations become:

\[
\frac{d C_{b,j}}{dt} = -\frac{3}{r_p^2} \frac{1 - \varepsilon_b}{\varepsilon_b} D_j \left( \frac{\partial C_{p,j}}{\partial \rho} \right)_{\rho=1}
\]

where \(\varepsilon_b\) is the bulk porosity.
\[
\frac{\partial C_{p,j}}{\partial t} = \frac{D_j}{r_p^2 \rho^2} \frac{\partial}{\partial \rho} \left[ \rho^2 \frac{\partial C_{p,j}}{\partial \rho} \right] + \frac{1 - \varepsilon_p}{\varepsilon_p} v_j \rho_{sola} \mathbf{R}^p
\] (3.43)

At \( t=0 \)

\[ C_{b,j} = C_{b0,j}, \quad C_{p,j} = C_{p0,j} \] (3.44)

At \( \rho=0 \)

\[ \frac{\partial C_{p,j}}{\partial \rho} = 0 \] (3.45)

At \( \rho=1 \)

\[ \left. \frac{\partial C_{p,j}}{\partial \rho} \right|_{\rho=1} = B_i \left( C_{b,j} - C_{p,j} \right) \] (3.46)

where \( B_i = \frac{k_i r_p}{D_j} \) is the Biot number for the \( j \) component.

### 3.6.2 Numerical Solution

The system of partial differential equations (Equations 3.42 to 3.46) was solved by the method of lines (MOL) using orthogonal elements, with B-splines as base functions through numerical package PDECOL (Madsen and Sincovec, 1979). This library is specially designed for the solution of the system of equations in partial derivatives with the structure

\[ \frac{\partial \mathbf{u}}{\partial t} = \mathbf{f} \left( t, \mathbf{x}, \mathbf{u}, \frac{\partial \mathbf{u}}{\partial \mathbf{x}}, \frac{\partial^2 \mathbf{u}}{\partial \mathbf{x}^2} \right) \]

and it has been used in the simulation of the adsorption/convection process for the particle (Lu et al., 1992), in the solution of the cyclic adsorption process PSA (Pressure Swing Adsorption) (Lu et al., 1993) and for the PSA with chemical reaction (Lu and Rodrigues, 1994). For the particular case involved in the mathematical model shown here, the global mass balances for all components, represented by Equation 3.42, are ordinary differential equations of first order in function of \( C_{b,j} \) but coupled with the internal variables of the inside the particle through the flow conditions for the bulk/intraparticle fluid (see Equation 3.46) and can not be incorporated in PDECOL when the diffusion in the external film is not negligible. For the negligible external mass transfer (\( B_i \rightarrow \infty \)), the boundary condition 3.46 can be replaced by the simpler one:

\[ \rho=1 \quad C_{b,j} = C_{p,j} \bigg|_{\rho=1} \] (3.47)
and introduced directly in the Equation 3.42 instead of Equation 3.43 for $\rho = 1$. For this particular case, the system of equations obtained can be solved easily with PDECOL, introducing the initial and boundary conditions 3.44 and 3.45, respectively, but leaving "free" the boundary condition 3.47.

When the external resistance is not negligible, Equation 3.47 is not valid and Equations 3.42 and 3.43 must be integrated simultaneously. In the study of the PSA system taking into account dead volumes at both ends of the column, (Lu et al, 1993) solved the conservation equations inside the adsorption column using PDECOL, while the dead volume regions were modelled as perfectly mixed tanks coupled to PDECOL with a fourth order Runge-Kutta method. In this work, the situation is similar, but with only one external perfect mixed volume in contact with the solid phase (see Figure 3.19). An auxiliary system of equations in partial derivatives defined as:

$$
\rho = 1 \quad \frac{\partial C_{b,j}}{\partial t} = - \frac{3}{r_p^2} \frac{1 - \varepsilon_b}{\varepsilon_b} D_f \left( \frac{\partial C_{p,j}}{\partial \rho} \right)_{\rho=1}
$$

$$
0 \leq \rho < 1 \quad \frac{\partial C_{b,j}}{\partial t} = 0
$$

was introduced, forcing a "phantom distributed external solution concentration" within the particle.

![Figure 3.19 Schematic figure of the batch reactor model.](image)
At this moment it is important to introduce the following additional observations:

a) For $\rho = 0$ the Equation 3.43 is not defined and should be substituted by a limiting expression that using the L'Hopital rule is transformed in:

$$\frac{\partial C_{p,j}}{\partial t} = 3 \frac{D_j}{r_p^2} \frac{\partial^2 C_{p,j}}{\partial \rho^2} + \frac{1 - \varepsilon_p}{\varepsilon_p} \rho \rho_{solid} R_p^p$$  \hspace{1cm} (3.50)

b) The group of Equations 3.48 and 3.49 have been written with partial derivatives instead total derivatives as in Equation 3.42 in order to recall that now $C_{b,j}$ are function of $t$ and $\rho$. Nevertheless, the values of $C_{b,j}$ inside the beads have not physical meaning with the exception of the values obtained at $\rho = 1$, which correspond to the values of the external concentration of the mixed tank.

c) The Equations 3.48 and 3.49 are solved by PDECOL introducing them in the vector $\vec{f}$ defined as the generic vectorial equation of the system $\frac{\partial \vec{u}}{\partial t} = f \left( t, x, \vec{u}, \frac{\partial \vec{u}}{\partial x}, \frac{\partial^2 \vec{u}}{\partial x^2} \right)$ that is required by PDECOL and not through the boundary conditions routine. At the same time, it is not introduced additional boundary conditions at $\rho = 1$ for the variables $C_{b,j}$, since the numerical problem becomes full determined at $\rho = 1$ with the solution of Equations 3.48 and 3.49 together with the initial conditions. For $\rho = 0$, the symmetry boundary condition is also used:

$$\rho = 0 \quad \frac{\partial C_{b,j}}{\partial \rho} = 0$$  \hspace{1cm} (3.51)

d) An important condition for the correct working of PDECOL is the consistency between initial and boundary conditions at time $t = 0$. The boundary condition 3.46 is only compatible “automatically” with the initial conditions 3.44 if $C_{b,j}(0) = C_{p,j}(0)$. However, in the general case, this is not verified, so the compatibility between initial and boundary conditions is achieved by the introduction of the following equation:

$$C_{b,j} - C_{p,j} \bigg|_{\rho = 1} = \frac{1}{B_{i,j}} \frac{\partial C_{p,j}}{\partial \rho} \bigg|_{\rho = 1} + \left( C_{b0,j} - C_{p0,j} \right) \exp(-Mt)$$  \hspace{1cm} (3.52)
Equation 3.52 work as a “switch” allowing to pass from the initial to the required boundary conditions walking through a smooth path, avoid an abrupt jump or discontinuity that could break PDECOL starting process. This type of “valve equation” was also use by (Lu et al, 1992), where $M$ is a valve parameter that must be fixed in order to have a negligible impact in the temporary solution of process before the starting condition. It can be verified that Equation 3.52 is transformed in an identity for $t = 0$ changing to the original conditions (see Equation 3.46) for higher values of $t$.

e) For all simulations a tolerance value EPS equal to $10^{-7}$ was fixed and 20 elements with a uniform spatial grid were used.

### 3.6.3 Results and Discussion

For the numerical study the rate expression 3.26 was used, where the activities of the components are relative to the liquid phase inside the catalyst pores.

**Negligible external mass transfer resistance**

To study the presence of internal mass transfer resistance, several experiments were performed with different pellet diameters, temperatures and initial molar ratio of reactants. The stirrer speed was high enough to avoid the external film resistance.

The diffusivities in multicomponent liquid mixture were estimated by the modified Wilke-Chang equation, proposed by Perkins and Geankoplis (see Appendix D).

In order to validate the internal mass transfer resistance estimation, experiments using catalyst with different pellets diameter were performed. The experimental data were compared with the simulated results. Two models were considered: one that includes the diffusion of the species inside the particle (diffusion model) and the other that considers that the controlling mechanism is the reaction step, so the diffusion inside the particle could be negligible (equilibrium model). In this case the concentration inside the particle is equal to the bulk concentration and Equation 3.43 is reduced to:

$$\frac{\partial C_{p,j}}{\partial t} = \frac{1 - \varepsilon_p}{\varepsilon_p} \nu_j \rho_{s,\text{solid}} \mathcal{R} \quad (3.53)$$

where $\mathcal{R}$ is the reaction rate relative to the bulk concentration.
In order to clarify the existence of internal mass transfer resistance in the experiments performed with the smallest pellet diameter, the experimental data were compared with the predicted by the equilibrium and diffusion models (see Figure 3.20).

If the internal mass transfer resistance is high, the diffusion of the reactants from the bulk to the particle is not sufficiently fast to compensate the converted reactants, resulting in a concentration profile inside the pellet. This profile causes a decreased average reaction rate relative to that when the concentration inside the particle is equal to the surface concentration (equilibrium model). If the simulated results obtained with the diffusion and equilibrium model are identical, the controlling mechanism is the reaction at the solid surface and therefore the diffusion inside the particle is negligible. Accordingly to this and from the comparison between diffusion and equilibrium models, it is possible to conclude that the measured kinetic results have limitations due to internal mass transfer resistances.

In order to determine the true kinetic constant, a new optimization of the kinetic data was performed. The estimation of the kinetic constant was carried out with a non-linear regression subroutine that uses the Levenberg-Marquardt method to minimise the sum of residual squares (SRS) between the experimental and calculated molar fraction of all components:

\[
SRS = \sum_{i=1}^{4} \sum_{j=1}^{4} (x_{i,\text{exp}} - x_{i,\text{theo}})^2
\]  

(3.54)

The theoretical molar fraction values \( x_{i,\text{theo}} \) were calculated by the proposed model, in absence of external mass transfer. The values of the true kinetic constant for the model 2 (expressed in terms of activities and molar fractions) are presented in Table 3.20

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Model 2 (activities)</th>
<th>Model 2 (molar fraction)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( k_c ) (mol g' min')</td>
<td>RS ( 2.9 \times 10^{-3} )</td>
</tr>
<tr>
<td>16</td>
<td>0.605</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>0.807</td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>1.481</td>
<td></td>
</tr>
</tbody>
</table>
Figure 3.20  Comparison between experimental and simulated kinetic curves:
$V_{atm}=2.17$, $P=6$ atm, $m_{\text{w}}=0.5$ g and $d_2=267$ $\mu$m. a) $T=16$ °C; b) $T=20$ °C; c) $T=26$ °C.
The kinetic model expressed in terms of activities is slightly more accurate than the model expressed in terms of molar fractions. But the last one is much simpler and also provides good results. The temperature dependence of kinetic constants was fitted with the Arrhenius equation (see Figure 3.21), leading to:

Activities: $k_{0_c} = 3.32 \times 10^{11} \text{ mol g}^{-1} \text{ min}^{-1}$; $E_{a_c} = 65.1 \text{ kJ mol}^{-1}$; $R^2 = 0.991$

Molar fractions: $k_{0_c} = 1.40 \times 10^{12} \text{ mol g}^{-1} \text{ min}^{-1}$; $E_{a_c} = 68.2 \text{ kJ mol}^{-1}$; $R^2 = 0.994$

It is verified that the true activation energy increased of about 40% of the apparent value.

![Figure 3.21](image)

*Figure 3.21*  Representation of experimental values of ln $k$ as function of $1/T$ and linear fitting.

The comparison between the experimental values and the theoretical models (apparent and true kinetic), for all temperatures and initial composition, is shown in Figure 3.22, Figure 3.23 and Figure 3.24.

The experimental and simulated values of molar fraction of ethanol, acetaldehyde and acetal as function of time, for the experiments using catalyst pellets with 267, 477 and 854 $\mu$m diameter are shown in Figure 3.25. The agreement between the experimental data and the results simulated with the diffusion model lead us to conclude that the mass transfer parameters are well predicted by the correlations above mentioned.
Figure 3.22  Comparison between experimental points and optimized kinetic curves (apparent kinetic and true kinetic+pore diffusion): $T=16$ °C, $P=6$ atm, $w_{\text{cat}}=0.5$ g and $d_p=267$ µm. a) $r_{A/B}=1.44$; b) $r_{A/B}=2.18$; c) $r_{A/B}=3.35$. 
Figure 3.23  Comparison between experimental points and optimized kinetic curves (apparent kinetic and true kinetic+pore diffusion): $T=20^\circ C$, $P=6$ atm, $w_{ad}=0.5$ g and $d_p=267$ μm. a) $r_{A/B}=1.47$; b) $r_{A/B}=2.18$; c) $r_{A/B}=3.34$. 
Figure 3.24  Comparison between experimental points and optimized kinetic curves (apparent kinetic and true kinetic+pore diffusion): $T=26^\circ C$, $P=6$ atm, $w_{\text{avg}}=0.5$ g and $d_p=267$ μm. a) $r_{A/B}=1.51$; b) $r_{A/B}=2.18$; c) $r_{A/B}=3.12$. 
Figure 3.25  Effect of catalyst particle diameter on the molar fraction of ethanol, acetaldehyde and acetal as a function of time: $T=20 \, ^{\circ}\mathrm{C}$, $r_{A/B}=2.17$, $P=6 \, \text{atm}$ and $w_{\text{cat}}=1.5 \, \text{g}$. a) $d_p=267 \, \mu\text{m}$; b) $d_p=477 \, \mu\text{m}$; c) $d_p=854 \, \mu\text{m}$. Points are experimental data, lines are simulated results.
Analysing the internal concentration profiles (see Figure 3.26) it is possible to conclude that the pore diffusion is the controlling mechanism. The effectiveness factor could be evaluated at each time by knowing the concentration inside the particle.

**Figure 3.26** Effect of catalyst particle diameter on the internal concentration profile of ethanol, experimental conditions of Figure 3.25. a) $t=5$ min; b) $t=50$ min; c) $t=100$ min.
Defining the effectiveness factor as:

$$\eta = \frac{\langle R \rangle}{R_s} = 3 \int R \frac{\rho^2 R \, d\rho}{R_s}$$

(3.55)

where $R_s$ is the kinetic rate at surface conditions and $\langle R \rangle$ is the average kinetic rate defined as:

$$\langle R \rangle = \frac{\int_r r^2 R \, dr}{\int_r r^2 \, dr}$$

(3.56)

The time evolution of the effectiveness factor, for different particle diameter is represented in Figure 3.27.

![Figure 3.27](image)

**Figure 3.27** Effect of catalyst particle diameter on the effectiveness factor history.

It is interesting to notice that when the equilibrium is reached, the rates of the direct and the reverse reactions are equal, meaning that reaction rate $\langle R \rangle$ is zero, both at the surface as inside the particle. This should imply that the effectiveness factor was not defined:

$$\eta_w = \lim_{t \to \infty} \frac{\langle R \rangle}{R_s} = 0$$

(3.57)
In order to clarify the meaning of the value obtained by numerical integration, the values of the effectiveness factor for the same experiments were calculated assuming an infinite bath. The steady state profiles obtained in an infinite bath are shown in Figure 3.28. The corresponding effectiveness factors are presented at Table 3.21.

![Diagram showing concentration profiles](image)

**Figure 3.28** Effect of catalyst particle diameter on the ethanol and acetal internal concentration profiles at steady state, for an infinite bath.

**Table 3.21** Comparison of the effectiveness factors obtained in a batch reactor and in an infinite bath, at steady state, for different particle diameters.

<table>
<thead>
<tr>
<th>d_p (µm)</th>
<th>Effectiveness factor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Batch reactor</td>
</tr>
<tr>
<td>267</td>
<td>0.469</td>
</tr>
<tr>
<td>477</td>
<td>0.291</td>
</tr>
<tr>
<td>812</td>
<td>0.172</td>
</tr>
</tbody>
</table>

For better understanding, a slab of porous catalyst where a first-order reversible chemical reaction (A ⇌ B) takes place is studied in Appendix F. The main conclusions are:

- the effectiveness factor, for an infinite bath, is independent on the surface composition;
the effectiveness factor for the batch reactor, assuming a pseudo steady-state (at each time the internal profiles are in equilibrium with the surface composition by making zero the time derivative of the particle concentration), is equal to the value obtained in the infinite bath.

For the acetal synthesis is not possible to obtain the same results, since all properties are being estimated instantaneously and locally. The difference between the internal profiles inside the particle in the steady state for a batch reactor and for an infinite bath, affects the values of the properties (total molar concentration, viscosity of the mixture, activity coefficients and molecular diffusivities of components in the mixture) and therefore the effectiveness factors obtained are different.

In order to identify the controlling mechanism, it was defined a dimensionless parameter, the Thiele modulus:

$$\phi_A = \frac{r_p}{3} \sqrt{\frac{\rho_p k_c}{D_{es} C_{es}}}$$  

(3.58)

where \( r_p \) is the particle radius, \( \rho_p \) is the particle density, \( k_c \) is the kinetic constant, \( D_{es} \) is the effective diffusivity of ethanol at the surface and \( C_{es} \) is the ethanol concentration at the surface. For values greater than unity, the internal diffusion is the limiting step. The variation of the effectiveness factor with the Thiele modulus and the temperature was evaluated by using the infinite bath approach. The values used for the simulations are presented at Table 3.22. It was also considered the particle density \( \rho_p = 1205 \text{ g/l} \), the internal porosity \( \varepsilon_p = 0.48 \) and the tortuosity \( \tau = 2 \). Graphical representation of the effectiveness factor versus the Thiele modulus is available as Figure 3.29.

<table>
<thead>
<tr>
<th>Table 3.22</th>
<th>Parameters used for effectiveness factor evaluation in an infinite bath.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Molecular Diffusivity (cm²/min)</td>
</tr>
<tr>
<td>Ethanol</td>
<td>Acetaldehyde</td>
</tr>
<tr>
<td>10 °C</td>
<td>1.4×10⁻³</td>
</tr>
<tr>
<td>20 °C</td>
<td>1.1×10⁻³</td>
</tr>
</tbody>
</table>
The temperature will affect all properties estimation, but the effect on effectiveness factor dependence on Thiele modulus is small.

![Graph](image)

*Figure 3.29* Variation of the effectiveness factor with the Thiele modulus and temperature.

The relation between the effectiveness factor and the Thiele modulus (see Figure 3.30), when the internal diffusion is the controlling mechanism is given by:

- \( T = 10 \degree C \):
  \[
  \ln \eta = -0.936\ln \phi_A + 0.036; \quad R^2 = 0.9995
  \]

- \( T = 20 \degree C \):
  \[
  \ln \eta = -0.913\ln \phi_A + 0.250; \quad R^2 = 0.9986
  \]

![Graph](image)

*Figure 3.30* Dependence of the effectiveness factor on the Thiele modulus.
3.7 Conclusions

An automated experimental set-up was developed and used to carry out thermodynamic and kinetic studies of diethylacetal synthesis in liquid phase, catalyzed by the acid resin Amberlyst 18.

The thermodynamic equilibrium constant was measured in the temperature range of 20-60 °C at 10 bar: \( \ln K_a = 1270/T - 3.07 \) and \( \ln K_A = 1467/T - 4.20 \), using the equilibrium constant expressed in activities and molar fractions, respectively. The standard molar reaction properties were obtained at 298 K: \( \Delta H^0 = -10.56 \text{ kJ mol}^{-1} \), \( \Delta G^0 = -2.94 \text{ kJ mol}^{-1} \) and \( \Delta S^0 = -25.56 \text{ J mol}^{-1} \text{ K}^{-1} \). The standard molar properties of formation of acetal in the liquid phase at 298 K were estimated: \( \Delta H_f^0 = -476.5 \text{ kJ mol}^{-1} \), \( \Delta G_f^0 = -243.5 \text{ kJ mol}^{-1} \) and \( S_f^0 = 343.2 \text{ J mol}^{-1} \text{ K}^{-1} \).

Kinetic experiments showed that the pressure does not affect the reaction rate for the temperature range of 10-25 °C. Because of the strong non-ideality of the liquid reaction mixture, the reaction rate model was formulated in terms of activities. The rate-controlling step, the chemical reaction between adsorbed molecules, was formulated by analogy with homogeneous catalysis. The measured reaction rates were in good agreement with the proposed rate expression and the model constants dependence on temperature was found by Arrhenius equation. In order to simplify the modelling simulation, the kinetic model was simplified by using molar fractions instead of activities. The agreement between experimental and simulated results was good. In order to verify the existence of internal mass transfer resistance, it was developed a model including pore diffusion. Since the simulated results with the diffusion model were different from those using the equilibrium model, it was possible to conclude that the kinetic experiments were performed with mass transfer limitations. The experimental data were optimized in order to get the true kinetic constant. The proposed kinetic law, expressed in activities is:

\[
R = k_e \frac{a_A a_B}{K_{eq} a_C a_D} \left(1 + K_D a_D\right)^2
\]

and the parameters are
\[ k_c (\text{mol/g.min}) = 3.3 \times 10^{11} \exp \left[ -\frac{7824}{T (K)} \right] \]

\[ K_p = 6.4 \times 10^5 \exp \left[ -\frac{4003}{T (K)} \right] \]

The activation energy of reaction is 65.0 kJ mol\(^{-1}\).

The rate equation will be used in the modelling simulation of the continuous reactor for the synthesis of diethylacetal. In order to relate the average rate of reaction with the reaction rate at the surface, it was found the relation between the effectiveness factor and the Thiele modulus, when the internal diffusion is the controlling mechanism (\(\ln \phi_A > 1\)):

\[ T=10 \, ^\circ\text{C}: \quad \ln \eta = -0.936 \ln \phi_A + 0.036 \]

\[ T=20 \, ^\circ\text{C}: \quad \ln \eta = -0.913 \ln \phi_A + 0.250 \]

where the Thiele modulus, related to ethanol, is defined as:

\[ \phi_A = \frac{r_p}{3} \sqrt[3]{\frac{\rho_p k_c}{D_{ij} C_{d,i}}} \]

### 3.8 Notation

- **a** liquid phase activity
- **A** peak area for Equation 3.1
- **A_p** external exchange area between the bulk fluid and the particles
- **Bi** Biot number
- **C** concentration (mol/l)
- **C_{b,i}** bulk concentration (mol/l)
- **C_{p,i}** concentration inside the particle (mol/l)
- **D_{ij}** effective diffusivity of species \(j\) inside the pores (cm\(^2\)/min)
\(d_p\)  average pellet diameter (\(\mu m\))

\(E_{a,\alpha}\)  reaction activation energy (J mol\(^{-1}\))

\(f_i\)  response factor (Equation 3.1)

\(K_{eq}\)  equilibrium reaction constant

\(K_x\)  equilibrium constant based on molar fractions

\(K_y\)  equilibrium constant based on activity coefficients

\(K_c\)  equilibrium constant based on concentrations

\(K_a\)  equilibrium constant based on activities

\(K_s\)  equilibrium adsorption constant

\(K_p\)  correction factor

\(k_e\)  kinetic constant (mol g\(^{-1}\) min\(^{-1}\))

\(k_{0,e}\)  Arrhenius constant for Equation 3.33 (mol g\(^{-1}\) min\(^{-1}\))

\(K_{0,a}\)  Arrhenius constant for Equation 3.34

\(k_f\)  external film coefficient (cm/min)

\(m\)  mass (g)

\(n\)  number of moles (mol)

\(\Delta H^o\)  standard enthalpy of reaction (J mol\(^{-1}\))

\(\Delta H^f\)  standard enthalpy of formation (J mol\(^{-1}\))

\(\Delta H_s\)  enthalpy of adsorption (J mol\(^{-1}\))

\(\Delta G^o\)  standard Gibbs energy of reaction (J mol\(^{-1}\))

\(\Delta G^f\)  standard Gibbs energy of formation (J mol\(^{-1}\))

\(\Delta S^o\)  standard entropy of reaction (J mol\(^{-1}\) K\(^{-1}\))

\(P\)  pressure (atm)

\(r\)  radial position (cm)

\(R\)  gas constant (J mol\(^{-1}\) K\(^{-1}\))

\(r_p\)  particle radius (\(\mu m\))

\(r_{A/B}\)  initial molar ratio of reactants
\( R \) reaction rate (mol g\(^{-1}\) min\(^{-1}\))
\( R_s \) reaction rate at surface conditions (mol g\(^{-1}\) min\(^{-1}\))
\( \langle R \rangle \) average reaction rate (mol g\(^{-1}\) min\(^{-1}\))
\( R'' \) reaction rate relative to the local pore concentration (mol g\(^{-1}\) min\(^{-1}\))
\( S'' \) standard entropy of formation (J mol\(^{-1}\) K\(^{-1}\))

\( t \) time coordinate (min)
\( T \) temperature (K)
\( V_{ml} \) liquid molar volume (cm\(^3\) mol\(^{-1}\))
\( x_i \) molar fraction
\( X \) conversion of the limiting reactant
\( V \) volume of solution (ml)
\( V_{liq} \) total volume of reactant mixture (ml)
\( V_p \) total volume of the particles (ml)
\( w_{cut} \) mass of dry catalyst (g)

**Greek letters**

\( \nu_i \) stoichiometric coefficient
\( \theta_0 \) fraction of vacant sites
\( \gamma \) activity coefficient
\( \rho \) dimensionless radial coordinate
\( \eta \) effectiveness factor
\( \varepsilon_p \) particle porosity
\( \phi \) Thiele modulus
\( \rho_p \) particle density (g/l)
\( \rho_{solid} \) true density of the resin (g/l)
\( \varepsilon_b \) bulk porosity
\( \theta_i \) fraction of sites occupied by species i
Subscripts

- initial value
- $A$ ethanol
- $B$ acetaldehyde
- $C$ acetal
- $D$ water
- $e$ equilibrium
- $exp$ experimental data
- $gas$ vapour phase
- $i$ relative to component $i$
- $l$ relative to limiting reactant
- $liq$ liquid phase
- $theo$ theoretical data

3.9 References


4. The Fixed Bed Adsorptive Reactor

The synthesis of diethylacetal from ethanol and acetaldehyde was performed in a laboratory and pilot scale fixed bed adsorptive reactors. Two acid resins were tested: Amberlyst 18 and Amberlyst 15, both supplied from Rohm and Haas. Adsorption and reaction experiments were undertaken at constant temperature and atmospheric pressure. Experimental results of dynamic adsorption of binary non-reactive mixtures are reported and used to obtain multicomponent adsorption equilibrium isotherms of Langmuir type. The reaction kinetics reported in the previous chapter for Amberlyst 18 was used in the model of the adsorptive reactor, which also included axial dispersion, external and internal mass-transfer resistances and multicomponent Langmuir isotherms. Model equations were solved by orthogonal collocation on finite elements (OCFE) implemented by the PDECOL package, using the measured model parameters and was validated by experimental data for reaction and regeneration steps, with good accuracy.

4.1 Introduction

Most known methods of acetal production involve the acid-catalyzed equilibrium controlled reaction of acetaldehyde and ethanol (Bramwyche et al, 1950), according to the reaction:

\[ 2 \text{Ethanol (A)} + \text{Acetaldehyde (B)} \rightleftharpoons \text{Acetal (C)} + \text{Water (D)} \]

Traditionally, mineral or carboxylic acids are used as catalyst (Morrison and Boyd, 1983). The disadvantage of using soluble catalysts is that they must be neutralized after reaction. Therefore, heterogeneous catalysts of the strongly acid resin type are used. These catalysts have the advantage of being easily separated from reaction product and having a long lifetime.
Resins are of particular interest since they act like catalyst for the acetalization reaction and as a selective adsorbent to the species involved in the process (Mazzotti et al., 1996; Mazzotti et al., 1997). Lately, the development of multifunctional reactors using acid resins as catalyst is being implemented in the production of oxygenated fuel additives (MTBE, ETBE, TAME, etc.), where reaction is of the type: A + B → C. Among all available technologies, the reactive distillation is the most used in that field when the boiling point of the desired product, C, is different from the reactants boiling points (Sundmacher and Hoffmann, 1996; Higler et al., 2000). In the case of acetalization, where the two products, acetal and water, have boiling temperatures of 102 °C and 100 °C, respectively, the use of an adsorptive chromatographic reactor seems to be a feasible and economical solution. The application of chromatographic reactors to equilibrium controlled reactions (Sardin et al., 1993; Carta, 1991) leads to conversions higher than the equilibrium since one of the products is being removed from the reaction zone. Perhaps one of the most interesting chromatographic reactors is the Simulated Moving Bed Reactor (SMBR). This technology has been applied to reversible reactions catalyzed by acid resins (Kawase et al., 1996; Mazzotti et al., 1996) and also to biochemical reactions (Azevedo and Rodrigues, 2001; Barker et al., 1992). However, some authors first studied the dynamic behaviour of the fixed bed adsorptive reactor to validate kinetic and adsorption data and to provide a better understanding of the performance of chromatographic reactors (Lode et al., 2001; Mazzotti et al., 1997; Kawase et al., 1999). A number of mathematical models have been developed to explain the kinetic behaviour of the fixed bed adsorptive reactor and to estimate the breakthrough curves. The mechanism of adsorption and reaction on a catalyst includes external diffusion, internal diffusion, the adsorption and the reaction at the solid surface. The intraparticle diffusion may occur by molecular diffusion, Knudsen diffusion and the surface diffusion, depending on the pores size, the adsorbate concentrations and others conditions. Figure 4.1 shows a schematic illustration of the mass transfer mechanisms that may occur in a fixed bed adsorptive reactor. The mass transfer effects are due to four main mechanisms: axial mixing in the bulk mobile phase percolating between the stationary phase particles in the column (axial dispersion); the mass transfer of molecules between the bulk mobile phase and the external surface of the stationary phase particles (external mass transfer); the diffusive migration through the pores inside the particles (internal diffusion); and the surface diffusion.
Ion exchange resins are produced through a copolymerization procedure with styrene and divinyl-benzene used as cross-linking agent. The acid groups, containing hydrogen ions in the from of sulfonic groups, are attached to the polymeric matrix developed in the gel phase by long polystyrene chains fixed by bridges of divinyl-benzene, leading to a stable and rigid structure (Quinta-Ferreira et al., 1996). This structure can be of gel-type resins (continuous microporous matrix) or macroreticular-type resins. Macroporous resins, such as Amberlyst 18 (A18) and Amberlyst 15 (A15), have macropores, which allows significant increase in the reaction rate between nonpolar molecules or high molecular weight (Quinta-Ferreira and Rodrigues, 1993). The macroreticular ion exchange resins show bidisperse pore distribution (Caetano et al., 1994; Ihm et al., 1996). The resin particles are considered to be an ensemble of cellular microspheres and most of the active sites are reported to lie within these microspheres (Ihm et al., 1996). The reactant species should first diffuse through the macropores to the external surface of microspheres and then penetrate into the gel phase. The pore size distribution of the ion exchange resin depends upon the degree of cross-linking of the polymer matrix. The sulfonic groups constitute a dense network structure by forming hydrogen bonds between them, therefore the diffusion of polar compounds into the microspheres is expected to be strongly influenced by the interaction with the catalyst structure (Oktar et al., 1999).

The adsorption and reaction processes over catalysts with bidisperse pore size distribution have been widely studied in the literature. The first and more used model was developed by Ruckenstein, who considers a spherical macroporous pellet to be an assembly of small microspheres (Ruckenstein et al., 1971). The adsorbate diffuses into macropores, adsorbs on the
macropore walls, and also diffuses into the micropores and is adsorbed there. Recently, this model was used to determine the effectiveness of bidisperse catalysts (Leitão et al, 1994), to study adsorption induced convection in the macropores of a bidisperse adsorbent particle (Taqvi et al, 1997). Latter, it was adopted an equivalent model, considering microspheres as homogeneous gel particles, where the adsorbed phase diffuses (Ruthven and Loughlin, 1972).

Turner proposed a model structure where the solid network is described by the branched micro-macropore model, including macropores for the transport and micropores to provide capacity of adsorption or reaction (Turner, 1958), which was also used later by Villermaux (Villermaux et al, 1987). This model was also applied for the analysis of diffusion and reaction in a catalyst with a bidisperse pore structure (Tartarelli et al, 1970). Recently, the Turner structure of a bidisperse model was adopted to study adsorption, because of its simplicity, the geometry of macro and micropores and the diffusivities within pores is then well defined (Petersen, 1991; Silva and Rodrigues, 1999, see Appendix G).

The ratio of the diffusion times in the macro and micropores obtained from adsorption experiments of methanol and isobutylene in gas phase over A15, was found to be of the order of magnitude of unity. Therefore, in the analysis of rate data for etherification reactions, both macro and micropore diffusion resistances should be taken into consideration (Oktar et al, 1999). The analysis of the pure component batch adsorption experiments of ethanol, methanol and 2-methyl-2-butene on Amberlyst 15, using n-heptane as inert solvent, showed that the surface diffusion had significant contribution in the total diffusion flux into a macroreticular resin catalyst (Dogu et al, 2003).

The aim of this work is to study the synthesis of diethylacetal in a fixed bed adsorptive reactor, in view of future implementation of the process in a Simulated Moving Bed Adsorptive Reactor. Adsorption and reaction experiments were carried out at constant temperature and atmospheric pressure. The multi-component adsorption parameters were obtained by performing binary adsorptive experiments in absence of reaction. The model for the adsorptive reactor includes axial dispersion, external and internal mass-transfer resistances, constant temperature and multicomponent Langmuir isotherms, and it was solved by orthogonal collocation by finite elements, using the measured model parameters.
4.2 The Chromatographic Reactor

4.2.1 Experimental Apparatus

The experiments have been performed in a laboratory-scale jacketed glass column that was maintained at constant temperature, through a thermostatic bath at 15 °C, at atmospheric pressure (see Figure 4.2). All experiments were performed with analytical grade chemicals (purity > 99 %) from Sigma-Aldrich (U.K.). The experimental breakthrough curves were obtained by analysing with a gas chromatograph, small samples withdrawn at different times from the column exit.

![Figure 4.2](image)  
*Experimental set-up (configuration: top-down flow direction).*
The column was packed with a sulfonic acid ion exchange resin. Two types of resins, Amberlyst 18 and Amberlyst 15 (see Table 4.1), were used to perform the experiments.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Amberlyst 18</th>
<th>Amberlyst 15</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manufacturer</td>
<td>Rohm and Haas</td>
<td>Rohm and Haas</td>
</tr>
<tr>
<td>Concentration of acid sites (eq H(^+)/kg)</td>
<td>4.5</td>
<td>4.7</td>
</tr>
<tr>
<td>Surface area (m(^2)/g)</td>
<td>30</td>
<td>45</td>
</tr>
<tr>
<td>Average pore diameter (nm)</td>
<td>43</td>
<td>24</td>
</tr>
</tbody>
</table>

Amberlyst 18 and Amberlyst 15 are ion exchange resins with co-polymer structure of styrene-divinyl benzene that swell selectively when they are brought in contact with the liquid phase. The swelling ratio (ratio between the swollen and dry volume of the resin) depends upon the fluid composition. The swelling is due to the sorption of the different components of the mixture, depending on their relative affinities to the resin. The interaction between component and polymer matrix is caused by the interaction between the component and the acid site, the sulfonic acid group. The penetrability to acid sites depends on interactions between the pairs of components and the pairs of component and polymer matrix. Diffuse reflectance FT-IR spectra of methanol and ethanol on Amberlyst 15 indicate that alcohol molecules are adsorbed by forming hydrogen bridges with –SO\(_3\)H sites of the resin and among themselves. Some of the alcohol molecules were found to be strongly chemisorbed by dissociation of one or two hydrogen atoms (Dogu et al., 2001). The character of the resin is mainly determined by its structure, e.g. cross-linking degree and functional groups. The polymeric resins that contain sulfonic acid functional groups exhibit a strong selectivity for polar species. For Amberlyst 15 the swelling ratio for water, ethanol, acetic acid and ethyl acetate is, respectively, 1.52, 1.48, 1.30 and 1.22 (Mazzotti et al., 1997), that is in agreement with the polarity of the components.

So, it is expected for the system studied here that the order of increasing affinity of the components to the resin is: acetal, ethanol, acetaldehyde and water. The effect of swelling yields changes in the length and in the bulk porosity of the fixed bed reactor, but during its operation, no variation in the bed length was noticed. Table 4.2 shows the characteristics of the fixed bed column.
Table 4.2  Characteristics of the fixed bed columns.

<table>
<thead>
<tr>
<th></th>
<th>Amberlyst 18</th>
<th>Amberlyst 15</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid weight (g)</td>
<td>46</td>
<td>40</td>
</tr>
<tr>
<td>Length (L) cm</td>
<td>28</td>
<td>23</td>
</tr>
<tr>
<td>Internal diameter cm</td>
<td>2.2</td>
<td>2.6</td>
</tr>
<tr>
<td>Radius of the particle (r) μm</td>
<td>239</td>
<td>400</td>
</tr>
<tr>
<td>External void fraction (ε)</td>
<td>0.39</td>
<td>0.40</td>
</tr>
<tr>
<td>Internal void fraction (ε)</td>
<td>0.39</td>
<td>0.40</td>
</tr>
<tr>
<td>Bulk density (ρs) kg/m³</td>
<td>390</td>
<td>390</td>
</tr>
</tbody>
</table>

In order to determine the Peclet number and the bed porosity, pulse experiments of tracer were performed using a blue dextran solution (5 kg/m³). Samples of 0.2 cm³ were injected under different flow rates and the column response was monitored using a UV-VIS detector at 300 nm. The bed porosity was calculated from the stoichiometric time of the obtained experimental curves. By calculating the second moment of the experimental curves, an average Peclet number was obtained for the range of flow rates to be used in the fixed bed experiments. Figure 4.3 shows two different tracer experiments and the respective values of bed porosity and Peclet number are presented in Table 4.3.

![Figure 4.3](image1.png)  
Figure 4.3  Tracer experiments using a blue dextran solution. a) Amberlyst 18; b) Amberlyst 15. Points are experimental values and lines are simulated curves.
Table 4.3 Results obtained from tracer experiments.

<table>
<thead>
<tr>
<th></th>
<th>Q (ml/min)</th>
<th>τ (min)</th>
<th>ε</th>
<th>σ²</th>
<th>Pe</th>
</tr>
</thead>
<tbody>
<tr>
<td>run 1</td>
<td>5.0</td>
<td>8.33</td>
<td>0.392</td>
<td>0.506</td>
<td>273.8</td>
</tr>
<tr>
<td>run 2</td>
<td>7.5</td>
<td>5.58</td>
<td>0.393</td>
<td>0.234</td>
<td>265.7</td>
</tr>
<tr>
<td>run 3</td>
<td>18.0</td>
<td>2.67</td>
<td>0.405</td>
<td>0.047</td>
<td>303.1</td>
</tr>
<tr>
<td>run 4</td>
<td>20.8</td>
<td>2.20</td>
<td>0.386</td>
<td>0.031</td>
<td>310.3</td>
</tr>
<tr>
<td>run 5</td>
<td>25.0</td>
<td>1.89</td>
<td>0.399</td>
<td>0.026</td>
<td>276.5</td>
</tr>
</tbody>
</table>

4.2.2 Mathematical Model

A rigorous modelling of the sorption in the swelling polymer should include an appropriate model, as the modified Flory-Huggins, to predict the polymer-phase activities (Mazzotti et al., 1996). However, for densely cross-linked resins bearing highly polar groups on almost every monomer, these effects are poorly understood and this model should be regarded as an empirical tool to correlate the sorption equilibrium data and to predict the behaviour of multicomponent mixtures (Lode et al., 2001). For this reason, an alternative approach based on the multicomponent Langmuir model was considered. It was shown that thermodynamic consistency requires that the total molar capacity of the resin should be equal for all species. For physical adsorption of molecules of widely different size such an assumption is unrealistic. Pöpken states that using a Langmuir-type adsorption isotherm based on mass instead of adsorbed amount, where the total adsorbed mass per mass of catalyst was kept the same for all species, results in further improvement of the fitting result (Pöpken et al., 2000). It should also be mentioned that the underlying assumptions of the Langmuir model, that is monolayer adsorption to energetically equal binding sites, do not describe the actual physical phenomena of adsorption. However, the Langmuir model should be regarded as an analytical description rather than a physical model which is able to represent satisfactorily the experimental adsorption data.

The mathematical model used to describe the dynamic behaviour of the fixed bed adsorber/reactor considers the following assumptions:

- The flow pattern is described by the axial dispersed plug flow model;
External and internal mass-transfer for adsorbable species are combined in a global resistance;

Isothermal process.

Constant column length and packing porosity are assumed.

The model equations are constituted by the following system of four second order partial differential equations in the bulk concentration of the \( i \)th component, \( C_i \), four ordinary differential equations in the average concentration of the \( i \)th component into the particle pores, \( \bar{C}_{p,i} \), and four algebraic equations in the adsorbed concentration in equilibrium with \( \bar{C}_{p,i} \), \( q_i \):

**Bulk fluid mass balance to component \( i \):**

\[
\epsilon \frac{\partial C_i}{\partial t} + \frac{\partial (u C_i)}{\partial z} + (1 - \epsilon) \frac{\partial}{\partial z} \left( \frac{3}{r_p} K_l \left( C_i - \bar{C}_{p,i} \right) \right) = \epsilon D_{av} \frac{\partial}{\partial z} \left( C_i \frac{\partial x_i}{\partial z} \right) \quad (4.1)
\]

**Pellet mass balance to component \( i \):**

\[
\frac{3}{r_p} K_l \left( C_i - \bar{C}_{p,i} \right) = \epsilon_p \frac{\partial \bar{C}_{p,i}}{\partial t} + (1 - \epsilon_p) \frac{\partial q_i}{\partial t} - v_i \rho_p \mu_i(\bar{C}_{p,i}) \quad (4.2)
\]

**Adsorption equilibrium isotherm to component \( i \):**

\[
q_i = \frac{Q_i K_i \bar{C}_{p,i}}{1 + \sum_{j=1}^{n} K_j \bar{C}_{p,j}} \quad (4.3)
\]

together with the initial and Danckwerts boundary conditions:

\[
t = 0 \quad C_i = \bar{C}_{p,i} = C_{i,0} \quad (4.4)
\]

\[
z = 0 \quad u C_i - \epsilon D_{av} C_i \frac{\partial x_i}{\partial z} \bigg|_{z=0} = u C_{i,F} \quad (4.5)
\]

\[
z = L \quad \frac{\partial C_i}{\partial z} \bigg|_{z=L} = 0 \quad (4.6)
\]
Subscripts $F$ and $0$ refer to the feed and initial states, respectively, $u$ is the superficial velocity, $K_L$ is the global mass transfer coefficient, $D_{av}$ is the axial dispersion coefficient, $t$ is the time variable, $z$ is the axial coordinate, $v_i$ is the stoichiometric coefficient of component $i$, $\rho_b$ is the bulk density, $\eta$ is the effectiveness factor of the reaction and $\beta$ is the apparent kinetic rate of the chemical reaction relative to the bulk liquid phase; and $Q_i$ and $K_i$ represent the total molar capacity per unit volume of resin and the equilibrium constant for component $i$, respectively.

Variations in the superficial velocity and in the total concentration of the liquid phase can be accounted for, by assuming the ideal volume additivity of the components within the liquid phase, that is $\sum C_i V_{ml,i}=1$. However, velocity and total concentration variations in the simulations under examination are small and can be neglected without significantly affecting the model accuracy.

Introducing the dimensionless variables for space $\zeta=\frac{z}{L}$ and time $\theta=\frac{t}{\varepsilon L / u}$ and the parameters:

**Peclet number**

$$P_e=\frac{u L}{\varepsilon D_{av}}$$  \hspace{1cm} (4.7)

**Damköhler number**

$$D_a=\frac{\rho_b k_e \varepsilon L}{u}$$  \hspace{1cm} (4.8)

**Number of mass transfer units**

$$K_L^*=\frac{e L}{u r_p} K_i$$  \hspace{1cm} (4.9)

The model Equations 4.1 and 4.2 become:

$$\frac{\partial C_i}{\partial \theta} + \frac{\partial C_i}{\partial \zeta} + K_L^* - \frac{1}{\varepsilon} \left( C_i - C_{p,i} \right) = \frac{1}{P_e} \frac{\partial^2 C_i}{\partial \zeta^2}$$  \hspace{1cm} (4.10)

$$K_L^* \left( C_i - C_{p,i} \right) = \varepsilon_p \frac{\partial C_{p,i}}{\partial \theta} + (1-\varepsilon_p) \frac{\partial q_i}{\partial \theta} - v_i D_a f \left( C_{p,i} \right)$$  \hspace{1cm} (4.11)

with the initial and boundary conditions:

$$\theta=0 \quad C_i = C_{p,i} = C_{i,0}$$  \hspace{1cm} (4.12)
\[ \zeta = 0 \quad \frac{C_i - \frac{1}{Pe} \frac{\partial C_i}{\partial \zeta}}{C_{i,\text{ref}}} = 0 \quad (4.13) \]

\[ \zeta = 1 \quad \frac{\partial C_i}{\partial \zeta} \bigg|_{\zeta=1} = 0 \quad (4.14) \]

The proposed model considers a global mass transfer coefficient \( K_L \) defined as:

\[ \frac{1}{K_L} = \frac{1}{k_e} + \frac{1}{\varepsilon_p k_i} \quad (4.15) \]

wherein \( k_e \) and \( k_i \) are, respectively, the external and internal mass transfer coefficients to the liquid phase.

Santacesaria showed that the internal mass transfer coefficient varies in time, and the calculation of the rigorous value requires the solution of the complete model equations inside particles (Santacesaria et al., 1982). As an approximation, the mean value estimated by the Equation 4.15 (Glueckauf, 1955) was used:

\[ k_i = \frac{5 D_m / \tau}{r_p} \quad (4.16) \]

The external mass transfer coefficient was estimated by the Wilson and Geankoplis correlation (Ruthven, 1984):

\[ Sh_p = \frac{1.09}{\varepsilon} (Re_p Sc)^{0.33} \quad 0.0015 < Re_p < 55 \quad (4.17) \]

where \( Sh_p \) and \( Re_p \) are, respectively, the Sherwood and Reynolds numbers, relative to particle:

\[ Sh_p = \frac{k_e d_p}{D_m} \quad (4.18) \]

\[ Re_p = \frac{\rho d_p u}{\mu} \quad (4.19) \]

and \( Sc \) is the Schmidt number:

\[ Sc = \frac{\mu}{\rho D_m} \quad (4.20) \]
The system of partial differential equations represented by Equations 4.10 to 4.14 is solved by the method of the lines (MOL) using orthogonal collocation in finite elements, with B-splines as base functions through numerical package PDECOL (Madsen and Sincovec, 1979). Fifty subintervals for spatial discretization along the $\zeta$-axis were used, with two internal collocation points in each subinterval, resulting in 200/400 time dependent ordinary differential equations for adsorption/reaction simulations. For all simulations, a tolerance value EPS equal to $10^{-7}$ was fixed.

4.3 Results and Discussion

4.3.1 Binary adsorption experiments

The breakthrough curves of ethanol, acetal and water were measured in the absence of reaction. The resin was saturated with a certain component A and then the feed concentration of component B was changed stepwise. The adsorption parameters were optimized by minimizing the difference between experimental and theoretical number of moles adsorbed/desorbed for all adsorption experiments:

$$n_{\text{exp}}^{\text{ads}} = Q \int [C_f - C_{\text{ads}}(t)] \, dt$$ \hspace{1cm} (4.21)

$$n_{\text{exp}}^{\text{des}} = Q \int [C_{\text{ads}}(t) - C_f] \, dt$$ \hspace{1cm} (4.22)

$$n_{\text{theo}}^{\text{ads}} = \varepsilon + (1 - \varepsilon) C_f + (1 - \varepsilon) (1 - \varepsilon) \left[ q(C_f) - q(C_0) \right]$$ \hspace{1cm} (4.23)

$$n_{\text{theo}}^{\text{des}} = \varepsilon + (1 - \varepsilon) C_f + (1 - \varepsilon) (1 - \varepsilon) \left[ q(C_0) - q(C_f) \right]$$ \hspace{1cm} (4.24)

$$f_{\text{ob}} = \sum_{k=1}^{N} \left[ \left( n_{\text{exp}}^{\text{ads}} - n_{\text{theo}}^{\text{ads}} \right)^2 + \left( n_{\text{exp}}^{\text{des}} - n_{\text{theo}}^{\text{des}} \right)^2 \right]$$ \hspace{1cm} (4.25)
Then the mass transfer parameters were estimated from the equations above, after the tortuosity being optimized from the experimental data by "best fit" procedure. For all simulations, the mixture viscosity and the diffusivity of each component in the liquid mixture were calculated at each time and at any axial position, and therefore the mass transfer parameters also depend on the liquid composition.

4.3.1.1 Adsorption results for Amberlyst 18

It has to be noticed that the hydrodynamic regime has an important effect on experimental results and the difference in densities of the species (see Table 4.4) can lead to axial backmixing driven by natural convection. The concentration fronts moving within the column are hydrodynamically stable if the component above the front is less dense than the component below the front. In order to obtain reproducibility in the experimental results, the correct flow direction (bottom-up or top-down) has to be chosen. As an example, for a breakthrough experiment where acetal is fed to a column initially saturated with ethanol, the liquid flow direction must be bottom-up, due to the higher density of acetal as compared to the ethanol as shown in Figure 4.4. So, the correct liquid flow direction was considered in all experiments performed.

| Table 4.4 | Adsorption equilibrium isotherms over A18 and component densities at 15 °C. |
|-----------|-----------------------------|---------------------|---------|
| Component | \( Q \) (mol/ l\(_{oa}\)) | \( K \) (mol/ l) | \( \rho \) (g/ l) |
| Ethanol   | 25.9                        | 0.195              | 795     |
| Acetaldehyde | 35.4                     | 0.173              | 784     |
| Acetal    | 15.9                        | 0.071              | 836     |
| Water     | 60.7                        | 0.310              | 1003    |
In order to compare the selectivity of the resin to the components, two different experiments performed in the fixed bed column are illustrated in Figure 4.5a and Figure 4.5b; in both cases, top-down flow was used. In Figure 4.5a, ethanol displaces water, which initially saturates the resin. Since the resin preferentially adsorbs water, the concentration front of ethanol has a dispersive character. In Figure 4.5b, ethanol displaces acetal, that is the weakest adsorbed component, and in this case the breakthrough front of ethanol is self-sharpening.
In a breakthrough experiment, where component A displaces the component B, the total amount of A necessary to saturate the column is given by the product between the volumetric flowrate and the area over the breakthrough curve limited by the feed concentration (Equation 4.23). The product between the flowrate and the area under the elution curve gives the total amount of component B that was initially saturating the column (Equation 4.24). In Figure 4.6a and Figure 4.6b, the concentration history of ethanol and water are shown. In the breakthrough of ethanol, Figure 4.6a, the errors between the experimental and simulated amounts of ethanol fed and water displaced are 1.2 and 0.5 %, respectively. Comparing the amount of ethanol fed in the experiment of Figure 4.6b with the amount of ethanol displaced by water in the experiment of Figure 4.6a, the error obtained is 2.0 %. For water, the error between the amount fed, Figure 4.6a, and the amount eluted, Figure 4.6b, is 2.0 %.

It was not possible to perform the breakthrough experiments with acetaldehyde, because acetaldehyde reacts with itself to give an acetaldehyde trimer (paraldehyde). So the adsorption parameters were determined by optimization of the reaction data.

![Figure 4.6](image)

**Figure 4.6** Breakthrough experiments: outlet concentration of ethanol and water as a function of time.  
*a* water displacing ethanol; $Q = 16.7$ ml/min; bottom-up direction flow.  
*b* ethanol displacing water; $Q = 23.5$ ml/min; top-down direction flow. Points are experimental values and lines are simulated curves.
4.3.1.2 Adsorption results for Amberlyst 15

All binary adsorption experiments performed with Amberlyst 18 (in the previous section) used pure components, for example, pure acetal replacing pure ethanol. In order to obtain more equilibrium points for the adsorption parameters over Amberlyst 15, binary mixtures were used to perform the experiments. Two sizes of columns were tested: one at pilot scale with 86 cm length and the other at laboratory scale with 23 cm length. Table 4.5 summarizes the conditions of the binary adsorption experiments.

<table>
<thead>
<tr>
<th>Adsorption</th>
<th>Run 1</th>
<th>Run 2</th>
<th>Run 3</th>
<th>Run 4</th>
<th>Run 5</th>
<th>Run 6</th>
<th>Run 7</th>
<th>Run 8</th>
<th>Run 9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetal</td>
<td>Acetal</td>
<td>Acetal</td>
<td>Ethanol</td>
<td>Water</td>
<td>Water</td>
<td>Ethanol</td>
<td>Acetal</td>
<td>Acetal</td>
<td>Ethanol</td>
</tr>
<tr>
<td>Desorption</td>
<td>Ethanol</td>
<td>Ethanol</td>
<td>Acetal</td>
<td>Ethanol</td>
<td>Ethanol</td>
<td>Water</td>
<td>Ethanol</td>
<td>Ethanol</td>
<td>Acetal</td>
</tr>
<tr>
<td>L (cm)</td>
<td>86</td>
<td>86</td>
<td>86</td>
<td>86</td>
<td>86</td>
<td>86</td>
<td>23</td>
<td>23</td>
<td>23</td>
</tr>
<tr>
<td>Q (ml/min)</td>
<td>2.6</td>
<td>3.7</td>
<td>3.2</td>
<td>8.0</td>
<td>9.2</td>
<td>9.0</td>
<td>12.0</td>
<td>12.7</td>
<td>12.7</td>
</tr>
<tr>
<td>T (°C)</td>
<td>15.0</td>
<td>15.0</td>
<td>15.0</td>
<td>15.0</td>
<td>15.0</td>
<td>15.0</td>
<td>10.0</td>
<td>10.0</td>
<td>10.0</td>
</tr>
<tr>
<td>C_{A,0} (mol/l)</td>
<td>17.13</td>
<td>9.38</td>
<td>5.09</td>
<td>17.17</td>
<td>15.69</td>
<td>12.89</td>
<td>17.16</td>
<td>8.26</td>
<td>3.13</td>
</tr>
<tr>
<td>C_{B,0} (mol/l)</td>
<td>0.00</td>
<td>3.21</td>
<td>4.98</td>
<td>0.26</td>
<td>5.04</td>
<td>14.05</td>
<td>0.00</td>
<td>3.64</td>
<td>5.75</td>
</tr>
<tr>
<td>C_{A} (mol/l)</td>
<td>9.35</td>
<td>5.08</td>
<td>17.15</td>
<td>15.66</td>
<td>12.94</td>
<td>17.10</td>
<td>8.24</td>
<td>3.12</td>
<td>17.15</td>
</tr>
<tr>
<td>C_{B} (mol/l)</td>
<td>3.21</td>
<td>4.98</td>
<td>0.00</td>
<td>5.13</td>
<td>13.91</td>
<td>0.49</td>
<td>3.66</td>
<td>5.75</td>
<td>0.00</td>
</tr>
</tbody>
</table>

* component A: ethanol; component B: acetal or water.

The optimization of the adsorbed/desorbed number of moles of each component, for all experiments, lead to the adsorption parameters represented in Table 4.6. For these values of adsorption parameters the error percentage between the number of moles adsorbed/desorbed for each component, in all experiments was lower than 2% for the experiments realized at 15 °C and lower than 5% for the experiments performed at 10 °C, as shown in Table 4.7.
Table 4.6  Adsorption equilibrium isotherms over A15.

<table>
<thead>
<tr>
<th>Component</th>
<th>( Q ) (mol/( l_{eq} ))</th>
<th>( K ) (mol/( l ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>14.3</td>
<td>1.43</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>20.1</td>
<td>1.58</td>
</tr>
<tr>
<td>Acetal</td>
<td>11.45</td>
<td>0.09</td>
</tr>
<tr>
<td>Water</td>
<td>44.7</td>
<td>2.01</td>
</tr>
</tbody>
</table>

Table 4.7  Experimental and theoretical values for the number of moles adsorbed/desorbed.

<table>
<thead>
<tr>
<th></th>
<th>Run 1</th>
<th>Run 2</th>
<th>Run 3</th>
<th>Run 4</th>
<th>Run 5</th>
<th>Run 6</th>
<th>Run 7</th>
<th>Run 8</th>
<th>Run 9</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n_{exp} ) (mol)</td>
<td>-1.664</td>
<td>-1.008</td>
<td>2.679</td>
<td>-0.802</td>
<td>-1.035</td>
<td>1.834</td>
<td>-0.709</td>
<td>-0.456</td>
<td>1.159</td>
</tr>
<tr>
<td>( n_{exp} ) (mol)</td>
<td>0.683</td>
<td>0.415</td>
<td>-1.106</td>
<td>2.587</td>
<td>3.338</td>
<td>-5.918</td>
<td>0.291</td>
<td>0.184</td>
<td>-0.474</td>
</tr>
<tr>
<td>( \Delta n_A ) (%)</td>
<td>0.02</td>
<td>1.17</td>
<td>0.01</td>
<td>0.00</td>
<td>1.84</td>
<td>1.09</td>
<td>3.20</td>
<td>4.32</td>
<td>0.07</td>
</tr>
<tr>
<td>( \Delta n_B ) (%)</td>
<td>0.05</td>
<td>0.00</td>
<td>0.75</td>
<td>0.00</td>
<td>1.83</td>
<td>1.16</td>
<td>3.94</td>
<td>4.21</td>
<td>0.90</td>
</tr>
</tbody>
</table>

* component A: ethanol; component B: acetal or water.

The comparison between experimental and simulated results is presented at Figure 4.7, Figure 4.8 and Figure 4.9. It was verified that the mass balance closes for a set of experiments where the column was initially saturated with pure ethanol, and ethanol was replaced by acetal or water, and finally the column was regenerated with pure ethanol. For example, considering the runs 1, 2 and 3, the total amount of ethanol desorbed during runs 1 and 2 was 2.672 moles, that were replaced with 1.098 moles of acetal. During the regeneration step, 2.679 moles of ethanol were needed to displace 1.106 moles of acetal, leading to an error was less than 1 %.
Figure 4.7  Breakthrough experiments performed with ethanol and acetal in the column packed with Amberlyst 15 with 85 cm of length. a) acetal displacing ethanol (run 1). b) acetal displacing ethanol (run 2). c) ethanol displacing acetal (run 3).
Experimental data: (□) ethanol; (◆) acetal. (—) Model results.
Figure 4.8  Breakthrough experiments performed with ethanol and water in the column packed with Amberlyst 15 with 85 cm of length. a) water displacing ethanol (run 4), b) water displacing ethanol (run 5), c) ethanol displacing water (run 6). Experimental data: (□) ethanol; (♣) water; (—) Model results.
Figure 4.9  Breakthrough experiments performed with ethanol and acetal in the column packed with Amberlyst 15 with 23 cm of length. a) acetal displacing ethanol (run 7). b) acetal displacing ethanol (run 8). c) ethanol displacing acetal (run 9).

Experimental data: (□) ethanol; (◆) acetal. (—) Model results.
4.3.2 Kinetic experiments

4.3.2.1 Kinetic results for Amberlyst 18

In a typical reaction experiment, a mixture of ethanol and acetaldehyde is continuously fed to the chromatographic reactor initially saturated with ethanol. Since the feed mixture is less dense than ethanol, the direction flow adopted was from the top to bottom of the column. In the regeneration experiment, ethanol was used as desorbert and the top-down flow was adopted, because the reaction mixture present within the column is heavier than pure ethanol.

Two reaction experiments, where the feed was a mixture of ethanol and acetaldehyde almost at the stoichiometric ratio, and the column was initially saturated with ethanol were performed. The time evolution of the outlet concentrations is shown in Figure 4.10. As the acetaldehyde enters the column, it is adsorbed and reacts with the adsorbed ethanol, in the resin phase. Acetal and water are formed in stoichiometric amounts, but the resin adsorbs preferentially water, whereas acetal is soon desorbed and carried by the fluid stream along the column. Since one of the products is removed from the reaction medium, the acetalization proceeds until consumption of acetaldehyde. This process continues until the resin is completely saturated with acetaldehyde and water. When the resin reaches equilibrium sorption, the selective separation of acetal and water is not possible anymore. Local compositions remain constant and the steady state is achieved, and a reactive mixture at the equilibrium composition constitutes the outlet stream. The difference in the areas below the outlet concentration curves of acetal and water is due to the difference in the adsorbed amounts in the resin, since both products are formed in the same stoichiometric amount. In this case, the model predictions are quite good.

It is interesting to notice that there are two concentration fronts. The first one is a separative front of acetal and ethanol, which comes out between 4 and 11 minutes (Figure 4.10). The second front is a reactive front where acetalization and separation of the products occurs and it comes out at 12 minutes. These phenomena are better understood with the analysis of propagation of these composition fronts. This is only possible by considering the simulated profiles in the same experimental operating conditions of Figure 4.10. Figure 4.11a and Figure 4.11b illustrate the concentration profiles for all species, at times 3 and 9 minutes, respectively,
where four different regions are shown. Zone I corresponds to the steady-state zone and includes the steady-state reaction zone Ia at the entrance of the reactor. This reaction zone corresponds to the consumption of the acetaldehyde until the equilibrium composition ($C=2.9$ mol/l), due to the reaction taking place in a zone where the steady-state has already been achieved. When the equilibrium conversion is reached (at $\zeta=0.25$ and $t=9$ min, in Figure 4.11b), the reactant concentrations do not change until a second transition occurs (zone II). This zone corresponds to the reactive front zone that travels along the column at constant velocity without changing its shape. Although the equilibrium concentration has been reached, in this zone reaction occurs until complete consumption of acetaldehyde since ethanol is in great excess with respect to acetaldehyde and water displaces acetal from the stationary phase. In this zone, a front of water is observed, since the resin is preferentially adsorbing water, while it is produced. That front exhibits constant pattern behaviour, since it propagates along the column at constant velocity without changing its shape. The acetal fluid concentration increases in zone II since acetal is immediately desorbed as it is produced. In zone III, there are only acetal and ethanol and it corresponds to a separative front where acetal is eluting the ethanol initially present in the column (zone IV), as it is illustrated in Figure 4.11a.
Figure 4.11 Internal concentration profiles of all species in fluid phase inside the column, during the reaction experiment of Figure 4.10; (a) \( t = 3 \text{ min} \); (b) \( t = 9 \text{ min} \).

The two adsorptive fronts are shown at Figure 4.12, which represents the concentration profiles for each species at times 1, 3, 6 and 9 minutes. The acetal produced is immediately desorbed, increasing the acetal fluid concentration. After the reactive front zone, there are only acetal and ethanol in a separate front where acetal is eluting the ethanol initially present on the column. Since ethanol has more affinity to the resin than acetal, this front is dispersive, as shown in Figure 4.12a and Figure 4.12c. The other adsorptive front moves together with the reaction front: acetaldehyde and water fronts concentration exhibit constant pattern behaviour, since they propagate along the column at constant velocity (at about 2.2 cm/min for acetaldehyde and at about 1.9 cm/min for water, in Figure 4.12b and Figure 4.12d) without changing its shape. Since water is being preferentially adsorbed by the resin while it is produced, the velocity of the water front is lower than that of the acetaldehyde front.

Finally, the two reaction zones can be better visualized if the calculated reaction rate profiles inside the column at different times are plotted in Figure 4.13. The maximum reaction rate is observed at the entrance of the reactor and then decreases exponentially until \( \zeta \approx 0.4 \) (for \( t = 9 \text{ min} \)) and this zone corresponds to the steady-state reaction zone. The second reaction zone is moving along the column at constant velocity (at about 2 cm/min, in Figure 4.13) and is travelling together with the concentration fronts of acetaldehyde and water, which velocities are \( \approx 2.2 \text{ cm/min} \) and \( \approx 1.9 \text{ cm/min} \), respectively, according to Figure 4.12b and Figure 4.12d.
Figure 4.12  Internal concentration profiles of each species in fluid phase inside the column, at different times, during the reaction experiment of Figure 4.10; (a) ethanol; (b) acetaldehyde; (c) acetal; (d) water.

Figure 4.13  Calculated reaction rate profiles inside the column for the experiment in Figure 4.10 at different times.
In order to assess the mass transfer resistances, the values of the external, internal and global mass transfer coefficients are shown in Table 4.8; it is clear that the internal diffusion is the controlling mechanism.

**Table 4.8** Mass transfer coefficients estimated at 15 °C, at the inlet of the column for a reaction experiment where the feed is a mixture of ethanol and acetaldehyde at stoichiometric ratio and the flowrate is 14.5 ml/min: particle radius $r_p = 239 / 327$ μm.

<table>
<thead>
<tr>
<th>Component</th>
<th>$K_e$ (cm/min)</th>
<th>$K_i$ (cm/min)</th>
<th>$K_L$ (cm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>0.462 / 0.355</td>
<td>0.113 / 0.079</td>
<td>0.041 / 0.029</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>0.468 / 0.359</td>
<td>0.115 / 0.080</td>
<td>0.041 / 0.030</td>
</tr>
<tr>
<td>Acetal</td>
<td>0.323 / 0.248</td>
<td>0.066 / 0.046</td>
<td>0.024 / 0.017</td>
</tr>
<tr>
<td>Water</td>
<td>0.739 / 0.569</td>
<td>0.228 / 0.159</td>
<td>0.080 / 0.057</td>
</tr>
</tbody>
</table>

In Figure 4.14, the comparison between the bulk and the average particle concentrations is shown, for the run of Figure 4.10, at time 3 minutes. At the entrance of the reactor, ethanol and acetaldehyde being consumed by reaction inside the particle and since the mass transfer is not sufficiently high, the average particle concentration is lower than the bulk concentration.

**Figure 4.14** Calculated bulk concentration (dashed line) and average particle concentration (continuous line) profiles inside the column for the run shown in Figure 4.10, at 3min.
Two reaction experiments, Figure 4.15a and Figure 4.15b, were realized with a bigger pellet diameter \(d_p = 654 \, \mu\text{m}\) at different flowrate and temperature, in order to validate the mass transfer parameters estimation. The mass transfer resistance increases (see Table 4.8) and the agreement between experimental and simulated results is quite good. The non-ideality of the system is observed by analysing the activities coefficients calculated by the UNIFAC method. In a typical experiment, the activity coefficients ranges are: [1.01-1.10] for ethanol, [1.163-1.32] for acetaldehyde, [0.66-1.53] for acetal and [1.32-1.91] for water.

**Figure 4.15** Concentration histories in a fixed bed adsorptive reactor, initially saturated with ethanol and then fed with ethanol and acetaldehyde \((C_{\text{initial}} = 12.3 \, \text{mol/l} \text{ and } C_{\text{initial}} = 5.5 \, \text{mol/l})\), packed with Amberlyst 18 with particle diameter \(d_p = 654 \, \mu\text{m}\). Experimental conditions: a) \(Q = 20.5 \, \text{ml/min}, T = 15 \, ^\circ\text{C}\). b) \(Q = 13.5 \, \text{ml/min}, T = 10 \, ^\circ\text{C}\).

After the steady-state is achieved, and before starting a new reaction experiment, it is necessary to regenerate the column. This step requires the use of a solvent to remove the adsorbed species. Ethanol was used as desorbent, although it is possible to use acetaldehyde to regenerate the resin. In Figure 4.16, the regeneration step relative to the run represented in Figure 4.10 is shown. Acetal and acetaldehyde are the weakly adsorbed species and are the first to be desorbed. Water is strongly adsorbed and has much more affinity to the resin than ethanol, so large amounts of ethanol are needed to complete displacement of water. Again, in the regeneration step, the agreement between model predictions and experimental results is satisfactory.
Figure 4.16 Concentration histories in the regeneration step of a fixed bed adsorptive reactor. The initial profiles in the bed are those at the final steady state of the run in Figure 4.10. Experimental conditions: \( Q = 14.5 \text{ ml/min} \), \( C_{\text{in}} = 17.0 \text{ mol/l} \) and \( C_{\text{bo}} = 0.0 \text{ mol/l} \).

4.3.2.2 Kinetic results for Amberlyst 15

In order to verify if the rate law obtained with Amberlyst 18 fits the kinetic data acquired with Amberlyst 15, two kinetic experiments were carried out in a batch reactor (see Figure 4.17). The simulations were performed with the pore diffusion model, using the Amberlyst 18 kinetic parameters. The catalysis with A15 is slightly slower than that with A18. Since both catalysts have approximately the same concentration of acid sites, the small deviation could be explained by the mass transfer controlling mechanism inside the particle. The model used in the prediction of the kinetic curves on A15 considers pore diffusion, neglecting the surface diffusion. Since the resin it is an agglomerate of small microspheres, it is possible that surface diffusion occurs. The average pore diameter of A15 is half of A18 and the surface area is 150% higher; this indicates that A15 has more microspheres with smaller diameter than A18. Because of this, the surface diffusion resistance could be more significant in the overall mass transfer mechanism inside the A15 particle than at A18. Anyway, the simulated curves predict satisfactory the Amberlyst 15 kinetic experimental results and the A18 kinetic parameters could be used to describe the adsorptive fixed bed reactor packed with A15. Figure 4.18 shows the production and regeneration steps for a typical experiment performed in a laboratory scale column, packed with A15. The agreement between experimental and simulated results is quite good.
To ensure that the behaviour of the fixed bed adsorptive reactor is well described for different range of compositions, a kinetic experiment was performed in a pilot scale column packed with A15, initially saturated with a mixture of ethanol and water. Then, a mixture containing ethanol, acetaldehyde and water was fed to the column until the equilibrium has been reached (Figure 4.19a) and the regeneration of the resin was performed with pure ethanol (Figure
4.19b). All adsorptive and reactive concentration fronts are well predicted by the proposed model.

![Graphs showing concentration histories](image)

**Figure 4.19** Concentration histories in a fixed bed adsorptive reactor packed with Amberlyst 15 with particle diameter $d_p = 700 \mu m$ and 86 cm of length, at 15°C. Experimental conditions: a) Production step: column initially saturated with a mixture of ethanol/water and then fed with a mixture of ethanol/acetaldehyde/water ($C_{A0} = 10.6$ mol/l, $C_{B0} = 5.2$ mol/l and $C_{D0} = 5.2$ mol/l) at $Q = 9.2$ ml/min. b) Regeneration step with pure ethanol at $Q = 9.0$ ml/min.

### 4.4 Conclusions

The dynamic behaviour of fixed bed adsorptive reactor for the synthesis of diethylacetal, using acid resin catalysts (Amberlyst 18 and Amberlyst 15) was studied.

The adsorption data were obtained by performing dynamic binary adsorption experiments, in the absence of reaction, at 288 K, in a laboratory scale column. The adsorption parameters were optimized by minimizing the difference between experimental and theoretical number of moles adsorbed/desorbed for all adsorption experiments. It was verified that the mass balance closes for a set of experiments were the column was initially saturated with pure ethanol, ethanol was replaced by acetal or water, and finally the column was regenerated with pure ethanol. Comparing the adsorption parameters obtained for each resin is shown in Table 4.9. Amberlyst 18 has higher adsorption capacity than Amberlyst 15, but the adsorption equilibrium constants over A18 are smaller than those over A15. The adsorption parameters obtained for A15 are more accurate since the experiments were performed with a HPLC pump, while the experiments over A18 were carried out with a peristaltic pump. For A15,
binary mixtures were used for each pair of components, allowing the determination of more equilibrium adsorption points and therefore to find the best set of adsorption parameters, since the optimization process was very affected by the initial guess and leads to several local minima.

<table>
<thead>
<tr>
<th>Component</th>
<th>Amberlyst 18</th>
<th>Amberlyst 15</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$Q$ (mol/ $l_{ad}$)</td>
<td>$K$ (mol/ l)</td>
</tr>
<tr>
<td>Ethanol</td>
<td>25.9</td>
<td>0.195</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>35.4</td>
<td>0.173</td>
</tr>
<tr>
<td>Acetal</td>
<td>15.9</td>
<td>0.071</td>
</tr>
<tr>
<td>Water</td>
<td>60.7</td>
<td>0.310</td>
</tr>
</tbody>
</table>

A mathematical model for the adsorptive reactor was developed, including axial dispersion, mass-transfer resistances, constant temperature, multicomponent Langmuir adsorption isotherms and reaction rate expressed in terms of activities. The theoretical model considers two mass transfer resistances in series: the external film and the diffusion inside the pores. The internal mass transfer coefficients were estimated by the Glueckauf approximating equation and the Wilson and Geankoplis correlation was used to estimate the external mass transfer coefficients. Model equations were solved by orthogonal collocation by finite elements, using the measured model parameters. The model was validated by comparison with the experimental results obtained for the production and regeneration steps. It was observed a quite good agreement between model predictions and experimental data for both catalysts. The model is able to predict the response of adsorptive reactors with different lengths for a wide range of initial/feed compositions. The model developed as well as the reaction and adsorption data for Amberlyst 15 will be applied in the analysis of the Simulated Moving Bed Reactor.
4.5 Notation

\( a \) - liquid phase activity

\( C \) - liquid phase concentration (mol/m\(^3\))

\( C_T \) - total liquid phase concentration (mol/m\(^3\))

\( \overline{C}_p \) - average liquid phase concentration inside the particle (mol/m\(^3\))

\( d_p \) - particle diameter (m)

\( D_a \) - Damköhler number

\( D_{ax} \) - axial dispersion (m\(^2\)/s)

\( D_m \) - molecular diffusivity (m\(^2\)/s)

\( D_{Am} \) - diffusion coefficient for a dilute solute \( \mathcal{A} \) into a mixture (m\(^2\)/s)

\( K \) - Langmuir equilibrium parameter (m\(^3\)/mol)

\( k_i \) - internal mass transfer coefficient (m/s)

\( k_e \) - external mass transfer coefficient (m/s)

\( k_c \) - kinetic constant (mol/kg\(_{res}\).s)

\( K_{eq} \) - equilibrium constant

\( K_r \) - adsorption constant in equation 6

\( K_g \) - global mass transfer coefficient (m/s)

\( K' \) - number of mass transfer units

\( l \) - bed length (m)

\( Pe \) - Peclet number

\( q \) - solid phase concentration in equilibrium with the fluid concentration inside the particle (mol/m\(^3\)\(_{res}\))
\( Q \) - adsorption capacity (mol/m\(^3\)_{res})

\( \mathfrak{R}^p \) - reaction rate relative to fluid concentration inside the particle (mol/kg_{res.s})

\( r_p \) - particle radius (m)

\( Re_p \) - Reynolds number relative to particle

\( Sh_p \) - Sherwood number relative to particle

\( Sc \) - Schmidt number

\( T \) - temperature (K)

\( t \) - time (s)

\( t_a \) - stoichiometric time defined in equation 20 (s)

\( u \) - superficial velocity (m/s)

\( V_m \) - molar volume in the liquid phase (m\(^3\)/mol)

\( x \) - liquid phase molar fraction

\( z \) - axial coordinate (m)

**Greek letters**

\( \varepsilon \) - bulk porosity

\( \varepsilon_p \) - porosity of pellet

\( \gamma \) - activity coefficient

\( \mu \) - fluid viscosity (kg/m.s)

\( v \) - stoichiometric coefficient

\( \rho \) - liquid density (kg/m\(^3\))

\( \rho_b \) - bulk density (kg_{res}/m\(^3\))

\( \theta \) - dimensionless time coordinate
\[ \tau \text{ - tortuosity} \]
\[ \zeta \text{ - dimensionless axial coordinate} \]

**Subscripts**

\[ i \text{ - relative to component } i (i= A, B, C, D) \]
\[ F \text{ - relative to the feed} \]
\[ 0 \text{ - relative to initial conditions} \]

**Superscripts**

\[ p \text{ - relative to particle} \]

### 4.6 References


5. The Simulated Moving Bed Reactor

Diethylacetal was produced and separated from the reactive mixture in a SMBR pilot unit Licosep 12-26 (Novasep, France) with twelve columns packed with the acid resin Amberlyst 15 (Rohm and Haas). Experimental results are described by the mathematical model based on the TMBR strategy. The influence of feed composition, mass transfer, switching time in the SMBR performance is studied. The performance criteria were the raffinate and extract purities, productivity, solvent consumption and acetaldehyde conversion. The concept of separation region is used the operating conditions of existing SMBR equipment applied to the production of diethylacetal.

5.1 Introduction

The combination of a chemical or biochemical reaction and a chromatographic separation process in a single unit operation may improve reaction conversion as well as the separation efficiency. Besides, performing two unit operations in a single piece of equipment may reduce capital costs. For the last thirty years, the concept of chromatographic reactors has been extended to continuous processes in order to benefit from those features as enhanced productivity and decreased solvent consumption. Continuous mode of operation has been achieved by means of moving the adsorbent or simulating its motion. This is possible by such equipment configurations as simulated moving bed (Hashimoto et al., 1983), countercurrent moving-bed (Fish and Carr, 1989; Petroulas et al., 1985), rotating annular chromatograph (Sardini and Barker, 1993) and semicontinuous countercurrent chromatographic reactor-separator (Ganetsos et al., 1993). Perhaps one of the most interesting physical implementations
of a chromatographic reactor-separator is the Simulated Moving Bed Reactor (SMBR). The countercurrent motion of the stationary phase is simulated by applying an intelligent scheme of valve switchings on a set of fixed beds. In such a reactor, reaction occurs either in the mobile or stationary phase. In the latter, the catalyst is supported or immobilised in the solid adsorbent, which promotes the separation of the reaction products. In the case of reactions catalyzed by acid sites, the use of acid ion exchange resins, as Amberlyst 15, is very interesting since the resin acts both as catalyst as well as a selective adsorbent. Moreover, since the acetalization is chemical equilibrium controlled, the removal of the reaction products leads to reactants conversion above the equilibrium limit. Because of this the diethylacetal production and separation in a SMBR seems to be a feasible process.

5.1.1 The Simulated Moving Bed concept

The Simulated Moving Bed (SMB) is a continuous chromatographic counter-current process developed in 1960s by Universal Oil Products (Broughton and Gerhold, 1961). The first patent was licensed as the SORBEX process and issued for a number of large-scale separations in the petrochemical and sugar industries. Nowadays, the SMB technology has a wide range of applications, including the recently developed laboratory-scale pharmaceutical, fine chemistry and bio-separations. The SMB is based on the principles of True Moving Bed (TMB) concept. In the TMB (Figure 5.1) the liquid and the solid phases flow in opposite direction. The inlet (feed and eluent) and outlet (extract and raffinate) ports are fixed along the unit. According to the position of the inlet and outlet streams, four different sections could be distinguished: section I located between the eluent and extract streams; section II between the extract and feed streams; section III placed between feed and raffinate streams; section IV located between raffinate and eluent streams.

The major problem of TMB operation connected with the solid movement was overcome by the introduction of the SMB technology. The SMB unit consists of a set of inter-connected columns in series; the countercurrent flow of solid and liquid phases is simulated by the periodic shifting of inlets and outlets in the direction of the fluid flow (Figure 5.2).
Due to the switch of the inlet and outlet lines, each column changes the boundary conditions after the end of each switching time interval, depending on its location (section). This time dependence of the boundary conditions leads to cyclic steady-state for the SMB system, instead of a real steady-state present in the TMB approach; it means that, after the cyclic steady-state is achieved, the internal concentration profiles vary along the switch time interval, but they are identical at the same time for two consecutive cycles. The cyclic steady-state of the SMB is equivalent to the real steady-state of the TMB for high degree of subdivisions of the SMB adsorbent bed is used (Storti et al., 1988; Pais et al., 1998); hence, it is better to simulate and obtain the optimum operating conditions using the TMB model since it requires lower computing time. The cyclic behaviour of the SMB can be predicted from the steady-state model of the TMB, by considering the relation between the interstitial solid velocity $U_s$ and
the switching time \( t^* \) in SMB operation, i.e.:

\[
U_s = \frac{L_c}{t^*}
\]  

(5.1)

where \( L_c \) is the column length.

The equivalence between the SMB and the TMB systems is made by keeping constant the net-flow of the liquid relative to the solid:

\[
u_{j}^{SMB} = u_{j}^{TMB} + U_s
\]

(5.2)

where \( u_j \) is the interstitial fluid velocity in the \( j \) section of the moving bed. The ratio between the liquid and solid interstitial velocities in each section is given by:

\[
\gamma_j = \frac{u_j^{TMB}}{U_s}
\]

(5.3)

The successful design of SMB involves the right choice of the operation conditions (switching time period and flow rates in each section of the unit). The net flowrate has to be selected in each section in order to ensure the regeneration of adsorbent in section I, the desorption of the less adsorbed component in section II, the adsorption of the more adsorbed component in section III and the regeneration of the eluent in section IV. These conditions will guarantee the separation, since the more retained component, B, moves to the extract port with the solid phase and the less retained component, A, moves to raffinate port with the liquid phase. Since it is not adequate to search for suitable SMB operating conditions by trial and error procedures, great progress has been made by using the equilibrium model applied to the equivalent TMB, where axial mixing and mass transfer resistances are neglected and linear adsorption equilibrium is assumed (Ching and Ruthven, 1985; Nicoud, 1992). The analysis of the equivalent representation of a true moving bed under an equilibrium model leads to explicit inequality relations between liquid and solid interstitial velocities in the four TMB sections \((\gamma_j)\):

\[
K_B < \gamma_1 < \infty
\]

(5.4)

\[
K_A < \gamma_2 < \gamma_3 < K_B
\]

(5.5)

\[
0 < \gamma_4 < K_A
\]

(5.6)

where \( K_A \) and \( K_B \) are the adsorption equilibrium constants for the less and more retained components, respectively. With the equilibrium theory, it is possible to set the net flows in section I and IV that ensure the solid and eluent regeneration, respectively. Therefore the
design of the SMB consists in the determination of the set of pairs of net-flows in sections II and III that accomplish the desired separation. These space-operating parameters lead to the separation region (Triangle Theory) as shown in Figure 5.3.

![Figure 5.3 Separation region for the complete separation under the equilibrium theory.](image)

The equilibrium models are not able to link the product purities with the zone flowrates, zone lengths and mass transfer parameters; therefore, the resulting design can only serve as an initial guess for the SMB optimization (Ma and Wang, 1997). The suitable operating conditions (flowrates, switching time, feed concentration, etc.) and/or geometrical parameters (column dimensions, extra-column piping, etc.) could be obtained by use of a complete model that includes the mass transfer effects. The introduction of mass-transfer effects into SMB design described by the LDF approximation have shown that the separation region was considerably reduced when mass-transfer resistances are significant (Pais et al, 1997). Latter the concept of "separation region" was extended to "separation volumes", by accounting the effect of the net-flow in section I or IV on the separation regions in presence of mass-transfer resistance (Azevedo and Rodrigues, 1999). The constraints on zone I, II and III are more restrictive than those derived from equilibrium model, whereas the constraint on zone IV was less affected (Azevedo and Rodrigues, 1999; Minceva and Rodrigues, 2002).

Recently, the concept of the SMB has also been applied successfully to combine a reaction with chromatographic separation (Kawase et al, 1996; Mazzotti et al, 1996).
5.1.2 The SMB Reactor

Commonly, chemical processes were designed with reaction and separation units in series. Process integration by combining both steps of reaction and separation in one single unit may significantly reduce the costs for the whole process. Besides reactive distillation, reactive extraction or membrane reactors, the interconnection of chemical or biochemical reaction with chromatographic separation forms an attractive integrated process for producing high-purity products. For reactions in series or in parallel, it may be possible the selective separation of desired intermediate species. In addition, the SMBR also enhances the conversion, yield, selectivity and purity of the desired product beyond the levels predicted by thermodynamics for an equilibrium-limited reversible reaction, since the products are continuously removed from the reaction zone.

The first applications of the SMBR were for gas phase as the hydrogenation of 1,3,5-trimethylbenzene (Ray et al., 1994) and the oxidative coupling of methane (Tonkovich and Carr, 1994). Several applications for the liquid phase are, for biochemical reactions, the isomerization of glucose by action of glucose isomerase (Hashimoto et al., 1983), the inversion of sucrose by action of invertase (Meurer et al., 1996; Azevedo and Rodrigues, 2001) and the production of lactosucrose by action of b-fructofuranosidase (Kawase et al., 2001). For chemical reactions major examples are reversible reactions catalyzed by ion exchange resins. Examples are the esterification of acetic acid with b-phenyl alcohol (Kawase et al., 1996), the ethyl acetate synthesis on Amberlyst 15 (Mazzotti et al., 1996; Migliorini et al., 1999), the synthesis of bisphenol A from acetone and phenol (Kawase et al., 1999), esterification of acetic acid with methanol (Lode et al., 2001), synthesis of MTBE (Zhang et al., 2001). Another example is the dismutation of toluene into benzene and xylenes (Hotier et al., 2002).

The design and optimization of SMBR to carry out simultaneous and continuous reaction and separation are essential to define the feasibility of the process at industrial scale. The number of publications focusing on the design of non-reactive SMB’s is quite large. Nevertheless, the same may not be said of SMBR design (Fricke et al., 1999b; Migliorini et al., 1999), and about the optimization of the SMBR process (Dünnebier et al., 2000; Zhang et al., 2002) The design will define geometric and operating parameters that should lead not only to product separation but also to high reactant conversion. In Table 5.1 a list of recent publications for reversible reactions catalyzed by ion exchange resins and a summary of the main results are presented.
### Table 5.1 Recent publications on SMBR design, applied to reversible reactions catalyzed by resins.

<table>
<thead>
<tr>
<th>Reference/System</th>
<th>Results/Conclusions</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Kawase et al, 1999)</td>
<td>The influence of the secondary product (water) on the conversion of the limiting reactant (acetone); as the liquid-solid velocity ratio at section III decreases, water is more effectively removed from the reaction medium and the acetone conversion increases. But this leads to a higher solvent consumption in order to regenerate the resin, in section I.</td>
</tr>
<tr>
<td>Product: Bisphenol A</td>
<td></td>
</tr>
<tr>
<td>Resin: Amberlyst 31</td>
<td></td>
</tr>
<tr>
<td>(Migliorini et al, 1999)</td>
<td>The region in the operating parameter space, where complete conversion of the limiting reactant and complete separation of the products is achieved, is reported. The influence of the feed composition on the separation region is analysed.</td>
</tr>
<tr>
<td>Product: Ether Acetate</td>
<td></td>
</tr>
<tr>
<td>Resin: Amberlyst 15</td>
<td></td>
</tr>
<tr>
<td>(Fricke et al, 1999a)</td>
<td>The effect of process parameters on the SMBR performance for a reversible reaction of type A→B+C has been analysed. The maximum feed flowrate that can be used without falling short of the desired product purity and the specific desorbent consumption (Q_{des}/Q_i) were the performance criteria selected. Increasing the kinetic constant as well as the equilibrium constant, the value of the maximum feed increases and the specific desorbent consumption is reduced. It is pointed out that for adsorption limited by the mass transfer kinetics, the reactant has to be significantly less adsorbed than the more adsorbed product, but should adsorb more than the less adsorbed product.</td>
</tr>
<tr>
<td>Product: not specified</td>
<td></td>
</tr>
<tr>
<td>Resin: not specified</td>
<td></td>
</tr>
<tr>
<td>(Lode et al, 2001)</td>
<td>The concept of separation region for an SMBR is introduced for a reversible reaction of type A↔B+C. It is considered that the adsorptivity of the reactant is intermediate between those of the two products. The triangle region corresponding to the separation of B and C in a SMB unit is split into three different sub-regions, by representing the Henry constant of the reactant (Figure 5.4). The esterification of acetic acid with methanol is a bimolecular reaction of type A+B→C+D. This system is analogous to the previous one (A↔B+C) when one of the reactants is used as desorbent and therefore tends to be in excess in respect to the other. The influence of the feed composition, switching time and unit configuration in the separation region is studied.</td>
</tr>
<tr>
<td>Product: Methyl Acetate</td>
<td></td>
</tr>
<tr>
<td>Resin: Amberlyst 15</td>
<td></td>
</tr>
<tr>
<td>(Zhang et al, 2001)</td>
<td>The effects of the switching time, feed, solvent and products flow rates and the number of columns on the yield, selectivity and purity of the desired product (MTBE) and the conversion of the limiting reactant (TBA) were studied. The sensitivity study reveals that is not possible to maximize the yield and selectivity of MTBE simultaneously, as some of the operating parameters act in conflicting manner.</td>
</tr>
<tr>
<td>Product: MTBE</td>
<td></td>
</tr>
<tr>
<td>Resin: Amberlyst 15</td>
<td></td>
</tr>
<tr>
<td>(Fricke and Schmidtt-Traub, 2003)</td>
<td>The development of a new method to estimate the effect of the reaction on the design of a SMBR.</td>
</tr>
<tr>
<td>Product: not specified</td>
<td></td>
</tr>
<tr>
<td>Resin: not specified</td>
<td></td>
</tr>
</tbody>
</table>
In this chapter, the feasibility of the process of diethylacetal synthesis is proved experimentally using a SMBR pilot unit Licosep 12-26 (Novasep, France) with twelve columns packed with the acid resin Amberlyst 15 (Rohm and Haas). A mathematical model for a SMBR unit based on the TMBR strategy, using a suitable representation of the experimentally determined reaction kinetics and multicomponent adsorption equilibria, is developed and validated. The SMBR process is investigated through numerical simulation, in order to identify the governing design parameters.

5.2 The SMBR Unit

5.2.1 Experimental Apparatus

All SMBR experiments described in this thesis were performed in a pilot unit LICOSEP 12 26 by Novasep (Vandoeuvre-dès-Nancy, France). Twelve columns Superformance SP 230 x 26 (length x i.d., mm), by Götee Labortechnik (Mühlral, Germany), packed with the acid resin Amberlyst 15 (Rohm and Haas) were connected to the SMBR pilot unit. Each column is
jacketed to ensure temperature control and the jackets are connected to one another by silicone hoses and to a thermostat bath (Lauda). The operating temperature was 10°C. Between every two columns there is a four-port valve actuated by the control system. When required, the valves allow either pumping of feed/eluent into the system or withdrawal of extract/raffinate streams. Each of the inlet (feed and eluent) and outlet (extract and raffinate) streams is pumped by means of HPLC pumps. The recycling pump is a positive displacement three-head membrane pump (Milton Roy, Pont St. Pierre, France), which may deliver flowrates as low as 20 ml/min up to 120 ml/min. The other flows (desorbent, extract, feed and raffinate) are controlled by four Merck–Hitachi pumps (Merck–Hitachi models L-6000 and L-6200, Darmstadt, Germany), connected to computer via RS-232. The maximum flow-rate in the desorbed and extract pumps is 30 ml/min, while in the feed and raffinate pumps is 10 ml/min. The maximum allowable pressure is 60 bar. Between the twelfth and the first column there is a six-port valve, which is used to collect samples for internal concentration profile measurements. Figure 5.5 shows a side view of the pilot unit, where six columns are placed. The other six columns used in most experiments are placed on the other side. The equipment has its own process control software, which is able to accomplish the following tasks:

- Switch the inlet and outlet streams at regular time intervals (as assigned by user) by opening and closing on-off pneumatic valves;
- Keep steady and constant section flowrates as assigned;
- Keep suction pressure at the recycling pump around a set point assigned by the user (usually 1.5 bar).

All piping between columns consists of 1/16” i.d. tubing in order to minimize the dead volumes. The dead volume represented by the recycling pump accounts for 21 cm³. Its adverse effects on the unit performance is overcome by desynchronising the switches of the ports which are about to or have been shifted across the pump at each cycle. In such cases, the switch is delayed \( t_d \) minutes, as calculated from the following equation:

\[
  t_d (\text{min}) = \frac{21}{Q (\text{ml/min})} \quad \text{where} \quad \bar{Q} = \frac{\sum Q_i}{4}
\]
This feature is also built in the control software, so that the behaviour of the unit is identical to that of an ideal SMB with no dead volumes.

![Image of SMB pilot unit](image)

*Figure 5.5 SMB pilot unit LICOSSEP 12-26 at LSRE.*

Each of the twelve columns was subjected to tracer experiments in order to verify the homogeneity of packing and determine bed porosity under the flowrates of 15-40 ml/min. As described in the previous chapter, the bed porosity and the Peclet number were calculated from the stoichiometric time and the second moment of the obtained experimental curves. By calculating the second moment of the experimental curves, an average Peclet number was obtained for the range of flow rates to be used in the fixed bed experiments. The mean value obtained for porosity was 0.40. It was verified that the axial mixing did not vary significantly from column to column and in the flow range studied. The mean value obtained for the Peclet number was \( Pe = 290 \). Figure 5.6 shows the obtained experimental pulse for one of the
columns as compared to the simulation results using $Pe = 300$. The columns were all assumed to be homogeneously packed with axial mixing accounted for by assigning $Pe = 300$ in the range of flowrates to be used in the SMB. The characteristics of the SMB columns used in the simulations are presented at Table 5.2.

Table 5.2 Characteristics of the simulated moving bed columns.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length ($L$)</td>
<td>23 cm</td>
</tr>
<tr>
<td>Internal diameter</td>
<td>2.6 cm</td>
</tr>
<tr>
<td>Radius of the particle ($r_p$)</td>
<td>400 μm</td>
</tr>
<tr>
<td>External void fraction ($\varepsilon$)</td>
<td>0.40</td>
</tr>
<tr>
<td>Internal void fraction ($\varepsilon_i$)</td>
<td>0.40</td>
</tr>
<tr>
<td>Peclet number</td>
<td>300</td>
</tr>
<tr>
<td>Bulk density ($\rho_s$)</td>
<td>390 kg/m³</td>
</tr>
</tbody>
</table>

Figure 5.6 Tracer experiments performed with one SMB column, using a blue dextran solution. Points are experimental values and lines are simulated curves.
5.2.2 Mathematical Model

As stated before in the beginning of this section, the SMBR modelling strategy is more precise than the TMBR model since it depicts the actual physical equipment operation. It allows the visualization of the axial movement of concentration profiles and the variations in extract and raffinate concentrations within a period. However, it demands considerably higher computational effort than the TMBR strategy, especially when a large number of columns are involved. For this case the cyclic behaviour of the SMBR can be predicted from the steady-state model of the TMBR with good accuracy. Therefore, the mathematical model used to describe the SMBR performance is based on the TMBR strategy considering axial dispersion flow for the bulk fluid phase, plug flow for the solid phase, linear driving force (LDF) for the particle mass transfer rate and multicomponent adsorption equilibria. Constant column length and packing porosity are also assumed. The model equations are

Bulk fluid mass balance to component $i$ at section $j$:

$$
\varepsilon \frac{\partial C_y}{\partial t} + \varepsilon u_j \frac{\partial C_y}{\partial z} + (1 - \varepsilon) \frac{3}{r_p} K_{L,i} \left( C_y - \bar{C}_{p,y} \right) = D_{a,i,j} \frac{\partial^2 C_y}{\partial z^2} \tag{5.7}
$$

where $C_y$ and $\bar{C}_{p,y}$ are the bulk and average particle concentrations at fluid phase of species $i$ in section $j$ of the TMBR, respectively, $K_{L,i}$ is the global mass transfer coefficient of component $i$, $\varepsilon$ is the bulk porosity, $t$ is the time variable, $z$ is the axial coordinate, $D_{a,i,j}$ and $u_j$ are the axial dispersion coefficient and the interstitial velocity at section $j$, respectively, and $r_p$ is the particle diameter.

Pellet mass balance to component $i$ at section $j$:

$$
U_s \left[ \varepsilon_p \frac{\partial \bar{C}_{p,y}}{\partial z} + (1 - \varepsilon_p) \frac{\partial q_y}{\partial z} \right] + \frac{3}{r_p} K_{L,i} \left( C_y - \bar{C}_{p,y} \right) = \varepsilon_p \frac{\partial \bar{C}_{p,y}}{\partial t} + (1 - \varepsilon_p) \frac{\partial q_y}{\partial t} - V_i \rho_p \eta \mathcal{R} \tag{5.59}
$$

where $q_y$ is the adsorbed phase concentration of species $i$ in section $j$ in equilibrium with $\bar{C}_{p,y}$, $U_s$ is the solid velocity and $\varepsilon_p$ is the particle porosity, $V_i$ is the stoichiometric coefficient of component $i$, $\rho_p$ is the particle density, $\eta$ is the effectiveness factor of the catalyst and $\mathcal{R}$ is the rate of the chemical reaction relative to the bulk liquid phase.
Initial and Danckwerts boundary conditions:

\[ t = 0 \quad C_{y} = \overline{C}_{y,p,0} = C_{y,0} \]  
(5.8)

\[ z = 0 \quad u_{j} C_{y} - D_{m,j} \frac{\partial C_{y}}{\partial z} \bigg|_{z=0} = u_{j} C_{y,F} \]  
(5.9)

\[ z = L_{j} \quad \frac{\partial C_{y}}{\partial z} \bigg|_{z=L_{j}} = 0 \quad \text{and} \quad \overline{C}_{j,y,L_{j}} = \overline{C}_{j,y+1,0} \]  
(5.10)

where subscripts \( F \) and \( 0 \) refer to the feed and initial states, respectively.

Multicomponent adsorption equilibrium isotherm:

\[ q_{ij} = \frac{Q_{adh,i} K_{i} \overline{C}_{p,ij}}{1 + \sum_{i=1}^{k} K_{i} \overline{C}_{p,ij}} \]  
(5.11)

where \( Q_{adh,i} \) and \( k_{i} \) represent the total molar capacity per unit volume of resin and the equilibrium constant for component \( i \), respectively.

Mass balances at the nodes of the inlet and outlet lines of the TMBR

**Eluent node:**

\[ C_{y+1,0} = \frac{u_{4}}{u_{1}} C_{y,L_{j}} \]  
(5.12)

**Extract node:**

\[ C_{y+1,0} = C_{y,L_{j}} \]  
(5.13)

**Feed node:**

\[ C_{y+1,0} = \frac{u_{2}}{u_{3}} C_{y,L_{j}} + \frac{u_{F}}{u_{3}} C_{i,F} \]  
(5.14)

**Raffinate node:**

\[ C_{y+1,0} = C_{y} \]  
(5.15)

with the relations between fluid velocities in the four zones of the TMBR:

\[ u_{1} = u_{4} + u_{P}, \quad u_{2} = u_{1} - u_{X}, \quad u_{3} = u_{2} + u_{F}, \quad u_{4} = u_{3} - u_{R} \]  
(5.16)

where \( u_{1}, u_{2}, u_{3} \) and \( u_{4} \) are the fluid velocities at sections I, II, III and IV, respectively. The subscripts \( D, \ X, \ F \) and \( R \) refer to the desorbent, extract, feed and raffinate streams, respectively.
**SMBR performance criteria**

The SMBR process performance will be evaluated accordingly the following criteria:

**Raffinate Purity (%)**:

\[
PUR = \frac{C_{C,R}}{C_{B,R} + C_{C,R} + C_{D,R}} \times 100
\]  
(5.17)

**Extract Purity (%)**:

\[
UX = \frac{C_{D,X}}{C_{B,X} + C_{C,X} + C_{D,X}} \times 100
\]  
(5.18)

**Acetaldehyde Conversion (%)**:

\[
X = 1 - \frac{Q_A C_{B,X} + Q_R C_{B,R}}{Q_C C_{B,F}}
\]  
(5.19)

**Raffinate Productivity (mol/min/l)**:

\[
PR = \frac{Q_R C_{C,R}}{(1 - e) V_{ml}}
\]  
(5.20)

**Desorbent consumption (l/mol)**:

\[
DC = \frac{\left[ Q_D C_{A,D} + Q_L (C_{A,F} - 2 X C_{B,F}) \right] V_{ml}}{Q_R C_{C,R}}
\]  
(5.21)

The productivity is defined just for the raffinate stream, since acetal is the desired product. The definition of desorbent consumption just takes into consideration the amount of ethanol that is used as desorbent, and not the ethanol consumed in the reaction.

Model equations were numerically solved by using the gPROMS- general PROCess Modelling System (gPROMS, 2003), a software package for modelling and simulation of processes with both discrete and continuous as well as lumped and distributed characteristics. The mathematical model involves a system of partial and algebraic equations (PDAEs). Third order orthogonal collocation method in finite elements (OCFEM) was used in the discretisation of axial domain. Twenty equal elements per section with two collocation points in each element were used. The system of ordinary differential and algebraic equation (ODAEs) was integrated over time using the DASOLV integrator implement in gPROMS. For all simulations was fixed a tolerance value equal to $10^{-5}$. 
5.3 Results and Discussion

The SMBR experiments were performed under conditions of incomplete adsorbent regeneration in section 1, due to equipment specifications. The recycle pump was operated at the minimum flow-rate (20 ml/min). For the desorbent the maximum flow-rate (30 ml/min) was not used, since the system was not stable.

The choice of the feed composition was limited by cavitation problems in the feed pump. It was preferable to use pure acetaldehyde in order to achieve higher productivity and lower desorbent consumption. A test with pure acetaldehyde feed stream was performed, but acetaldehyde evaporation occurred in the feed pump. Pure ethanol was used as desorbent.

Three experiments of diethylacetal synthesis were carried out at 10°C in the SMBR unit, with 3 columns per section. The feed composition was a mixture of ethanol and acetaldehyde, with 51% acetaldehyde molar fraction \( C_{A,F} = 8.57 \text{ mol/l}, \ C_{B,F} = 8.96 \text{ mol/l} \). The flow rates of feed, raffinate and extract streams were \( Q_F = 3 \text{ ml/min} \) and \( Q_R = 8 \text{ ml/min} \). The other experimental conditions and the SMBR experimental and simulated (inside brackets) performance criteria are presented at Table 5.3. The pseudo steady state concentration profiles obtained experimentally at the middle of the switching time after 10 cycles are compared with the steady state profiles simulated by the TMBR model in Figure 5.7.

<table>
<thead>
<tr>
<th>Run 1</th>
<th>Run 2</th>
<th>Run 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>( t^* = 3.50 \text{ min} )</td>
<td>( t^* = 3.75 \text{ min} )</td>
<td>( t^* = 4.00 \text{ min} )</td>
</tr>
<tr>
<td>( Q_D = 23.5 \text{ ml/min} )</td>
<td>( Q_D = 22.7 \text{ ml/min} )</td>
<td>( Q_D = 24.0 \text{ ml/min} )</td>
</tr>
<tr>
<td>( Q_4 = 20.5 \text{ ml/min} )</td>
<td>( Q_4 = 21.3 \text{ ml/min} )</td>
<td>( Q_4 = 20.0 \text{ ml/min} )</td>
</tr>
<tr>
<td>( C_{C,R} = 2.37 \text{ mol/l} )</td>
<td>( C_{C,R} = 3.00 \text{ mol/l} )</td>
<td>( C_{C,R} = 2.90 \text{ mol/l} )</td>
</tr>
<tr>
<td>PUR = 79.1 (87.3) %</td>
<td>PUR = 84.1 (90.2) %</td>
<td>PUR = 87.2 (90.0) %</td>
</tr>
<tr>
<td>PUX = 97.8 (95.2) %</td>
<td>PUX = 95.2 (97.4) %</td>
<td>PUX = 96.1 (98.3) %</td>
</tr>
<tr>
<td>PR = 21.5 (24.7) mol/l.min</td>
<td>PR = 27.3 (27.1) mol/l.min</td>
<td>PR = 26.3 (23.8) mol/l.min</td>
</tr>
<tr>
<td>DC = 1.16 (1.01) l/mol</td>
<td>DC = 0.88 (0.89) l/mol</td>
<td>DC = 0.97 (1.07) l/mol</td>
</tr>
<tr>
<td>X = 97.7 (98.6) %</td>
<td>X = 98.1 (98.7) %</td>
<td>X = 98.2 (99.0) %</td>
</tr>
</tbody>
</table>
Figure 5.7  Experimental and simulated concentration profiles in a SMBR at the middle of a switching time at cyclic steady-state (10th cycle). a) run 1; b) run 2; c) run 3.
The stationary steady state predicted with the TMBR model describes well the SMBR cyclic steady state at the middle of the switching time behaviour for all three experimental runs, in terms of internal concentration profiles. Therefore, the influence of feed composition, switching time, mass transfer and length of the section in the SMBR performance parameters will be studied with the TMBR modelling approach. For the above studies, a reference case was selected. The operating conditions for this case are presented at Table 5.4; the kinetic and adsorption parameters are those defined in Chapters 3 and 4. The design of the SMBR takes into account the minimum raffinate purity of 95%, a minimum desorbent consumption and a maximum productivity. The extract purity is not an important parameter since water in a secondary product.

<table>
<thead>
<tr>
<th>Operating Conditions</th>
<th>Performance Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t^* = 3.70 \text{ min}$</td>
<td>PUR=97.9 %</td>
</tr>
<tr>
<td>$Q_D = 50.0 \text{ ml/min}$</td>
<td>PUX=99.9 %</td>
</tr>
<tr>
<td>$Q_k = 10 \text{ ml/min}$</td>
<td>PR=32.5 mol/l.min</td>
</tr>
<tr>
<td>$Q_R = 25 \text{ ml/min}$</td>
<td>DC=1.69 l/mol</td>
</tr>
<tr>
<td>$Q_A = 35 \text{ ml/min}$</td>
<td>X=99.7 %</td>
</tr>
<tr>
<td>$C_{4,F} = 8.57 \text{ mol/l}$</td>
<td></td>
</tr>
<tr>
<td>$C_{8,F} = 8.96 \text{ mol/l}$</td>
<td></td>
</tr>
<tr>
<td>Configuration: 3-3-3-3</td>
<td></td>
</tr>
</tbody>
</table>

### 5.3.1 Effect of feed composition

Ethanol is used both as desorbent and reactant; higher desorbent flow-rate is necessary for complete regeneration of adsorbent in section I. In the reaction sections (II and/or III) the ethanol reacts with the acetaldehyde that is fed to the system. If the ethanol that enters in SMBR unit in the desorbent stream is enough to convert the acetaldehyde that is being fed
using a feed of pure acetaldehyde, this should lead to the best performance of the SMBR unit, since for the same desorbent flow rate more acetal is being produced. However, the influence of feed composition on the acetal purity, productivity and ethanol consumption (Figure 5.8) shows that a feed containing 70-80 % molar of acetaldehyde leads to a better performance. A deeper understanding of the unit behavior is possible by analyzing the internal concentration profiles (Figure 5.9).

![Graph a) Purity and conversion vs. acetaldehyde in feed](image)

![Graph b) Productivity and desorbent consumption vs. acetaldehyde in feed](image)

**Figure 5.8** Effect of the feed composition (molar percentage of acetaldehyde) in the performance parameters: a) raffinate and extract purities and acetaldehyde conversion; b) productivity and desorbent consumption.
Figure 5.9  Effect of the feed composition (molar percentage of acetaldehyde) in the steady state concentration profiles of ethanol, acetaldehyde, acetal and water. Legend: 100 % (red line); 80 % (green line); 70 % (black line); 60 % (blue line).

The acetaldehyde internal profile is distributed in sections II and III, where the reaction occurs; sections I and IV plays the same role as in a SMB system. For concentration of acetaldehyde higher than 80% the conversion is lower than 95% (Figure 5.8) and the unreacted acetaldehyde goes to the raffinate stream leading to impure acetal (Figure 5.9). The reason of this behaviour is that section II is characterized by a lack of ethanol and the reaction is chemical equilibrium controlled. Higher acetaldehyde concentrations will lead to higher excess of unreacted acetaldehyde and consequently the raffinate stream is contaminated. Below 70 % of acetaldehyde at feed, this is completed consumed near the feed port and the SMBR unit operates like an SMB to separate acetal from water.

The ideal feed composition will depend on the desorbent flowrate (pure ethanol) and the feed that will be processed; acetaldehyde concentration should be high enough to increase the productivity without leading to a lack of ethanol in the reaction zone (II and III).
5.3.2 Effect of switching time

The switching time sensitivity analysis was conducted for two situations:

i) the feed is a 50% mixture of acetaldehyde (Figure 5.10): the acetaldehyde is completely consumed and appears only near the feed port, and the SMBR unit plays as a SMB unit;

ii) the feed is a 70% mixture of acetaldehyde (Figure 5.11): in this case, the acetaldehyde is not instantaneously consumed and section II and III are used as reactive and separative zones.

---

Figure 5.10 Effect of the switching time (51 % molar percentage of acetaldehyde in feed) in the performance parameters: a) raffinate and extract purities and acetaldehyde conversion; b) productivity and desorbent consumption.
For a 50% acetaldehyde feed composition the best performance achieved is a productivity of 33 mol/l/min and a desorbent consumption of 1.7 l/mol, for switching time range 3.7-4.1 min. The increase of acetaldehyde feed concentration to 70% leads to a maximum productivity of 45 mol/l/min with a minimum desorbent consumption of 1.2 l/mol for a switching time of 4 min. In this case the switching time plays a fundamental role both for the reaction and the separation goals as shown in Figure 5.12.
Acetaldehyde is the middle adsorbed component when compared with ethanol and water. If the conditions of sections II and III guarantee the acetal/water separation ($t^* = 3.7 - 4.1$ min), the switching time will affect the acetaldehyde net-flow and acetaldehyde appears only in section II ($t^* = 3.7$ min) or in section III ($t^* = 4.1$ min) or at both ($t^* = 3.9$ min), and the residence time of acetaldehyde in that sections should be enough to achieve complete reaction.

5.3.3 Effect of mass transfer resistance

The mass transfer resistances are very important for the separation region that allows a given purity, mainly for high degree of purity. For that reason, the sensibility analysis of the global mass transfer coefficient on the SMBR performance parameters is presented at (Figure 5.13).
The raffinate purity increases from 97.9\% (reference case) to 99.5\% by making the global mass transfer coefficients calculated instantaneously and locally twice bigger than at the reference case.

![Graph](image)

**Figure 5.13** Sensitivity analysis to mass transfer resistance (51\% molar percentage of acetaldehyde in feed, $t^* = 3.7$ min) in the performance parameters: a) raffinate and extract purities and acetaldehyde conversion; b) productivity and desorbent consumption.
5.3.4 Separation Region

The numerical procedure used to define the separation region consists on fixing at the same time the value of switching time and the values of flow-rate in section I and IV. These conditions are those from Table 5.4. Keeping the flow-rates in section I and IV constant leads to constant desorbent flow-rate. By setting the $\gamma_i$ values for sections I ($\gamma_i = 4.30$) and IV ($\gamma_i = 0.515$) a region of separation is defined in a $\gamma_2, \gamma_3$ plane.

The separation region is located within the region between the diagonal $\gamma_2 = \gamma_3$, the horizontal line $\gamma_3 = 0.515$ and $\gamma_3$ axis. The diagonal $\gamma_2 = \gamma_3$ corresponds to zero feed flow-rate, therefore $\gamma_i$ must be higher than $\gamma_2$. The horizontal branch $\gamma_3 = 0.515$ corresponds to zero raffinate flow-rate.

The algorithm for the construction of the separation region starts by setting a low value of the feed flow rate (0.02 ml/min) and the value of $\gamma_3$ equal to 0.515. Then, the $\gamma_3$ values were consecutively incremented by a step of 0.001, sufficiently small to provide precise determination of the separation region. For each $\gamma_3$, the value of $\gamma_i$ was calculated from the mass balance in the feed node. The purities of extract and raffinate were calculated for each pair of $(\gamma_3, \gamma_i)$. The values that guarantee the minimum 95% purity in both extract and raffinate were selected to build the separation region. At the end of this cycle, the line of separation corresponding to the feed flow rate is defined and then the feed flow rate is increased to higher value. The simulation procedure ends with the last value of the feed flow rate, which gives extract and raffinate purities equal to 95% (vertex of the separation region). Above that feed flow-rate value the purity requirement cannot be fulfilled for any pair of values of $(\gamma_3, \gamma_i)$.

Figure 5.14 shows two separation regions for a 95% purity criteria:

i) Reversible reaction with the true kinetic of diethylacetel synthesis;

ii) Considering that the reaction is irreversible and infinitively fast.
Both separation regions present a plateau at $\gamma_3 = 2.82$ and 2.95 for reversible and fast irreversible reaction, respectively. This is due to the reactive front constituted by acetaldehyde and water that travels along section III, as in the fixed bed reactor, and reaches the raffinate port (see Figure 5.15).

The movement of the reaction front is observed in the raffinate purity history (Figure 5.16). At the beginning of the SMBR operation the acetal produced is separated from the reactive zone and reaches the raffinate port (purity increases). At the same time the water that is produced is strongly adsorbed by the resin and carried out with the solid phase to zone IV, decreasing slightly the raffinate purity. After that, it was expected that after 10 cycles (444 min), since both purities remain constant, that the steady state was achieved. Only by analysis of the time evolution of the internal concentration profiles was possible to see that there was a reactive front moving along the section III, and when it arrives at raffinate port the purity decreases again.
Figure 5.15  Time evolution of the concentration profiles of acetaldehyde, acetal and water ($\gamma_1=4.302; \gamma_2=1.632; \gamma_3=2.844; \gamma_4=0.515$). Legend: $t=400$ min (green line); $t=600$ min (blue line); $t=800$ min (red line); $t=1000$ min (black line).
Figure 5.16 Time evolution of purities of extract and raffinate ($\gamma_1 = 4.302; \gamma_2 = 1.632; \gamma_3 = 2.844; \gamma_4 = 0.515$).

The separation zone for equimolar binary mixtures acetal/water, acetal/acetaldehyde and acetaldehyde/water were also determined imposing a 95% purity, without reaction, as shown in Figure 5.17.

Figure 5.17 Separation regions ($\gamma_1 = 4.30; \gamma_4 = 0.515$), 95% purity.
All separation region have different shape and position imposed from the selectively between the components of the binary mixture and the desorbent selectivity relative to both components (intermediate desorbent for the mixtures acetal/water, acetal/acetalddehyde and less adsorbed desorbent for acetalddehyde/water). The reactive separation zone comprises parts of all three regions.

5.4 Conclusions

The SMBR for acetal production was studied experimentally and by simulation. The experimental studies were described using the TMBR modelling strategy. The mathematical model assumes axial dispersion flow for the bulk fluid phase, plug flow for the solid phase, linear driving force (LDF) for the particle mass transfer rate and multicomponent adsorption equilibria. The kinetic and adsorption parameters obtained from batch and fixed bed reactor experiments were used in the prediction of the SMBR performance. The stationary steady state predicted with the TMBR model describes satisfactory the experimental SMBR cyclic steady state at the middle of the switching time behaviour, in terms of internal concentration profiles.

The influence of feed composition, switching time and mass transfer on the SMBR performances was analysed by simulation. The ideal feed composition will depend on the desorbent flowrate (pure ethanol) and the feed that will be processed; acetalddehyde concentration should be high enough to increase the productivity without leading to a lack of ethanol in the reaction zone (II and III). For high acetalddehyde concentrations, the switching time plays a fundamental role on the SMBR unit in or to both reaction and separation goals to be accomplish simultaneously. The reactive system is quite complex and the operating conditions should be chosen carefully, since there are contradictory effects of the variables involved in the SMBR process.

The right choice of the operation parameters leads to complete acetalddehyde conversion and high purity products (raffinate and extract). The separation regions for 95% purity were determined using the separation zone methodology for the case (i) reversible reaction and (ii) irreversible infinitively fast reaction. Both regions are similar and present a plateau at $\gamma = 2.82$ and 2.95, respectively, due to the reactive front with constant pattern behaviour along section III (reaction zone).
The separation zone for equimolar binary mixtures acetal/water, acetal/acetaldehyde and acetaldehyde/water were also determined imposing a 95% purity, without reaction. All separation regions have different shape and position imposed from the selectivity between the components of the binary mixture and the desorbent selectivity relative to both components (intermediate desorbent for the mixtures acetal/water, acetal/acetaldehyde and less adsorbed desorbent for acetaldehyde/water). The reactive separation zone comprises parts of all three regions.

5.5 Notation

$C$ - liquid phase concentration (mol/m$^3$)

$\bar{C}_p$ - average liquid phase concentration inside the particle (mol/m$^3$)

$d_p$ - particle diameter (m)

$D_m$ - axial dispersion (m$^2$/s)

$DC$ - desorbent consumption (m$^3$/mol)

$K$ - Langmuir equilibrium parameter (m$^3$/mol)

$K_L$ - global mass transfer coefficient (m/s)

$L_c$ - column length (m)

$Pe$ - Peclet number

$PR$ - raffinate productivity (mol/s/m$^3$)

$PUR$ - raffinate purity (%)

$PUX$ - extract purity (%)

$q$ - solid phase concentration (mol/m$^3_{sol}$)

$Q_{ad}$ - adsorption capacity (mol/m$^3_{sol}$)
$Q$ - volumetric flow rate (m$^3$/s)

$\mathcal{R}$ - reaction rate (mol/kg$_{res.}$s)

$r_p$ - particle radius (m)

$t$ - time (s)

$t^*$ - switching time (min)

$u$ - interstitial fluid velocity (m/s)

$U_x$ - interstitial solid velocity (m/s)

$V_m$ - molar volume in the liquid phase (m$^3$/mol)

$X$ - acetaldehyde conversion (%) 

$z$ - axial coordinate (m)

**Greek letters**

$\varepsilon$ - bulk porosity

$\varepsilon_p$ - particle porosity

$\nu$ - stoichiometric coefficient

$\gamma$ - ratio between the liquid and solid interstitial velocities

$\eta$ - effectiveness factor of the catalyst

$\rho_b$ - bulk density (kg/m$^3$)

$\rho_p$ - particle density (kg/m$^3$)

**Subscripts**

D - relative to the desorbent
i - relative to component \(i (i= A, B, C, D)\)

\(F\) - relative to the feed

\(R\) - relative to the raffinate

SMB - relative to a SMB process

\(X\) - relative to the extract

\(0\) - relative to initial conditions

TMB - relative to a TMB process

5.6 References


6. Conclusions and Suggestions for Future Work

The goal of this work was the development of a method for the diethylacetal production from the reaction between ethanol and acetaldehyde catalyzed by acid resins. The main results and conclusions are the following:

An automated experimental set-up was developed and used to measure thermodynamic and kinetics of diethylacetal synthesis in liquid phase. The equilibrium constant was measured in the temperature range of 20-60 °C and pressure of 10 bar: \( \ln K_p = 1270 / T - 3.07 \).

The standard molar reaction properties were obtained at 298 K: \( \Delta H^0 = -10.56 \text{ kJ mol}^{-1} \), \( \Delta G^0 = -2.94 \text{ kJ mol}^{-1} \) and \( \Delta S^0 = -25.56 \text{ J mol}^{-1} \text{ K}^{-1} \). The standard molar properties of formation of acetal in the liquid phase at 298 K were estimated: \( \Delta H_f^0 = -476.5 \text{ kJ mol}^{-1} \), \( \Delta G_f^0 = -243.5 \text{ kJ mol}^{-1} \) and \( S_f^0 = 343.2 \text{ J mol}^{-1} \text{ K}^{-1} \).

The kinetics over Amberlyst 18 was studied in the temperature range of 10-25 °C. Because of the strong non-ideality of the liquid reaction mixture, the reaction rate model was formulated in terms of activities. The measured reaction rates were limited by diffusion inside the particle. A batch reactor mathematical model that includes pore diffusion inside the particle was developed and used to get the true kinetic rate expression from the experimental kinetic data. The proposed kinetic law, expressed in activities is:

\[
\mathcal{R} = k_c \frac{a_A a_B}{K_{eq} a_A} \frac{a_c a_d}{(1 + K_D a_d)^2}
\]
and the parameters are

\[ k_c (\text{mol/g.min}) = 3.3 \times 10^{11} \exp \left[ -\frac{7824}{T (K)} \right] \]

\[ K_d = 6.4 \times 10^5 \exp \left[ -\frac{4003}{T (K)} \right] \]

The activation energy of reaction is 65.0 kJ mol\(^{-1}\).

In order to relate the average rate of reaction with the reaction rate at the surface the relation between the effectiveness factor and the Thiele modulus, when the internal diffusion is the controlling mechanism (\(\ln \phi_A > 1\)) was found:

\[ T = 10 \, ^{\circ}C: \quad \ln \eta = -0.936 \ln \phi_A + 0.036 \]

\[ T = 20 \, ^{\circ}C: \quad \ln \eta = -0.913 \ln \phi_A + 0.250 \]

where the Thiele modulus, related to ethanol, is defined as:

\[ \phi_A = \frac{r_p}{3} \sqrt[3]{\frac{D_p k_c}{D_A C_{As}}} \]

The dynamic behaviour of fixed bed adsorptive reactor for the synthesis of diethylacetal, using acid resin catalysts was studied. The adsorption data were obtained for Amberlyst 18 and Amberlyst 15, by performing dynamic binary experiments at 15 °C:

<table>
<thead>
<tr>
<th>Component</th>
<th>Amberlyst 18</th>
<th>Amberlyst 15</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Q , (\text{mol/} , l_m))</td>
<td>(K , (\text{mol/} , l))</td>
</tr>
<tr>
<td>Ethanol</td>
<td>25.9</td>
<td>0.195</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>35.4</td>
<td>0.173</td>
</tr>
<tr>
<td>Acetal</td>
<td>15.9</td>
<td>0.071</td>
</tr>
<tr>
<td>Water</td>
<td>60.7</td>
<td>0.310</td>
</tr>
</tbody>
</table>

A mathematical model for the isothermal adsorptive reactor was developed, including axial dispersion, mass-transfer resistances, multicomponent Langmuir adsorption isotherms and
reaction rate expressed in terms of activities. The theoretical model considers two mass transfer resistances in series: the film diffusion and the diffusion inside the pores. The model was validated by comparison with the experimental results obtained for the production and regeneration steps. The model is able to predict the response of adsorptive reactors with different lengths for a wide range of initial/feed compositions.

The SMBR for acetal production was studied experimentally and by simulation. The mathematical model uses the TMBR approach which considers axial dispersion flow for the bulk fluid phase, plug flow for the solid phase, linear driving force (LDF) for the particle mass transfer rate and multicomponent adsorption equilibria. The kinetic and adsorption parameters obtained from batch and fixed bed reactor experiments were used in the prediction of the SMBR performance. The stationary steady state predicted with the TMBR model describes the experimental SMBR cyclic steady state at the middle of the switching time, in terms of internal concentration profiles.

The influence of feed composition, switching time and mass transfer on the SMBR performances was analysed by simulations. The ideal feed composition will depend on the desorbent flowrate (pure ethanol) and the feed that will be processed; acetaldehyde concentration should be high enough to increase the productivity without leading to a lack of ethanol in the reaction zone (II and III). For high acetaldehyde concentrations, the switching time plays a fundamental role on the SMBR unit in both reaction and separation goals to be accomplished simultaneously. The reactive system is quite complex and the operating conditions should be chosen carefully, since there are opposite effects of the variables involved in the SMBR process.

The right choice of the operating parameters leads to complete acetaldehyde conversion and high purity products (raffinate and extract). The separation regions for 95% purity were determined using the separation zone methodology for the case (i) reversible reaction and (ii) irreversible infinitively fast reaction. Both regions are similar and present a plateau at $\gamma = 2.82$ and 2.95, respectively, due to the reactive front with constant pattern behaviour along section III (reaction zone).

Simulated results show that high acetal purities are achieved for 100% acetaldehyde conversion. The main problem is associated with the high ethanol consumption, since water is strongly adsorbed by the resin. However, ethanol, as reactant, is needed in excess
in sections II and III in order to complete acetaldehyde conversion, and therefore, using large desorbent flow rate will allow the use of high acetaldehyde feed concentrations, leading to a maximum productivity and a minimum desorbent consumption.

This work was conducted to design a SMBR unit without optimization of the entire process. Further improvement will be expected if a systematic process optimization will be applied for the SMBR process using multiple objectives. It is suggested as future work the application of the Non-Dominated Sorting Genetic Algorithm (NSGA) for the diethylacetal synthesis in a SMBR unit.

Further work should include the use of asynchronous shifting of inlet/outlet ports during SMBR operation.

The extension of this methodology to the synthesis of other acetals (methanol+ acetaldehyde; propanol+ acetaldehyde) and green solvents (ethyl lactate) should be of interest. The analysis of alternative technologies (membrane reactors) must also be considered.
Appendix A: Octane and Cetane Numbers

Octane number

The octane quality of gasoline is described by the octane number. The octane number of a gasoline is determined by comparative measurements of its octane quality and that of binary mixtures having variable concentrations of n-heptane (low octane quality) and 2,2,4-trimethylpentane (isooctane; high octane quality). By definition the octane number of n-heptane is 0 and that of isooctane is 100. The octane numbers of mixtures are given by their percentage by volume of isooctane; octane numbers greater than 100 can be determined with lead-containing isooctane or toluene-containing mixtures. The determination of the octane number is carried out under two different running conditions: determination of the research octane number (RON) and determination of the motor octane number (MON).

Cetane number

The cetane number is used to described the ignition quality of diesel fuels. Like the octane number, the cetane number is obtained by comparative measurements. Mixtures of α-methylnaphthalene with very low ignition quality (cetane number 0) and cetane (n-hexadecane) with very high ignition quality (cetane number 100) are used as references. The cetane number of a reference mixture is given by the volume percentage of cetane in α-methylnaphthalene.
Appendix B: Calibration

Pure Component

The calibration was realized injecting different volumes of pure components at 15 °C. The volume is converted to number of moles using the molar volumes at 15 °C, see Table B.1.

<table>
<thead>
<tr>
<th>Component</th>
<th>Molar Volume (ml/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetaldehyde</td>
<td>55.728</td>
</tr>
<tr>
<td>Acetel</td>
<td>140.558</td>
</tr>
<tr>
<td>Ethanol</td>
<td>57.559</td>
</tr>
<tr>
<td>Water</td>
<td>17.880</td>
</tr>
</tbody>
</table>

The response factor, \( f \), defined as:

\[
 n_i = f_i \, A_i \tag{B.1}
\]

where \( n_i \) is the number of moles of component \( i \) (μmol) and \( A_i \) is the area of component \( i \) (u.a.).
### Ethanol

<table>
<thead>
<tr>
<th>V (µl)</th>
<th>A (u.a.)</th>
<th>n (µmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.298</td>
<td>1.737</td>
</tr>
<tr>
<td>0.1</td>
<td>0.294</td>
<td>1.737</td>
</tr>
<tr>
<td>0.3</td>
<td>0.818</td>
<td>5.212</td>
</tr>
<tr>
<td>0.3</td>
<td>0.796</td>
<td>5.212</td>
</tr>
<tr>
<td>0.5</td>
<td>1.310</td>
<td>8.687</td>
</tr>
<tr>
<td>0.5</td>
<td>1.312</td>
<td>8.687</td>
</tr>
</tbody>
</table>

### Acetal

<table>
<thead>
<tr>
<th>V (µl)</th>
<th>A (u.a.)</th>
<th>n (µmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.244</td>
<td>0.711</td>
</tr>
<tr>
<td>0.1</td>
<td>0.250</td>
<td>0.711</td>
</tr>
<tr>
<td>0.3</td>
<td>0.689</td>
<td>2.134</td>
</tr>
<tr>
<td>0.3</td>
<td>0.682</td>
<td>2.134</td>
</tr>
<tr>
<td>0.5</td>
<td>1.095</td>
<td>3.557</td>
</tr>
<tr>
<td>0.5</td>
<td>1.094</td>
<td>3.557</td>
</tr>
</tbody>
</table>

### Acetaldehyde

<table>
<thead>
<tr>
<th>V (µl)</th>
<th>A (u.a.)</th>
<th>n (µmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.315</td>
<td>1.794</td>
</tr>
<tr>
<td>0.1</td>
<td>0.205</td>
<td>1.794</td>
</tr>
<tr>
<td>0.3</td>
<td>0.798</td>
<td>5.383</td>
</tr>
<tr>
<td>0.3</td>
<td>0.795</td>
<td>5.383</td>
</tr>
<tr>
<td>0.5</td>
<td>1.274</td>
<td>8.972</td>
</tr>
<tr>
<td>0.5</td>
<td>1.229</td>
<td>8.972</td>
</tr>
</tbody>
</table>

### Water

<table>
<thead>
<tr>
<th>V (µl)</th>
<th>A (u.a.)</th>
<th>n (µmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.467</td>
<td>5.593</td>
</tr>
<tr>
<td>0.1</td>
<td>0.464</td>
<td>5.593</td>
</tr>
<tr>
<td>0.3</td>
<td>1.293</td>
<td>16.779</td>
</tr>
<tr>
<td>0.35</td>
<td>1.301</td>
<td>16.779</td>
</tr>
<tr>
<td>0.5</td>
<td>2.121</td>
<td>27.964</td>
</tr>
<tr>
<td>0.5</td>
<td>2.104</td>
<td>27.964</td>
</tr>
</tbody>
</table>

### Graphs

- **Ethanol**
  - n = 6.5547 A
  - $R^2 = 0.998$

- **Acetal**
  - n = 3.1997 A
  - $R^2 = 0.997$

- **Acetaldehyde**
  - n = 7.0876 A
  - $R^2 = 0.994$

- **Water**
  - n = 13.054 A
  - $R^2 = 0.998$
Multicomponent mixtures

The determination of species concentration in mixtures, it is first calculated the molar fraction of each species, accordingly to:

\[ x_i = \frac{f_i A_i}{\sum_n f_n A_n} \]  \hspace{1cm} (B.2)

The concentration is then evaluated using the liquid molar volumes:

\[ C_i = \frac{x_i}{\sum_n x_n V_{mi,n}} \]  \hspace{1cm} (B.3)

In order to verify the analysis accuracy for binary and quaternary mixtures, were prepared and analysed several standard mixtures with known concentration, as shown in Table B.2-B.4.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ethanol molar fraction</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Real</td>
<td>Calculated</td>
<td>Error (%)</td>
</tr>
<tr>
<td>1</td>
<td>0.2828</td>
<td>0.2879</td>
<td>1.81</td>
</tr>
<tr>
<td>2</td>
<td>0.5238</td>
<td>0.5234</td>
<td>-0.09</td>
</tr>
<tr>
<td>3</td>
<td>0.8004</td>
<td>0.7918</td>
<td>-1.09</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ethanol molar fraction</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Real</td>
<td>Calculated</td>
<td>Error (%)</td>
</tr>
<tr>
<td>1</td>
<td>0.204</td>
<td>0.223</td>
<td>9.24</td>
</tr>
<tr>
<td>2</td>
<td>0.523</td>
<td>0.534</td>
<td>2.17</td>
</tr>
<tr>
<td>3</td>
<td>0.793</td>
<td>0.794</td>
<td>0.39</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Component</th>
<th>molar fraction</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Real</td>
<td>Calculated</td>
<td>Error (%)</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.3178</td>
<td>0.3171</td>
<td>-0.22</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>0.2319</td>
<td>0.2364</td>
<td>1.93</td>
</tr>
<tr>
<td>Acetal</td>
<td>0.2025</td>
<td>0.1956</td>
<td>-3.41</td>
</tr>
<tr>
<td>Water</td>
<td>0.2478</td>
<td>0.2509</td>
<td>1.25</td>
</tr>
</tbody>
</table>
Example:

The chromatogram of a quaternary mixture sample is shown in Figure B.1 and the composition calculation is presented in Table B.5.

![Chromatogram Image]

**Figure B.1.** Typical chromatogram of a quaternary mixture.

**Table B.5. Composition of a quaternary mixture sample.**

<table>
<thead>
<tr>
<th>Component</th>
<th>Amount injected</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$A_i$</td>
<td>$n_i$</td>
<td>$x_i$</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.04639</td>
<td>0.304</td>
<td>0.4786</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>0.00610</td>
<td>0.043</td>
<td>0.0681</td>
</tr>
<tr>
<td>Acetal</td>
<td>0.04035</td>
<td>0.129</td>
<td>0.2031</td>
</tr>
<tr>
<td>Water</td>
<td>0.12178</td>
<td>0.158</td>
<td>0.2502</td>
</tr>
</tbody>
</table>
Appendix C: Safety Data

1. Acetaldehyde

1.1 General

*Synonyms*: ethanal, ethyl aldehyde, acetic aldehyde
*Molecular formula*: $\text{C}_2\text{H}_4\text{O}$
*CAS No.*: 75-07-0

1.2 Physical data

Appearance: colourless liquid
Melting point: -124 °C
Boiling point: 20 °C
Specific gravity: 0.78
Vapour pressure: 755 mm Hg at 20 °C
Vapour density: 1.52 (air = 1)
Flash point: -39 °C
Explosion limits: 4% - 57%
Autoignition temperature: 185 °C
Water solubility: miscible in all proportions

1.3 Stability

Stable. Substances to be avoided include strong oxidising agents, strong acids, reducing agents, alkalis, halogens, halogen oxides. Highly flammable. Vapour/air mixtures explosive over a very wide concentration range. May form peroxides in storage.

1.4 Toxicology

Harmful by inhalation, ingestion and through skin absorption. Some experiments with animals suggest that this substance may be anticipated to be a carcinogen. Contact with skin or eyes may cause severe irritation or burns. EC carcinogen category 3. Typical OES 37 mg/m3 (20 ppm) long-term, 92 mg/m3 (50 ppm) short-term.

Risk phrases:
- R12 Extremely flammable.
- R36 Irritating to eyes.
- R37 Irritating to respiratory system.
- R40 Possible risk of irreversible effects.

1.5 Personal protection

Safety glasses. Effective ventilation.

Safety phrases:
- S16 Keep away from sources of ignition.
- S33 Take precautionary measures against static discharges.
- S36 Wear suitable protective clothing.
- S37 Wear suitable gloves.
1.6 HAZARD SUMMARY

- Acetaldehyde can affect you when breathed in.
- Because this is a MUTAGEN, handle it as a possible cancer-causing substance // WITH EXTREME CAUTION.
- Exposure can cause you to become dizzy, light headed, and to pass out. It can irritate the eyes, nose, throat and lungs. Higher exposures can cause fluid in the lungs (pulmonary edema).
- Contact can severely burn the eyes. Repeated contact can cause rash and/or skin allergy.
- Acetaldehyde is a HIGHLY FLAMMABLE and REACTIVE chemical and is a DANGEROUS FIRE and EXPLOSION HAZARD.

1.7 HOW TO DETERMINE IF YOU ARE BEING EXPOSED

- Exposure to hazardous substances should be routinely evaluated. This may include collecting air samples. Under OSHA 1910.20, you have a legal right to obtain copies of sampling results from your employer. If you think you are experiencing any work-related health problems, see a doctor trained to recognize occupational diseases. Take this Fact Sheet with you.
- The odor threshold only serves as a warning of exposure. Not smelling it does not mean you are not being exposed.

1.8 WORKPLACE EXPOSURE LIMITS

OSHA: The legal airborne permissible exposure limit (PEL) is 100 ppm averaged over an 8-hour workshift and 150 ppm, not to be exceeded during any (15 minute) work period.

ACGIH: The recommended airborne exposure limit is 100 ppm, which should not be exceeded at any time.

- Acetaldehyde is a MUTAGEN and may be a TERATOGEN. Mutagens may have a cancer risk. All contact with this chemical should be reduced to the lowest possible level.

1.9 WAYS OF REDUCING EXPOSURE

- Where possible, enclose operations and use local exhaust ventilation at the site of chemical release. If local exhaust ventilation or enclosure is not used, respirators should be worn.
- Wear protective work clothing.
• Wash thoroughly immediately after exposure to Acetaldehyde and at the end of the workshift.
• Post hazard and warning information in the work area. In addition, as part of an ongoing education and training effort, communicate all information on the health and safety hazards of Acetaldehyde to potentially exposed workers.

This Fact Sheet is a summary source of information of all potential and most severe health hazards that may result from exposure. Duration of exposure, concentration of the substance and other factors will affect your susceptibility to any of the potential effects described below.

**1.10 HEALTH HAZARD INFORMATION**

**Acute Health Effects**

The following acute (short-term) health effects may occur immediately or shortly after exposure to Acetaldehyde:

• Acetaldehyde can irritate the skin causing a rash or burning feeling on contact.
• Acetaldehyde can cause severe eye burns leading to permanent damage.
• Breathing Acetaldehyde can irritate the lungs causing coughing and/or shortness of breath. Higher exposures can cause a build-up of fluid in the lungs (pulmonary edema) a medical emergency, with severe shortness of breath.
• Inhaling a high concentration of the vapor may cause you to feel sleepy or dizzy, to pass out, or even die.

**Chronic Health Effects**

The following chronic (long-term) health effects can occur at some time after exposure to Acetaldehyde and can last for months or years:

**Cancer Hazard**

• Acetaldehyde causes MUTATIONS (genetic changes). Such chemicals may have a cancer or reproductive risk and there is limited evidence that Acetaldehyde causes cancer in animals.
• Many scientists believe there is no safe level of exposure to a carcinogen. Such substances may also have the potential for causing reproductive damage in humans.
Reproductive Hazard

- Acetaldehyde may be a teratogen in humans since it has been shown to be a teratogen in animals.

Other Long-Term Effects

- Acetaldehyde may cause a skin allergy. If allergy develops, very low future exposures can cause itching and a skin rash.
- Very irritating substances may affect the lungs. It is not known whether Acetaldehyde causes lung damage.
- Repeated exposure may cause chronic irritation of the eyes and skin.

Medical Testing

Before beginning employment and at regular times after that, the following are recommended:

- Lung function tests. If symptoms develop or overexposure is suspected, the following may be useful:
- Evaluation by a qualified allergist, including careful exposure history and special testing, may help diagnose skin allergy.
- Consider chest x-ray after acute overexposure.

Any evaluation should include a careful history of past and present symptoms with an exam. Medical tests that look for damage already done are not a substitute for controlling exposure. Request copies of your medical testing. You have a legal right to this information under OSHA 1910.20.

1.11 WORKPLACE CONTROLS AND PRACTICES

Unless a less toxic chemical can be substituted for a hazardous substance, ENGINEERING CONTROLS are the most effective way of reducing exposure. The best protection is to enclose operations and/or provide local exhaust ventilation at the site of chemical release. Isolating operations can also reduce exposure. Using respirators or protective equipment is less effective than the controls mentioned above, but is sometimes necessary.

In evaluating the controls present in your workplace, consider: (1) how hazardous the substance is, (2) how much of the substance is released into the workplace and (3) whether harmful skin or eye contact could occur. Special controls should be in place for highly toxic chemicals or when significant skin, eye, or breathing exposures are possible.
In addition, the following controls are recommended:

- Where possible, automatically pump liquid Acetaldehyde from drums or other storage containers to process containers.
- Before entering a confined space where Acetaldehyde is present, check to make sure sufficient oxygen (19%) exists.

Good WORK PRACTICES can help to reduce hazardous exposures. The following work practices are recommended:

- Workers whose clothing has been contaminated by Acetaldehyde should change into clean clothing promptly.
- Contaminated work clothes should be laundered by individuals who have been informed of the hazards of exposure to Acetaldehyde.
- Eye wash fountains should be provided in the immediate work area for emergency use.
- If there is the possibility of skin exposure, emergency shower facilities should be provided.
- On skin contact with Acetaldehyde, immediately wash or shower to remove the chemical. At the end of the workshift, wash any areas of the body that may have contacted Acetaldehyde, whether or not known skin contact has occurred.
- Do not eat, smoke, or drink where Acetaldehyde is handled, processed, or stored, since the chemical can be swallowed. Wash hands carefully before eating or smoking.

PERSONAL PROTECTIVE EQUIPMENT WORKPLACE CONTROLS ARE BETTER THAN PERSONAL PROTECTIVE EQUIPMENT.

However, for some jobs (such as outside work, confined space entry, jobs done only once in a while, or jobs done while workplace controls are being installed), personal protective equipment may be appropriate.

The following recommendations are only guidelines and may not apply to every situation.

Clothing

- Avoid skin contact with Acetaldehyde. Wear protective gloves and clothing. Safety equipment suppliers/manufacturers can provide recommendations on the most protective glove/clothing material for your operation.
- All protective clothing (suits, gloves, footwear, headgear) should be clean, available each day, and put on before work.
• ACGIH recommends Butyl Rubber as a good to excellent protective material.

Eye Protection
• Wear splash-proof chemical goggles and face shield when working with liquid, unless full facepiece respiratory protection is worn.
• Wear gas-proof goggles, unless full facepiece respiratory protection is worn.

Respiratory Protection
• **IMPROPER USE OF RESPIRATORS IS DANGEROUS.** Such equipment should only be used if the employer has a written program that takes into account workplace conditions, requirements for worker training, respirator fit testing and medical exams, as described in OSHA 1910.134.
• Where the potential exists for exposures over 100 ppm, use a MSHA/NIOSH approved full facepiece respirator with an organic vapor cartridge/canister. Increased protection is obtained from full facepiece powered-air purifying respirators.
• If while wearing a filter, cartridge or canister respirator, you can smell, taste, or otherwise detect Acetaldehyde, or in the case of a full facepiece respirator you experience eye irritation, leave the area immediately. Check to make sure the respirator-to-face seal is still good. If it is, replace the filter, cartridge, or canister. If the seal is no longer good, you may need a new respirator.
• Be sure to consider all potential exposures in your workplace. You may need a combination of filters, prefilters, cartridges, or canisters to protect against different forms of a chemical (such as vapor and mist) or against a mixture of chemicals.
• Where the potential for high exposures exists, use a MSHA/NIOSH approved supplied-air respirator with a full facepiece operated in the positive pressure mode or with a full facepiece, hood, or helmet in the continuous flow mode, or use a MSHA/NIOSH approved self-contained breathing apparatus with a full facepiece operated in pressure demand or other positive pressure mode.
• Exposure to 10,000 ppm is immediately dangerous to life and health. If the possibility of exposures above 10,000 ppm exists, use a MSHA/NIOSH approved self-contained breathing apparatus with a full facepiece operated in continuous flow or other positive pressure mode.
1.12 HANDLING AND STORAGE

- Prior to working with Acetaldehyde you should be trained on its proper handling and storage.
- Acetaldehyde is not compatible with STRONG OXIDIZERS, ACIDS, BASES, ALCOHOLS, AMMONIA, AMINES, PHENOLS, KETONES, HYDROGEN CYANIDE, HYDROGEN SULFIDE, ACID ANHYDRIDES, and HALOGENS.
- Store in tightly closed airtight containers in a cool, dark, well-ventilated area.
- Nitrogen or another inactive gas should be used as an "inert blanket" over liquid Acetaldehyde in storage containers.
- Sources of ignition, such as smoking and open flames, are prohibited where Acetaldehyde is handled, used, or stored.
- Metal containers involving the transfer of 5 gallons or more of Acetaldehyde should be grounded and bonded. Drums must be equipped with self-closing valves, pressure vacuum bungs, and flame arresters.
- Use only non-sparking tools and equipment, especially when opening and closing containers of Acetaldehyde.

**Hazard rating**

- FLAMMABILITY: 4=severe
- REACTIVITY: 2=moderate
- EXPLOSIVE GAS OR LIQUID POISONOUS GASES ARE PRODUCED IN FIRE

1.13 FIRE HAZARDS

- Acetaldehyde is a FLAMMABLE and EXPLOSIVE LIQUID or GAS.
- Use dry chemical, CO₂, or alcohol foam extinguishers.
- Use water spray to keep fire-exposed containers cool.
- POISONOUS GASES ARE PRODUCED IN FIRE.
- The vapor is heavier than air and may travel a distance to cause a fire or explosion far from the source.
- If employees are expected to fight fires, they must be trained and equipped as stated in OSHA 1910.156.
1.14 SPILLS AND EMERGENCIES

If Acetaldehyde is spilled or leaked, take the following steps:

- Restrict persons not wearing protective equipment from area of spill or leak until clean-up is complete.
- Remove all ignition sources.
- Ventilate area of spill or leak.
- Absorb liquids in vermiculite, dry sand, earth, or a similar material and deposit in sealed containers.

If Acetaldehyde is leaked, take the following steps:

- Restrict persons not wearing protective equipment from area of leak until clean-up is complete.
- Remove all ignition sources.
- Ventilate area of leak to disperse the gas.
- Stop flow of gas. If source of leak is a cylinder and the leak cannot be stopped in place, remove the leaking cylinder to a safe place in the open air, and repair leak or allow cylinder to empty.
- Keep Acetaldehyde out of a confined space, such as a sewer, because of the possibility of an explosion, unless the sewer is designed to prevent the build-up of explosive concentrations.
- It may be necessary to contain and dispose of Acetaldehyde as a HAZARDOUS WASTE. Contact your Department of Environmental Protection (DEP) or your regional office of the federal Environmental Protection Agency (EPA) for specific recommendations.

FOR LARGE SPILLS AND FIRES immediately call your fire department.

1.15 FIRST AID

Eye Contact
Immediately flush with large amounts of water. Continue without stopping for at least 30 minutes, occasionally lifting upper and lower lids. Seek medical attention immediately.

Skin Contact
Quickly remove contaminated clothing. Immediately wash area with large amounts of [soap and] water. Seek medical attention immediately.
Breathing

- Remove the person from exposure.
- Begin rescue breathing if breathing has stopped and CPR if heart action has stopped.
- Transfer promptly to a medical facility.
- Medical observation is recommended for 24 to 48 hours after breathing overexposure, as pulmonary edema may be delayed.

1.16 ECOLOGICAL INFORMATION

Acetaldehyde is a flammable liquid with a characteristic pungent odour. It is used to make paraaldehyde, acetic acid, butanol, perfumes, flavours, aniline dyes, plastics, and synthetic rubber. It is also used in silvering mirrors and in hardening gelatine fibbers. It can enter the environment through manufacturing effluents or spills.

1.17 ACUTE (SHORT-TERM) ECOLOGICAL EFFECTS

Acute toxic effects may include the death of animals, birds, or fish, and death or low growth rate in plants. Acute effects are seen two to four days after animals or plants come in contact with a toxic chemical substance. Acetaldehyde has high acute toxicity to aquatic life. No data are available on the short-term effects of acetaldehyde to terrestrial animals.

1.18 CHRONIC (LONG-TERM) ECOLOGICAL EFFECTS

Chronic toxic effects may include shortened lifespan, reproductive problems, lower fertility, and changes in appearance or behaviour. Chronic effects can be seen long after first exposure(s) to a toxic chemical.

Acetaldehyde has high chronic toxicity to aquatic life. No data are available on the long-term effects of acetaldehyde to plants, birds, or land animals.
2. Acetal

2.1 General

Synonyms: 1,1-diethoxyethane, diethylacetal

Molecular formula: C₆H₁₄O₂

 Structural: CH₃CH(OCH₂CH₃)

CAS No: 105-57-7

2.2 Physical data

Molecular Weight: 118
Vapour pressure at 20°C: 4.08 mm Hg
Melting point: -100°C
Boiling point: 102.7°C
Flash point: 36°C
Lower explosive limit: 1.7%
Upper explosive limit: 10.4%
Solubility in water at 20°C: 5%

2.3 Potential Hazards

Flammable, volatile liquid (Polar/Water-Miscible) May form peroxides in storage. Test for peroxides before use. Vapours may form explosive mixtures with air, and may travel to source of ignition and flash back. Vapours may spread along ground and collect in low or confined areas (sewers, basements, tanks). Containers may explode when heated.
2.4 Health

Inhalation or contact with material may irritate or burn skin and eyes. Fire may produce irritating, corrosive and/or toxic gases. Vapours may cause dizziness or suffocation.

2.5 Protective Clothing

Safety glasses. Effective ventilation.

2.6 Spill or Leak

Eliminate all ignition sources (no smoking, flares, sparks or flames in immediate area). All equipment used when handling the product must be grounded. Do not touch or walk through spilled material. Stop leak if you can do it without risk. Prevent entry into waterways, sewers, basements or confined areas. A vapour suppressing foam may be used to reduce vapours. Absorb or cover with dry earth, sand or other non-combustible material and transfer to containers. Use clean non-sparking tools to collect absorbed materials.

2.7 First Aid

Move victim to fresh air. Call emergency medical care. Apply artificial respiration if victim is not breathing. Remove and isolate contaminated clothing and shoes. In case of contact with substance, immediately flush skin or eyes with running water for at least 20 minutes. Wash skin with soap and water. Keep victim warm and quiet. Ensure that medical personnel are aware of the material(s) involved, and take precautions to protect themselves.

2.8 HEALTH HAZARD INFORMATION

Acute Health Effects

The following acute (short-term) health effects may occur immediately or shortly after exposure to Acetal:

- Acetal can irritate the skin and eyes.
- Breathing Acetal can irritate the nose and throat.
• High or repeated exposure to acetal can cause headache, dizziness and drowsiness.

Chronic Health Effects

The following chronic (long-term) health effects can occur at some time after exposure to Acetal and can last for months or years:

Cancer Hazard

• Cancer of the nose and mouth were found in Acetal production workers who were also exposed to other known carcinogenic Aldehydes. The contribution of Acetal to the development of these cancers has not been determined.

• Many scientists believe there is no safe level of exposure to a carcinogen. Such substances may also have the potential for causing reproductive damage in humans.

Reproductive Hazard

• Accordingly to the information presently available, Acetal has not been tested for its ability to affect reproduction.

Other Long-Term Effects

• Acetal has not been tested for other chronic (long-term) health effects.
3. Ethanol

3.1 General

*Synonyms:* ethyl alcohol, grain alcohol, fermentation alcohol, alcohol, methylcarbinol, absolute alcohol, absolute ethanol, anhydrous alcohol, alcohol dehydrated, algaem, anhydrol.

*Molecular formula:* C₂H₅OH

*CAS No.:* 64-17-5

3.2 Physical data

Appearance: colourless liquid

Melting point: -130 °C

Boiling point: 78 °C

Specific gravity: 0.789

Vapour pressure: 1.59

Flash point: 56 °F

Explosion limits: 3.3% - 24.5%

Autoignition temperature: 683 °F

Water solubility: miscible in all proportions

3.3 Stability

Stable. Substances to be avoided include strong oxidising agents, peroxides, acids, acid chlorides, acid anhydrides, alkali metals, ammonia, moisture. Forms explosive mixtures with air.
3.4 Toxicology

Causes skin and eye irritation. Ingestion can cause nausea, vomiting and inebriation; chronic use can cause serious liver damage. Note that "absolute" alcohol, which is close to 100% ethanol, may nevertheless contain traces of 2-propanol, together with methanol or benzene. The latter two are very toxic, while "denatured" alcohol has substances added to it which make it unpleasant and possibly hazardous to consume.

Risk phrases:

- R11 Highly flammable.
- R20 Harmful by inhalation.
- R21 Harmful in contact with skin.
- R22 Harmful if swallowed.
- R36 Irritating to eyes.
- R37 Irritating to respiratory system.
- R38 Irritating to skin.
- R40 Possible risk of irreversible effects.

1.5 Personal protection

Safety glasses. Suitable ventilation.

Safety phrases:

- S7 Keep container tightly closed.
- S16 Keep away from sources of ignition.
- S24 Avoid contact with skin.
- S25 Avoid contact with eyes.
- S36 Wear suitable protective clothing.
- S37 Wear suitable gloves.
- S39 Wear eye / face protection.
- S45 In case of accident or if you feel unwell, seek medical advice immediately (show the label whenever possible.)
Appendix D: Thermodynamic Properties

1. Literature Available Data

The data presented in this section are from (Reid et al., 1987), excepted when mentioned.

1.2 Liquid Heat Capacity

\[ C_p = A + BT + CT^2 + DT^3 \]  \hspace{1cm} (D.1)

with \( C_p \) (J/mol.K) and \( T \) (K).

<table>
<thead>
<tr>
<th>Constants</th>
<th>Acetaldehyde</th>
<th>Ethanol</th>
<th>Water</th>
<th>Acetal *</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>7.716</td>
<td>9.014</td>
<td>32.240</td>
<td>277.46</td>
</tr>
<tr>
<td>B</td>
<td>1.823E-01</td>
<td>2.141E-01</td>
<td>1.924E-03</td>
<td>-5.157E-1</td>
</tr>
<tr>
<td>C</td>
<td>-1.007E-04</td>
<td>-8.390E-05</td>
<td>1.055E-05</td>
<td>1.914E-3</td>
</tr>
<tr>
<td>D</td>
<td>2.380E-08</td>
<td>1.373E-09</td>
<td>-3.596E-09</td>
<td>-1.067E-6</td>
</tr>
</tbody>
</table>

* calculated from correlation (see this appendix, at section 2.2). It is mentioned at NIST Handbook the value of \( C_{p,liq} = 237.7 \) J/mol.K., for temperature range 289-382 K. It is mentioned at (Perry, 1984) the value of \( C_{p,liq} = 256.87 \) J/mol.K., for temperature range 292-372 K.
1.2 Vapour Pressure

\[
\log P_v = A + \frac{B}{C + T} \tag{D.2}
\]

\[
\log P_{v,p} = \left(A x + B x^{1.5} + C x^{3} + D x^{6}\right) \left(1 - x\right) \tag{D.3}
\]

with \(P_v\) (bar) and \(T\) (K).

<table>
<thead>
<tr>
<th>Table D.2.</th>
<th>Constants used for vapour pressure calculation.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Acetaldehyde</td>
</tr>
<tr>
<td>Equation</td>
<td>1</td>
</tr>
<tr>
<td>A</td>
<td>-7.04687</td>
</tr>
<tr>
<td>B</td>
<td>0.12142</td>
</tr>
<tr>
<td>C</td>
<td>-2.66037E-02</td>
</tr>
<tr>
<td>D</td>
<td>-5.90300</td>
</tr>
<tr>
<td>T_{min} (K)</td>
<td>273.0</td>
</tr>
<tr>
<td>T_{max} (K)</td>
<td>Tc</td>
</tr>
</tbody>
</table>

* NIST Handbook

1.3 Reaction thermochemistry data

<table>
<thead>
<tr>
<th>Table D.3.</th>
<th>Standard reaction thermochemistry data.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Properties</td>
<td>Acetaldehyde</td>
</tr>
<tr>
<td>(\Delta H_i^\circ) (kJ/mol)</td>
<td>-196.4 *</td>
</tr>
<tr>
<td>(\Delta G_i^\circ) (kJ/mol)</td>
<td>-128.08</td>
</tr>
<tr>
<td>(S^0) (J/mol.K)</td>
<td>117.3 *</td>
</tr>
<tr>
<td>(\Delta H_v^0) (kJ/mol)</td>
<td>25.76 *</td>
</tr>
</tbody>
</table>

* NIST Handbook
** (Wagnan et al., 1982)
# (Smith and Van Hess, 1987)
& \(\Delta H^\circ_{t, gas} = -453.5 \pm 2.3 \text{ kJ/mol} \) (NIST Handbook)
2. Properties Estimation

The correlation presented in this section are from (Reid et al, 1987), excepted when mentioned.

2.1 Estimation of critical properties

Critical temperature, pressure and volume could be calculated with Joback modification of Lydersen’s method, using the following relations:

\[ T_c = T_b \left[ 0.584 + 0.965 \sum \Delta_T - \left( \sum \Delta_T \right)^2 \right] \]  

\[ P_c = \left( 0.113 + 0.00329 \eta_A - \sum \Delta_P \right)^2 \]  

\[ V_c = 17.5 + \sum \Delta_V \]  

The acentric factor \( \omega \) could be estimated from the value of the critical compressibility factor, \( Z_c \), accordingly to:

\[ Z_c = \frac{P_c V_c}{RT_c} = 0.291 - 0.080 \omega \]

2.2 Estimation of liquid heat capacity

The liquid heat capacity for acetal was calculated with group contributions for Missenar method, at several temperatures. The values are presented at Table D.4.

<table>
<thead>
<tr>
<th>Table D.4.</th>
<th>Heat capacity of acetal.</th>
</tr>
</thead>
<tbody>
<tr>
<td>T (K)</td>
<td>273</td>
</tr>
<tr>
<td>Cp (J/mol.K)</td>
<td>257.6</td>
</tr>
</tbody>
</table>

2.3 Estimation of molar volume

The molar volumes for all components were estimated with Gunn-Yamada method:
\[ V(\tau) = \frac{f(\tau)}{f(\tau^R)} V^R \]  
(D.8)

where

\[ f(\tau) = H_1 \left(1 - \omega H_2 \right) \]  
(D.9)

\[ H_1 = 0.33593 + 0.33953 \tau + 1.51941 \tau^2 - 2.02512 \tau^3 + 1.11422 \tau^4 \]  
(D.10)

\[ H_2 = 0.29607 - 0.09045 \tau - 0.04842 \tau^2 \]  
(D.11)

\[ T_r = \frac{T}{T_c} \text{ or } \frac{T^R}{T_c} \]  
(D.12)

\( V^R \) is the molar volume at the reference temperature \( T^R \) (cm\(^3\)/mol), \( \omega \) is the acentric factor and \( T_c \) is the critical temperature (K).

The Gunn-Yamada method could be used just in the case when the liquid molar volume is known at some temperature (reference temperature). The reference molar volumes are presented at Table D.5.

**Table D.5. Molar volumes at the reference temperature used for all calculations.**

<table>
<thead>
<tr>
<th>Components</th>
<th>Acetaldehyde</th>
<th>Ethanol</th>
<th>Acetal</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar volume - V (cm(^3)/mol)</td>
<td>56.625</td>
<td>54.389</td>
<td>142.21</td>
<td>18.051</td>
</tr>
<tr>
<td>Reference temperature - T(^R) (K)</td>
<td>293.0</td>
<td>293.0</td>
<td>293.0</td>
<td>293.0</td>
</tr>
</tbody>
</table>

2.4 Estimation of viscosity

The viscosity of pure component could be calculated by the Przetakiewicz and Sridhar method by using the Hildebrand-modified Batschinski equation:

\[ \eta = \frac{V_0}{E(V - V_0)} \]  
(D.13)
where $\eta_l$ is liquid viscosity (cP), $V$ is liquid molar volume (cm$^3$/mol) and the parameters $E$ and $V_0$ are defined below:

$$E = -1.12 + \frac{V_c}{12.94 + 0.10M - 0.23P_c + 0.0424T_f - 11.58(T_f/T_c)} = 17.567 \quad (D.14)$$

$$V_0 = 0.0085\omega T_c - 2.02 + \frac{V_m}{0.342(T_f/T_c) + 0.894} = 123.31 \quad (D.15)$$

where $T_c$ is critical temperature (K), $P_c$ is critical pressure (bar), $V_c$ is critical volume (cm$^3$/mol), $M$ is molecular weight (g/mol), $\omega$ is acentric factor (dimensionless), $T_f$ is freezing point (K) and $V_m$ is liquid molar volume at $T_m$ (cm$^3$/mol).

<table>
<thead>
<tr>
<th>Table D.6. Viscosity of acetal.</th>
</tr>
</thead>
<tbody>
<tr>
<td>T (°C)</td>
</tr>
<tr>
<td>η (cP)</td>
</tr>
</tbody>
</table>

### 2.5 Estimation of molecular diffusivity

The diffusivities in multicomponent liquid mixture were estimated by the modified Wilke-Chang equation, proposed by Perkins and Geankoplis:

$$D_{am} = 7.4 \times 10^{-8} \left( \frac{\phi M}{\mu V_{ml,A}^{0.6}} \right)^{1/2} T$$

$$\phi M = \sum_{j=1, j\neq A}^{n} x_j \phi_j M_j \quad (D.17)$$

where $D_{am}$ is the diffusion coefficient for a dilute solute $A$ into a mixture of $n$ components, $T$ is the temperature, $V_{ml,A}$ is the molar volume of the solute $A$, $x_j$ is the molar fraction for component $j$, $\phi_j$ is the association factor for component $j$, that is equal to 2.6 for water, 1.5
for ethanol and 1.0 for unassociated components. The mixture viscosity, $\mu$, was predicted by the generalized corresponding states method purposed by Teja and Rice (Teja and Rice, 1981).

3. References


Appendix E: Kinetic results for Amberlyst 18

1. Comparison between experimental and simulated results

The experiments were realized at pressure $P = 6$ atm, using a mass of catalyst of $w_{cat} = 0.5$ g, with pellet diameter $d_p = 267 \, \mu m$ at stirrer speed of 800 r.p.m. The figures below show the comparison between experimental and simulated results (model 2, using activities), for temperatures of 16, 20 and 26 $^\circ$C, for different initial ratio of reactants: 1.47, 2.17 and 3.34.

![Graph showing experimental and simulated number of moles of ethanol, acetaldehyde and products as function of time: $T = 16 \, ^\circ$C, $r_{A/B} = 1.44$.](image)

*Figure D.1* Experimental and simulated number of moles of ethanol, acetaldehyde and products as function of time: $T = 16 \, ^\circ$C, $r_{A/B} = 1.44.$
Figure D.2  Experimental and simulated number of moles of ethanol, acetaldehyde and products as function of time: $T = 16 \, ^\circ\text{C}$, $r_{\text{A/B}} = 2.18$.

Figure D.3  Experimental and simulated number of moles of ethanol, acetaldehyde and products as function of time: $T = 16 \, ^\circ\text{C}$, $r_{\text{A/B}} = 3.35$. 
Figure D.4  Experimental and simulated number of moles of ethanol, acetaldehyde and products as function of time: $T = 20 \, ^\circ\text{C}$, $r_{A/B} = 1.47$.

Figure D.5  Experimental and simulated number of moles of ethanol, acetaldehyde and products as function of time: $T = 20 \, ^\circ\text{C}$, $r_{A/B} = 2.18$. 
Figure D.6  Experimental and simulated number of moles of ethanol, acetaldehyde and products as function of time: $T = 20 \, ^\circ C$, $r_{A/\text{B}} = 3.34$.

Figure D.7  Experimental and simulated number of moles of ethanol, acetaldehyde and products as function of time: $T = 26 \, ^\circ C$, $r_{A/\text{B}} = 1.51$. 

Figure D.8  Experimental and simulated number of moles of ethanol, acetaldehyde and products as function of time: $T = 26\, ^\circ\mathrm{C}$, $r_{A/B} = 2.18$.

Figure D.9  Experimental and simulated number of moles of ethanol, acetaldehyde and products as function of time: $T = 26\, ^\circ\mathrm{C}$, $r_{A/B} = 3.12$. 
Appendix F: Effectiveness factor of a slab catalyst for reversible reaction \( A \rightleftharpoons B \)

In order to understand the concept of effectiveness factor in a batch reactor when the equilibrium is achieved, the case of a slab porous catalyst where a first-order reversible chemical reaction \( A \rightleftharpoons B \) takes place is studied. This is an extension of the work of Paiva and Malcata, 1997.

1. Effectiveness factor in an infinite bath

Let us consider a slab porous catalyst, as shown in figure.

Assuming a first-order reversible chemical reaction \( A \rightleftharpoons B \), the mass balance equations for an infinite bath at steady state are:

\[
D_A \frac{d^2 C_A}{dx^2} - (k_A C_A - k_B C_B) = 0 \quad \text{(F.1)}
\]

\[
D_B \frac{d^2 C_B}{dx^2} + (k_A C_A - k_B C_B) = 0 \quad \text{(F.2)}
\]
with the boundary conditions (i=A, B):

\[ x = 0 \quad \frac{dC_i}{dx} = 0 \quad \text{(F.3)} \]

\[ x = L_p \quad C_i = C_{i,s} \quad \text{(F.4)} \]

Since in the steady-state the sum of the diffusional fluxes of all species is zero, the mass balance to product B may be written as:

\[ D_A \frac{dC_A}{dx} + D_B \frac{dC_B}{dx} = 0 \quad \text{(F.5)} \]

Integration of equation (F.5) using the stated boundary condition yields:

\[ C_B = C_{B,s} + \frac{D_A}{D_B} \left( C_{A,s} - C_A \right) \quad \text{(F.6)} \]

The analytical solution for the internal concentration profile is (for all \( C_{A,0} \) and \( C_{B,0} \)):

\[ \frac{C_A}{C_{A,s}} = \frac{K_{eq} - r_s \cosh(\alpha x / L_p)}{K_{eq} + \gamma \cosh(\alpha)} + \frac{r_s + \gamma}{K_{eq} + \gamma} \quad \text{(F.7)} \]

where

- equilibrium constant: \( K_{eq} = k_A / k_B \)  
  \[ \text{(F.8)} \]
- diffusivities ratio: \( \gamma = D_A / D_B \)  
  \[ \text{(F.9)} \]
- surface concentrations ratio: \( r_s = C_{B,s} / C_{A,s} \)  
  \[ \text{(F.10)} \]
- Thiele modulus: \( \phi = L_p \sqrt{\frac{k_A}{D_A}} \)  
  \[ \text{(F.11)} \]
- modified Thiele modulus: \( \alpha = \phi \sqrt{1 + \gamma / K_{eq}} \)  
  \[ \text{(F.12)} \]

Defining the effectiveness factor as:
\[
\eta = \frac{1}{2AL} \int_L^0 \left[ k_A C_A(x) - k_B C_B(x) \right] dx \\
(F.13)
\]

after integration and algebraic rearrangement, become:

\[
\eta = \frac{\tanh(\alpha)}{\alpha} \\
(F.14)
\]

that is independent of the surface concentration.

As an example, let us consider the following parameter values:

\[
\begin{align*}
L_p &= 1 \times 10^{-3} \text{ m} \\
D_A &= 2 \times 10^{-8} \text{ m}^2/\text{s} \\
D_B &= 1 \times 10^{-8} \text{ m}^2/\text{s} \\
k_A &= 0.02 \text{ s}^{-1} \\
k_B &= 0.2 \text{ s}^{-1}
\end{align*}
\]

\[
\{ \begin{array}{c}
\gamma = 2 \\
\phi = 1 \\
\alpha^2 = 21
\end{array} \}
\]

\[
\eta = 0.21817
\]

2. Effectiveness factor in an batch reactor

The mass balance equations in a batch reactor for a transient state are:

- for the bulk:

\[
\frac{\partial C_{b, A}}{\partial t} = -\frac{A_p}{V_{liq}} \frac{D_A}{L_p} \frac{\partial C_A}{\partial x} \bigg|_{x=L_p} \\
(F.15)
\]

\[
\frac{\partial C_{b, B}}{\partial t} = -\frac{A_p}{V_{liq}} \frac{D_B}{L_p} \frac{\partial C_B}{\partial x} \bigg|_{x=L_p} \\
(F.16)
\]

\[
\frac{A_p}{V_{liq}} = \frac{1}{L_p} \frac{V_B}{V_{liq}} \\
(F.17)
\]
inside the particle:

\[ \varepsilon_p \frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial x^2} - (k_A C_A - k_B C_B) \]  \hspace{1cm} (F.18)

\[ \varepsilon_p \frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2} + (k_A C_A - k_B C_B) \]  \hspace{1cm} (F.19)

with the boundary conditions (i=A, B):

\[ x = 0 \hspace{1cm} \frac{dC_i}{dx} = 0 \]  \hspace{1cm} (F.20)

\[ x = L_p \hspace{1cm} C_i = C_{b,i} \]  \hspace{1cm} (F.21)

and initial conditions (i=A, B):

\[ t = 0 \hspace{1cm} C_i = 0 \]
\[ C_{b,i} = C_{i,x} \]  \hspace{1cm} (F.22)

For the values used in example before, the effect of \( V_p / V_{\text{iq}} \) (\( \varepsilon_p = 0.4 \)) on bulk concentration is shown in the figure below:

**Figure F.1** Effect of the parameter \( V_p / V_{\text{iq}} \) in the bulk concentration profiles.
For small value of $V_p/V_{liq}$ the bulk composition almost does not change with time (infinite bath) and the effectiveness factor tends to the value determined by the infinite bath, as shown in the table below:

<table>
<thead>
<tr>
<th>$V_p/V_{liq}$</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.22227</td>
</tr>
<tr>
<td>0.1</td>
<td>0.21900</td>
</tr>
<tr>
<td>0.01</td>
<td>0.21825</td>
</tr>
<tr>
<td>0.001</td>
<td>0.21818</td>
</tr>
</tbody>
</table>

**Table F.1** Effect of the parameter $V_p/V_{liq}$ in the bulk concentration profiles.

From the results obtained from the infinite bath model, where the effectiveness factor does not change with the external (surface) composition, it was reasonable to expect the same effectiveness factor for the batch reactor. However, Table F.1 shows that the effectiveness factor for finite bath (batch reactor) is different from that obtained with infinite bath. The explanation for such difference is that the internal concentration profile at a certain time is not in equilibrium with the surface concentration.

The internal concentration profiles were calculated from a complete batch reactor model and from a pseudo-steady state batch reactor model (the time derivative in Equation F.18 is zero), where the internal concentration profile is at each moment in equilibrium with the surface concentration. Figure F.2 shows the bulk concentration history from the transient and the pseudo steady-state models. The effectiveness factors obtained were 0.22227 and 0.21817, respectively. The internal concentration profiles, at various times, are shown in Figure F.3. It is possible to conclude:

- the effectiveness factor is independent on the surface composition, if the internal concentration profile is in equilibrium with the surface concentration;

- the effectiveness factor for the batch reactor, assuming a pseudo steady-state (at each time the internal profiles are in equilibrium with the surface composition), is equal to the value obtained in the infinite bath.
Figure F.2  Bulk concentration profiles: comparison between the transient and pseudo steady-state models; $V_p/V_{eq} = 0.5$.

Figure F.3  Internal concentration profiles: comparison between the transient and pseudo steady-state models, at several times.

References
Appendix G: Adsorption and Diffusion in Bidisperse Pore Structures

1. Abstract

Transient diffusion and adsorption processes of one component in a bidisperse pore system are studied. The solid network is described by the branched micro-macropore model. A criterion to identify the controlling mechanism: macropore diffusion, micropore diffusion or both is suggested. This criterion based in diffusional information and pellet geometry is compared with the criterion for bidisperse systems with homogeneous diffusion at the microscale level. The effects of the nature of adsorption isotherm (linear, Langmuir and irreversible) in concentration profiles and in uptake are analysed. The mathematical model is analytically solved for linear systems and solutions for the macropore or micropore diffusion control cases were also obtained. Numerical solutions of concentration in macro and micropores for the three isotherms were obtained using orthogonal collocation in finite elements. For irreversible systems an analytical expression for uptake is derived based in a simplified model. The time dependence of the uptake for the three possible mechanisms is also addressed.
2. Introduction

There are several processes in chemical engineering, e.g., heterogeneous catalytic reactions, adsorption, ion exchange, whose performance depends on the diffusional process inside the network structure of the solid. The exact knowledge of the solid network is crucial to simulate, design and optimise a process. Since most solids have an irregular and complex matrix, with respect to size and shape of the pores, there is a need to use models that describe as best as possible the porous structure.

Solids with a bidisperse pore size distribution are of particular interest because they provide large pores for transport and narrow pores for the adsorption capacity; therefore, there is a need to consider diffusion in both macro and micropores. The use of single pore diffusivities methods to model adsorption kinetics in bidisperse pore systems may lead to erroneous interpretation of experimental data.

The first and more used model was developed by Ruckenstein et al.\textsuperscript{1}, who considers a spherical macroporous pellet to be an assembly of small microspheres. The adsorbate diffuses into macropores, adsorbs on the macropore walls, and also diffuses into the micropores and is adsorbed there. Recently, this model was used by Leitão et al.\textsuperscript{2} to determine the effectiveness of bidisperse catalysts, by Tajiri et al.\textsuperscript{3} to study adsorption induced convection in the macropores of a bidisperse adsorbent particle. Latter, Ruthven and Loughlin\textsuperscript{4} adopted an equivalent model, considering microspheres as homogeneous gel particles, where the adsorbed phase diffuses. This model was used by Quinta-Ferreira and Rodrigues\textsuperscript{5} to study diffusion and reaction in ion exchange resin and by Silva and Rodrigues\textsuperscript{6} for analysis of ZLC technique for diffusivity measurements in bidisperse porous pellets. Similar models have been applied to different systems (Sun and Meunier\textsuperscript{7}; Bathia\textsuperscript{8}).

Turner\textsuperscript{9} proposed a model structure shown in Figure G.1, including macropores for the transport and micropores to provide capacity of adsorption or reaction, which was also used later by Villermaux et al.\textsuperscript{10}. Tartarelli et al.\textsuperscript{11} used this model for the analysis of diffusion and reaction in a catalyst with a bidisperse pore structure. Mann\textsuperscript{12} adopted an identical basic structure, arranged in a parallel bundle model, to simulate deactivation of a supported zeolite catalyst. Recently, Petersen\textsuperscript{13} adopted the Turner structure of a bidisperse model to study
adsorption in irreversible systems, because of its simplicity and because the geometry of macro and micropores and the diffusivities within pores are then well defined.

In this paper, we study the adsorption process in a bidisperse solid in a transient state considering linear, Langmuir and irreversible isotherms only at the micropore. Therefore, it is an extension of Ruckenstein’s work to nonlinear adsorption equilibrium with negligible macropore adsorption. The pore network was modelled using a Turner pore structure, because of its simplicity which allows easy visualization of concentration profiles inside macro and micropores. The objectives are:

- to analyse the influence of the nature of adsorption isotherm in concentration profiles inside the pellet;
- to analyse the time dependence of the uptake;
- to identify the regions corresponding to the various diffusion controlling mechanisms.
3. Theoretical Model

The network structure is represented in figure 1, in which all pores are assumed to be cylindrical and both macropores and micropores have uniform size. Macropore dimensions are the half-length ($L_e$) and the radius ($r_e$) and 1, and $r_e$ are the length and radius of micropores, respectively.

The particle is initially empty. At time zero a step change in the concentration of the adsorbate external of the particle is made. The adsorbate diffuses into the macropore and then into the micropores where it is adsorbed. Constant temperature and pressure are assumed.

The mass balance for macropore is:

$$\frac{\partial}{\partial z} \left[ -D_m \frac{\partial C_m}{\partial z} \right] + \frac{\partial C_m}{\partial t} + nP \frac{A_t}{A_m} \left( -D_m \frac{\partial C_m}{\partial y} \right) \bigg|_{z=0} = 0 \quad (G.1)$$

where $D_m$ and $D_m$ are the diffusivities of macro and micropore (m$^2$ s$^{-1}$), respectively, $C_m$ and $C_t$ are the concentration of adsorbate in macro and micropore (mol m$^{-3}$), respectively, $z$ is the spatial co-ordinate of macropore (m), $y$ is the spatial co-ordinate of micropore (m), $n$ is the number of micropores for superficial area of macropore (m$^{-2}$), $P$ is the macropore perimeter (m), $A_t$ and $A_m$ are the cross-section areas of macro and micropores (m$^2$), respectively, and $t$ is the time variable (s).

The first term of Equation (G.1) represents the variation of diffusional flux, the second the accumulation in the macropore volume and the third the diffusional flux at the micropore mouth.

The initial and boundary conditions are:

$$t = 0 \quad C_m = 0 \quad (G.2.a)$$

$$z = 0 \quad C_m = C_m \quad (G.2.b)$$

$$z = L_e \quad \frac{dC_m}{dz} = 0$$

Since adsorption occurs in micropores, the mass balance in a micropore volume element depends on the adsorption equilibrium isotherm. Three adsorption isotherms will be considered:

**Linear isotherm**

$$q = \frac{Q_0}{C_i} C_i \quad (G.3.a)$$
Langmuir isotherm

\[ q = Q \frac{kC_i}{1 + kC_i} \quad (G.3.b) \]

Irreversible isotherm

\[ q = Q_0 \quad (C_i > 0) \quad (G.3.c) \]

where \( q \) is the amount adsorbed per unit of micropore surface area (mol m\(^{-2}\)), and \( Q_0 \) is the adsorbed concentration at \( C_i \) concentration, \( k \) is the Langmuir constant (mol\(^{-1}\) m\(^2\)) and \( Q \) is the monolayer capacity (mol m\(^{-2}\)).

The mass balance for micropore for linear and Langmuir isotherms is:

\[ \frac{\partial}{\partial y} \left[ -D_i \frac{\partial C_i}{\partial y} \right] + \frac{\partial C_i}{\partial t} + \frac{P_i}{A_i} \frac{\partial q}{\partial t} = 0 \quad (G.4) \]

where \( P_i \) is the micropore perimeter (m).

The first term of Equation (G.2) is due to the variation of diffusional flux, the second and third to accumulation in the fluid and adsorbed phases in the micropore, respectively.

The initial and boundary conditions are:

\[ \begin{align*}
  \tau &= 0 \quad & C_i &= 0 \quad (G.5.a) \\
  y &= 0 \quad & C_i &= C_a \quad (G.5.b) \\
  y &= L_i \quad & \frac{d}{dy} C_i &= 0
\end{align*} \]

Since irreversible systems lead to a discontinuity in the adsorbed phase concentration it is necessary to write two mass balances in distinct zones of the micropore. Accordingly to the adsorption front model shown in Figure G.2, the conservation equations for micropore are:

- mass conservation of adsorbate in the diffusion zone:

\[ \frac{\partial}{\partial y} \left[ -D_i \frac{\partial C_i}{\partial y} \right] + \frac{\partial C_i}{\partial t} = 0 \quad (G.6) \]

- conservation equation for the front:

\[ -A_i D_i \frac{\partial C_i}{\partial y} \bigg|_{y=y^*} = P_i Q \frac{\partial y^*}{\partial t} \quad (G.7) \]

where \( y^* \) is the micropore position at which the adsorbate concentration is zero (Figure G.2).

The initial and boundary conditions are then:

\[ \begin{align*}
  \tau &= 0 \quad & C_i &= y^* = 0 \quad (G.8.a) \\
  y &= 0 \quad & C_i &= C_a \quad (G.8.b)
\end{align*} \]
Figure G.2  Moving adsorption front model, for irreversible isotherms.

Introducing the dimensionless variables:

- for fluid phase concentration in macro and micropore, respectively
  \[ \psi_a = \frac{C_a}{C_0}, \quad \psi_i = \frac{C_i}{C_0} \]

- for adsorbed phase concentration
  \[ \theta = \frac{q}{Q_0} \]

- for spatial co-ordinate in macro and micropore, respectively
  \[ \zeta = \frac{z}{L_m}, \quad \varphi = \frac{y}{L_i} \]

- for time co-ordinate
  \[ \tau = \frac{t}{\tau_{dd}} \]

and the parameters:

\[ \beta = 2 n \pi r_i^3 \frac{L_i}{r_a} \]

\[ \gamma = \frac{r}{\tau_{dd}} \]
\[ \kappa = \frac{2Q_0}{r_t C_0} \]

where \( \tau_d = \frac{r_t^2}{D_l} \) and \( \tau_{d_a} = \frac{r_a^2}{D_a} \).

The model equations become:

- **macropore mass balance**

\[
\frac{\partial^2 \psi_a}{\partial \zeta^2} + \beta \gamma \frac{\partial \psi_a}{\partial \omega} \bigg|_{\omega=0} = \gamma \frac{\partial \psi_a}{\partial \tau} \tag{G.9}
\]

with the initial and boundary conditions:

\begin{align*}
\tau &= 0 \quad \psi_a = 0 \quad \text{(G.9.a)} \\
\zeta &= 0 \quad \psi_a = 1 \quad \text{(G.9.b)} \\
\zeta &= 1 \quad \frac{d \psi_a}{d \zeta} = 0
\end{align*}

- **micropore mass balance**

for linear isotherm

\[
\frac{\partial^2 \psi_l}{\partial \omega^2} = (1 + \kappa) \frac{\partial \psi_l}{\partial \tau} \tag{G.10.1}
\]

for Langmuir isotherm

\[
\frac{\partial^2 \psi_l}{\partial \omega^2} = \left(1 + \kappa \frac{1 + k'}{1 + k' \psi_l \gamma} \right) \frac{\partial \psi_l}{\partial \tau} \tag{G.10.2}
\]

where \( \kappa' = k C_0 \) is the dimensionless Langmuir constant. The initial and boundary conditions for both Equations (G.10.1) and (G.10.2) are:

\begin{align*}
\tau &= 0 \quad \psi_l = 0 \quad \text{(G.10.a)} \\
\omega &= 0 \quad \psi_l = \psi_a \\
\omega &= 1 \quad \frac{d \psi_l}{d \omega} = 0
\end{align*}

- **micropore mass balance, for irreversible isotherm**

\[
\frac{\partial^2 \psi_l}{\partial \omega^2} = \frac{\partial \psi_l}{\partial \tau} \tag{G.11.1}
\]

\[
\frac{d \psi_l}{d \omega} \bigg|_{\omega=\omega^*} = -\kappa \frac{\partial \omega^*}{\partial \tau} \tag{G.11.2}
\]

and the initial and boundary conditions for Equations (G.11.1) and (G.11.2) are:
\[ \tau = 0 \quad \psi_i = \varphi^* = 0 \quad \text{(G.11.a)} \]
\[ \varpi = 0 \quad \psi_i = \psi \quad \text{(G.11.b)} \]
\[ \varpi = \varpi^* \quad \psi_i = 0 \quad (\varphi^* < 1) \quad \text{and} \quad \frac{d \psi_i}{d \varpi} = 0 \quad (\varphi^* = 1) \]

Several quantities are needed to understand the system behaviour:
- Dimensionless average micropore concentration, \( \psi_m \)

Neglecting micropore radial concentration gradients, \( \psi_m \) is defined as:
\[ \psi_{i,m} = \int_0^{L_i} \psi_i \, d\varpi = \int_0^{L_i} \psi_i \, d\varpi \quad \text{(G.12)} \]

- Fraction uptake, \( F \)

The total capacity of the particle for adsorbate for the concentration \( C_0 \) is:
\[ M_1 = (2 \pi r_c L_r) \left[ n \pi r_c L_\gamma Q_0 \right] \quad \text{(G.13)} \]

and the amount adsorbed at any time is:
\[ M = n \pi r_c L_\gamma \int_0^{L_c} q \, dy \, dz = n \pi r_c L_\gamma L_r L_c \int_0^{L_c} q \, d\varpi \, d\zeta \quad \text{(G.14)} \]

\[ = n \pi r_c L_\gamma L_r L_c L_\gamma Q_0 \psi_{i,m} \psi_i \quad \text{(for linear isotherm)} \quad \text{(G.14.a)} \]

\[ = n \pi r_c L_\gamma L_r L_c L_\gamma Q_0 (1 + k') \int_0^{L_c} \frac{\psi_i}{1 + k' \psi_i} \, d\varpi \, d\zeta \quad \text{(for Langmuir isotherm)} \quad \text{(G.14.b)} \]

\[ = n \pi r_c L_\gamma L_r L_c Q_0 \psi_i \, d\zeta \quad \text{(for irreversible isotherm)} \quad \text{(G.14.c)} \]

The fraction uptake is defined as \( F = M / M_1 \), and so:
\[ F = \int_0^{L_c} \frac{q}{Q_0} \, d\varpi \, d\zeta \quad \text{(G.15)} \]

\[ = \int_0^{L_c} \psi_{i,m} \, d\zeta \quad \text{(for linear isotherm)} \quad \text{(G.15.a)} \]

\[ = \int_0^{L_c} \frac{(1 + k') \psi_i}{1 + k' \psi_i} \, d\varpi \, d\zeta \quad \text{(for Langmuir isotherm)} \quad \text{(G.15.b)} \]

\[ = \int_0^{L_c} \varphi^* \, d\zeta \quad \text{(for irreversible isotherm)} \quad \text{(G.15.c)} \]
4. Analytical Solution for Linear Systems

Model equations might be analytically solved when the equilibrium adsorption isotherm is linear (see sub-Appendix G1). The expressions for macro and micropores concentrations and for the fraction adsorbed \( F \) are, respectively:

\[
\psi_n = 1 - \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} (-1)^n \frac{4 \pi (n + 0.5) \cos \left[ \pi (n + 0.5) (1 - z_m) \right] \exp\left(-z_m^2 \frac{\tau}{(1 + \kappa)}\right)}{\gamma z_m \left[ \frac{2z_m}{(1 + \kappa)} + \beta \left( \tan z_m + z_m (1 + \tan^2 z_m) \right) \right]}
\]  
(G.16)

\[
\psi_r = 1 - \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} (-1)^n \frac{4 \pi (n + 0.5) \cos \left[ \pi (n + 0.5) (1 - z_m) \right] \exp\left(-z_m^2 \frac{\tau}{(1 + \kappa)}\right) \cos\left(z_m (1 - \omega)\right)}{\gamma z_m \left[ \frac{2z_m}{(1 + \kappa)} + \beta \left( \tan z_m + z_m (1 + \tan^2 z_m) \right) \right] \cos z_m}
\]  
(G.17)

\[
F = 1 - \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} (-1)^n \frac{4 \tan z_m \exp\left(-z_m^2 \frac{\tau}{(1 + \kappa)}\right)}{\gamma z_m \left[ \frac{2z_m}{(1 + \kappa)} + \beta \left( \tan z_m + z_m (1 + \tan^2 z_m) \right) \right]}
\]  
(G.18)

where \( z_m \) are the roots of the transcendental equations:

\[
\lambda_n = - \pi^2 (n + 0.5)^2
\]  
(G.19)

\[
- \gamma \left( \frac{z_m^2}{1 + \kappa} + \beta z_m \tan z_m \right) = \lambda_n
\]  
(G.20)

5. Numerical Solution of the Problem

a) Linear and Langmuir adsorption isotherms

The complete solution of the pair of partial differential equations, Equations (G.9) and (G.10), was obtained by orthogonal collocation in finite elements. Hermite polynomials of third degree were used for micropore spatial discretization. The micropore was discretized in \( N \) subintervals, with two internal collocation points in each subinterval, resulting in \( 2N \) time ordinary differential equations for the micropore. This set of equations together with macropore conservation equation were integrated in PDECOL package\(^\text{14} \). For the macropore, \( M \) subintervals were used, with two internal collocation points in each subinterval, resulting in \( 2(2N+1)(M+1) \) time ordinary differential equations that were integrated to obtain macro and micropore concentrations.
In Figure G.3, numerical solutions using 10 subintervals in micro and macropore are compared with analytical solutions using 20 terms in the series for Equation (G.16) and 44 for Equation (G.17).

![Graph](image)

**Figure G.3** - Comparison of analytical and numerical solutions for linear isotherm with $\kappa = 10, \beta = 1, \gamma = 1$ and $t = 4\tau$.

a) Dimensionless macro pore fluid concentration $\psi_i$ versus $\zeta$.
b) Dimensionless micropore fluid concentration $\psi_i$ versus $\theta$ at $\zeta = 0.5$.

**b) Irreversible adsorption isotherm**

The integration of the system of partial differential equations constituted by Equations (G.9) and (G.11) consists of a moving boundary value problem with respect to diffusion equation of adsorbate - Equation (G.11.1). This moving boundary is located at $\sigma^*$ ($\tau$) and its velocity is given by Equation (G.11.2).

To solve this problem it is necessary to fix the moving boundary, which is possible with a variable change:

$$\omega^* = \frac{\sigma}{\sigma^*}$$  \hspace{1cm} (G.21)

It can be shown (sub-Appendix G2) that:

$$\frac{\partial \psi}{\partial \tau} = \frac{\partial \psi}{\partial \tau} + \frac{\partial \psi}{\partial \sigma} \left( \frac{\partial \sigma^*}{\partial \sigma} \frac{\partial \omega^*}{\partial \tau} \right)$$  \hspace{1cm} (G.22)
Using equation (G.22) and the new variable given by (G.21), equations (G.11.1) and (G.11.2) become:

\[
\frac{1}{(\alpha^*)^2} \frac{\partial^2 \psi_i}{\partial (\alpha^*)^2} + \frac{\alpha^*}{\alpha^*} \frac{\partial \psi_i}{\partial \tau} \frac{\partial \psi_i}{\partial \alpha^*} = \frac{\partial \psi_i}{\partial \tau} \tag{G.23.1}
\]

\[
\frac{d \psi_i}{d \alpha^*} \bigg|_{\alpha^*=1} = -\kappa (\alpha^*) \frac{\partial \alpha^*}{\partial \tau} \tag{G.23.2}
\]

and the initial and boundary conditions are now:

\[
\tau = 0 \quad \psi_i = 0 \quad \text{and} \quad \alpha^* = \alpha^*0 \quad \text{(G.23.a)}
\]

\[
\alpha^* = 0 \quad \psi_i = \psi_e \quad \text{(G.23.b)}
\]

\[
\alpha^* = 1 \quad \psi_i = 0 \quad (\alpha^* < 1) \quad \text{and} \quad \frac{d \psi_i}{d \alpha^*} = 0 \quad (\alpha^* = 1)
\]

The initial condition \( \alpha^* = 0 \), given by Equation (G.11.a), leads to \( \alpha^* = \infty \), so it is necessary to start the integration with a value of \( \alpha^* \) slightly up to zero (\( \alpha^*0 \)), Equation (G.23.a).

The numerical procedure was the above mentioned. The discretization of Equation (G.23.1) results in 2N time ordinary equations that together with macropore and front conservation equations were discretized in PDECOL. A total of 4(N+1)(M+1) time ordinary differential equations were integrated to obtain macro and micropore concentrations.

6. Results and Discussion

The diffusional parameter \( \gamma = \frac{\tau_{ik}}{\tau_{di}} = \left( \frac{L_i}{L_e} \right)^2 \frac{D_i}{D_e} \) gives the ratio between diffusional time constants of macro and micropore.

The parameter \( \beta \) can be written as:

\[
\beta = \frac{n \left( 2 \pi r_e L_e \right) \left( \pi r_i^2 L_i \right)}{\left( \pi r_e^2 L_e \right)} = \frac{\epsilon_i}{\epsilon_m}
\]

It depends on the structure geometry since represents the ratio of micro and macroporosity.

The proposed model for the pore network has a restriction, since the total section cross-area
of micropores \(|n(2\pi r_a L_a)(\pi r_a^2)|\) can not exceed the superficial area of macropore \((2\pi r_a L_a)\). So parameter \(\beta\) is restricted:

\[
\beta < \frac{2L_a}{r_a}
\]

Parameter \(\kappa\) represents the adsorption capacity. In the case of Langmuir there is another parameter that expresses the non-linearity of isotherm, \(K'\).

### a) Definition of a criterion to identify the controlling mechanism

The criterion that identifies the controlling mechanism, for high adsorption capacities (\(\beta \kappa \geq 1\)), is:

- \(\beta \gamma < 0.1\): micropore diffusion control. In this regime micropores have sharp concentration profiles and macropore have flat ones (see Figure G.4);
- \(\beta \gamma > 10\): macropore diffusion control. In this regime micropores have flat concentration profiles in and inside macropores there are sharp concentration profiles (see Figure G.5);
- \(0.1 < \beta \gamma < 10\): macropore-micropore diffusion control. In this regime there are concentration gradients in both macro and micropores.

**Figure G.4** Dimensionless concentration profiles, at various times, for linear isotherm with \(\kappa = 2000\), \(\beta = 1\) and \(\gamma = 0.1\): micropore diffusion control.

a) Macropore fluid concentration \(\Psi_a\) (\(200\) s; \(800\) s) and average micropore fluid concentration \(\Psi_m\) (\(200\) s; \(800\) s) versus \(\xi\).

b) Micropore fluid concentration \(\Psi\) versus \(\Omega\) at \(\zeta = 0.5\).
Figure G.5  Dimensionless concentration profiles, at various times, for linear isotherm with \( k = 2000, \beta = 1 \) and \( \gamma = 10 \): macro pore diffusion control.

a) Macro pore fluid concentration \( \psi_s \) (2000 s; 8000 s) and average micro pore fluid concentration \( \psi_{\text{av}} \) (2000 s; 8000 s) versus \( \zeta \).

b) Micro pore fluid concentration \( \psi_i \) versus \( \varpi \) at \( \zeta = 0.5 \).

It should be noted that the criterion based on the model of homogeneous diffusion for the micropores adopted by Ruthven and Loughlin\(^4\) and by Ruthven\(^13\) involves the value of \( (1 + \kappa) \beta \gamma \). This is because in that model the equilibrium isotherm equation only appears the macro pore concentration with the adsorption at the micropore mouth or surface of microparticles, while in our model we explicitly consider fluid phase concentration inside micropore in equilibrium with adsorbed phase concentration at the micropore surface, locally. This was also noticed by Liang et al.\(^{16}\) that concludes that the model of homogeneous diffusion in zeolite crystals uses apparent diffusivities in micropores that are related with effective ones by the expression:

\[
D_{\text{eff}} = \frac{D_s}{1 + \kappa} \tag{G.24}
\]

The adsorption capacity parameter, \( \kappa \), only affects the time needed to obtain a certain particle profile. In the case of a Langmuir isotherm, Figure G.6 show that for a different value of \( \kappa \) we could obtain the same profile provided we choose the right times.
The effect of the nature of the isotherm in the concentration profiles in the pellet for macropore diffusion control can be observed in Figure G.7. The adsorbate concentrations at macro and micropore for linear systems are greater than those for Langmuir and irreversible isotherms. But in irreversible systems the adsorbed phase concentration is higher than in the cases of linear and Langmuir isotherms. Figure G.8 shows in more detail what happens in the pellet for irreversible systems.

Figure G.7  Effect of the nature of adsorption isotherm in pellet dimensionless concentration profiles at time $t=500$ s, for $\kappa=100$, $\beta=10$ and $\gamma=0.1$ (macropore diffusion control).

a)  Macropore fluid phase concentration $\psi_\alpha$ versus $\zeta$.
b)  Micropore fluid phase concentration $\psi_f$ (linear, Langmuir, irreversible) and adsorbed phase concentration $\Theta$ (linear, Langmuir, irreversible) versus $\omega$ at $\zeta=1$. 
Figure G.8  Dimensionless fluid phase concentration profiles and adsorption front position, for irreversible isotherms with $\kappa=200$, $\beta=1$ and $\gamma=10$ at various times.

a)  Macropore concentration $\psi_e$ (--- 500 s; --- 1000 s), average micropore concentration $\psi_m$ (----- 500 s, ------ 1000 s) and adsorption front position $\omega^*$ (○ 500 s; ◊ 1000 s) versus $\zeta$.

b) Micro pore concentration $\psi$, versus $\omega$ at $\zeta=0.8$

We can identify three stages, at a given time. In the first one, the average micropore concentration of adsorbate is equal to the adsorbate concentration at macropore. This happens in the zone of pellet near to the surface, where the front of adsorption has already reached the end of micropore and the whole micropore has the same fluid phase concentration, the macropore concentration ($\psi_e$).

In an intermediate region, the micropore is saturated on the adsorbed phase ($\omega^*=1$), but the fluid phase is not. This stage is identified by an abrupt fall in the average micropore concentration. At the centre of the pellet, the adsorption front did not reach the end of micropore and both adsorbed and fluid phases are not saturated.

b) Effect of model parameters in adsorption uptake

Systems controlled by macropore diffusion are slowest than those controlled by micropore diffusion. For the limiting cases of macro and micropore diffusion control, this system could be modelled with a single pore. Crank\textsuperscript{17} verified that for these cases the fraction uptake $F$ is proportional to $t^{1/2}$. However, for a system where both macro and micropore diffusion are important, the fraction uptake $F$ is proportional to $t^{1/4}$. If we use the simplified mathematical
model proposed by Petersen with the parameters of this work to derive the expression for fraction uptake, we obtain:

\[
F = \left( \frac{t}{\kappa \tau_n / 2} \right)^{K_a} \left( \frac{3}{2} \beta_y \right)^{K_c}
\]  \hspace{1cm} (G.25)

This equation is valid while \( \alpha \psi_\|_{-\infty} < 1 \) and \( \psi_n \big|_{z=1} = 0 \). In Figure G.9 we compare the numerical solution of Equation (G.15,c) with the analytical solution given by Equation (G.25). The slight difference for times greater than 400 s is due to the fact that the model considered by Petersen neglected the adsorbate accumulation in the fluid phase inside micropores. Equation (G.25) shows perfectly the linearity between \( F \) and \( \beta y \) mentioned above.

![Graph showing comparison between numerical solution (Equation (G.15,c)) and analytical solution (Equation (G.25)) for fraction uptake \( F \), for irreversible isotherm with \( \kappa = 2000 \) and \( \beta y = 1 \).]

**Figure G.9**: Comparison between numerical solution (Equation (G.15,c)) and analytical solution (Equation (G.25)) for fraction uptake \( F \), for irreversible isotherm with \( \kappa = 2000 \) and \( \beta y = 1 \).

c) Effect of adsorption isotherm in uptake

The influence of the nature of the adsorption isotherm in fraction uptake is shown in Figure G.10. Linear systems are the slowest, followed by Langmuir systems, from the smallest to the greatest value of \( \kappa' \), and finally the irreversible systems. So, increasing the non-linearity of a
system with the same adsorption capacity $\kappa$ and same values of $\beta$ and $\gamma$, the process of adsorption is faster and the time needed to reach the equilibrium is lower.

![Graph showing fraction uptake $F$ vs time $t$ for different isotherms.](image)

*Figure 10 - Influence of the nature of adsorption isotherm in fraction uptake $F$, for systems with $\kappa = 2000$, $\beta=1$ and $\gamma = 10$.*

7. Conclusions

The competitive effects between macropore diffusion and micropore diffusion for the case of linear, Langmuir and irreversible adsorption equilibrium isotherms were analysed in an adsorbent with a bidisperse pore structure of Turner type in transient regime.

A criterion to identify the controlling mechanism, $\beta\gamma$, is suggested; for $\beta\gamma > 10$ macropore diffusion is the controlling mechanism, for $\beta\gamma < 0.1$ micropore diffusion is the controlling mechanism and for $0.1 < \beta\gamma < 10$ both macro and micropore diffusion are important.

Linear systems were analytically solved, for the three controlling mechanisms: macropore diffusion, micropore diffusion or both. The analytical solutions were compared with the numerical solutions and the agreement was good.

The adsorption uptake $F$ is proportional to $t^{1/2}$ for the limiting cases of macro or micropore diffusion control and is proportional to $t^{1/4}$ for the intermediate situation.
Adsorption uptake $F$ depends on the type of adsorption isotherm. The time needed to saturate the particle is lower for the case of irreversible isotherm, than for Langmuir and finally for linear isotherm for systems with the same adsorption capacity. Between systems with Langmuir isotherm, those with higher $k'$ are faster than those with low values of $k'$. Increasing the non-linearity of a system, the adsorption process becomes faster.

8. Notation

$A$ – pore section area (m$^2$)
$C$ – concentration of adsorbate in pore (mol m$^{-3}$)
$C_0$ – concentration of adsorbate at macropore mouth (mol m$^{-3}$)
$D$ – diffusivity (m$^2$ s$^{-1}$)
$D_{app}$ – apparent diffusivity, given by equation (24) (m$^2$ s$^{-1}$)
$F$ – fraction adsorbed, dimensionless
$k$ – Langmuir constant (mol$^{-1}$ m$^3$)
$k'$ – Langmuir constant, dimensionless
$L$ – pore length (m)
$M$ – total uptake at a given time (mol)
$m$ – linear isotherm decline (m)
$M_t$ – total uptake at equilibrium (mol)
$n$ – number of micropores per unit area of macropore surface (m$^{-2}$)
$P$ – pore perimeter (m)
$Q$ – monolayer capacity (mol m$^{-2}$)
$Q_0$ – adsorbed concentration in equilibrium with $C_0$ adsorbate concentration (mol m$^{-2}$)
$q$ – adsorbed amount per unit of superficial area of micropore (mol m$^{-2}$)
$r$ – pore radius (m)
$t$ – time (s)
$x$ – co-ordinate along micropore (m)
$z$ – co-ordinate along macropore (m)
Greek letters

\( \beta \) – pellet's geometry parameter, dimensionless
\( \epsilon \) – porosity, dimensionless
\( \gamma \) – diffusional parameter, dimensionless
\( \kappa \) – adsorption parameter, dimensionless
\( \Theta \) – adsorbed concentration, dimensionless
\( \tau \) – time, dimensionless
\( \tau_d \) – pore time constant, dimensionless
\( \bar{w} \) – coordinate along micropore, dimensionless
\( \bar{w}^* \) – adsorption front position, dimensionless
\( \psi \) – fluid concentration, dimensionless
\( \zeta \) – coordinate along macropore, dimensionless

Subscripts

\( a \) – macropore
\( i \) – micropore
\( \text{m} \) – average value

9. References


SUB-APPENDIX G1

Applying Laplace transforms relative to dimensionless time, the mass balance for micropore [Equation (G.10.1)] becomes:

\[ \frac{\partial^2 \tilde{\psi}_\varepsilon}{\partial \tilde{\sigma}^2} = (1 + \kappa) s \tilde{\psi}_\varepsilon \]  

(G1.1)

Considering the corresponding boundary conditions, the solution is:

\[ \tilde{\psi}_\alpha = \frac{\sinh \left(\sqrt{(1 + \kappa) s} (1 - \tilde{\sigma})\right)}{\cosh \sqrt{(1 + \kappa) s}} \]

(G1.2)

Applying Laplace transforms relative to dimensionless time, the macropore conservation equation [Equation (G.9)] becomes:

\[ \frac{\partial^2 \tilde{\psi}_\alpha}{\partial \tilde{\zeta}^2} + \beta \gamma \left. \frac{\partial \tilde{\psi}_\alpha}{\partial \tilde{\sigma}} \right|_{\tilde{\sigma} = 0} = \gamma s \tilde{\psi}_\alpha \]

(G1.3)

Inserting equation (G1.2) in the above equation we get:

\[ \frac{\partial^2 \tilde{\psi}_\alpha}{\partial \tilde{\zeta}^2} = \gamma \left( s + \beta \sqrt{(1 + \kappa) s} \tanh \sqrt{(1 + \kappa) s} \right) \tilde{\psi}_\alpha \]

(G1.4)

and the solution, using the corresponding boundary conditions, is:

\[ \tilde{\psi}_\alpha = \frac{1}{s} \frac{\cosh \sqrt{\lambda} (1 - \tilde{\zeta})}{\cosh \sqrt{\lambda}} \]

(G1.5)

where

\[ \lambda = \gamma \left( s + \beta \sqrt{(1 + \kappa) s} \tanh \sqrt{(1 + \kappa) s} \right) \]

(G1.6)

Equations (G1.5) and (G1.2) are easily inverted by introducing a new variable \( z = \sqrt{(1 + \kappa) s} \) and the time domain solution for the macro and micropore concentrations are, respectively:

\[ \psi_\alpha = \frac{1}{\gamma} \sum_{n = 0}^{\infty} \sum_{m = 0}^{\infty} (-1)^{n+m} 4 \pi (n + \frac{1}{2}) \cos \left( \pi (n + \frac{1}{2}) (1 - \tilde{\zeta}) \right) \exp \left( -z^2 \frac{\tau}{1 + \kappa} \right) \]

\[ \psi_\varepsilon = \frac{1}{\gamma} \sum_{n = 0}^{\infty} \sum_{m = 0}^{\infty} (-1)^{n+m} 4 \pi (n + \frac{1}{2}) \cos \left( \pi (n + \frac{1}{2}) (1 - \tilde{\zeta}) \right) \exp \left( -z^2 \frac{\tau}{1 + \kappa} \right) \cos \left( \frac{\pi z_{n,m}}{\sqrt{1 + \kappa}} \right) \cos \left( \frac{\pi z_{n,m}}{\sqrt{1 + \kappa}} \right) \]

where \( z_{n,m} \) and \( \lambda_n \) are the roots of the transcendental equations:
\[ \lambda_n = -\pi^2 \left( n + \frac{1}{2} \right)^2 \]  

\[ -\gamma \left( \frac{z_{n,m}^2}{1 + \kappa} + \beta z_{n,m} \tan z_{n,m} \right) = \lambda_n \]  

and \[ \varphi(\zeta) = \begin{cases} 
1, & \zeta = 0 \\
0, & \zeta > 0 
\end{cases} \]

Analytical expressions for the limiting cases macro or micropore diffusion control can be obtained as follows.

(a) Macropore diffusion control

In this case \( \zeta \to 0 \), so \( \zeta \tan \zeta \approx \zeta \); Equation (G1.10) becomes:

\[ \lambda_n = -\gamma \left( 1/(1 + \kappa) + \beta \right) \zeta^2 \]

and the solution is:

\[ \nu_n = -\sum_{n=1}^{\infty} \frac{2(-1)^n}{\pi (n + \frac{1}{2})} \cos \left( \pi (n + \frac{1}{2}) (1 - \zeta) \right) \exp \left[ -\frac{\pi^2 (n + \frac{1}{2})^2}{\gamma (1/(1 + \kappa) + \beta)} \right] \tau \]  

(b) Micropore diffusion control

In this case \( \lambda \to 0 \), so \( \lambda \approx 1 - \lambda^2 / 2 \); Equation (G1.5) becomes:

\[ \nu_n = -\frac{1 + \kappa}{z^2} \left( 1 - \zeta^2 \right) / 2 \]  

and the solution for micropore concentration in time domain is:

\[ \nu_n = -\sum_{n=1}^{\infty} \frac{2 (1 + \kappa) (2 \zeta - \zeta^3)}{\gamma z_m^2 + \beta (1 + \kappa) / 2 (z_m \tan z_m + z_m^2 / \cos z_m)} \exp \left( -z_m^2 \tau / (1 + \kappa) \right) \]  

where \( z_m \) are the roots of transcendental equation:

\[ \gamma \left( \frac{z_m^2}{1 + \kappa} + \beta z_m \tan z_m \right) = 2 \]  

Relatively to micropore concentration, we must consider residues resulting of the singularity \( \zeta_m = \pi (m + 1/2) \), and the time domain solution is:

\[ \psi_n = -\sum_{m=1}^{\infty} \frac{2 \cos \left( \frac{z_m (1 - \sigma)}{\rho z_m} \right)}{\sin z_m} \exp \left( -z_m^2 \tau / (1 + \kappa) \right) \]
SUB-APPENDIX G2

Let

\[ d\psi_i(\sigma, \tau) = \frac{\partial \psi_i}{\partial \sigma} \bigg|_{\tau} d\sigma + \frac{\partial \psi_i}{\partial \tau} \bigg|_{\sigma} d\tau \]  

(G2.1)

and in the new variables \( \sigma^+ \) and \( \tau \),

\[ d\psi_i(\sigma^+, \tau) = \frac{\partial \psi_i}{\partial \sigma^+} \bigg|_{\tau} d\sigma^+ + \frac{\partial \psi_i}{\partial \tau} \bigg|_{\sigma^+} d\tau \]  

(G2.2)

where

\[ d\sigma^+ = \frac{\partial \sigma^+}{\partial \sigma} \bigg|_{\tau} d\sigma + \frac{\partial \sigma^+}{\partial \tau} \bigg|_{\sigma} d\tau \]  

(G2.3)

The combination of Equations (G2.2) and (G2.3) gives:

\[ d\psi_i(\sigma^+, \tau) = \frac{\partial \psi_i}{\partial \sigma^+} \bigg|_{\tau} d\sigma^+ + \left[ \frac{\partial \psi_i}{\partial \tau} \bigg|_{\sigma} \frac{\partial \sigma^+}{\partial \sigma} \bigg|_{\tau} + \frac{\partial \psi_i}{\partial \sigma^+} \bigg|_{\tau} \frac{\partial \sigma^+}{\partial \tau} \bigg|_{\sigma} \right] d\tau \]  

(G2.4)

Since

\[ \frac{\partial \psi_i}{\partial \sigma} \bigg|_{\tau} = \frac{\partial \psi_i}{\partial \sigma^+} \bigg|_{\tau} \]  

(G2.5)

Equation (G2.4) may be written as

\[ d\psi_i(\sigma^+, \tau) = \frac{\partial \psi_i}{\partial \sigma^+} \bigg|_{\tau} d\sigma^+ + \left[ \frac{\partial \psi_i}{\partial \tau} \bigg|_{\sigma} \frac{\partial \sigma^+}{\partial \sigma} \bigg|_{\tau} + \frac{\partial \psi_i}{\partial \sigma^+} \bigg|_{\tau} \frac{\partial \sigma^+}{\partial \tau} \bigg|_{\sigma} \right] d\tau \]  

(G2.6)

Comparing Equations (G2.1) and (G2.6) we obtain:

\[ \frac{\partial \psi_i}{\partial \tau} \bigg|_{\sigma} + \frac{\partial \psi_i}{\partial \sigma^+} \bigg|_{\tau} \frac{\partial \sigma^+}{\partial \tau} \bigg|_{\sigma} = \frac{\partial \psi_i}{\partial \tau} \bigg|_{\sigma^+} + \frac{\partial \psi_i}{\partial \sigma^+} \bigg|_{\tau} \frac{\partial \sigma^+}{\partial \tau} \bigg|_{\sigma^+} \]  

(G2.7)

Inserting Equation (G.21) into Equation (G2.7) gives:

\[ \frac{\partial \psi_i}{\partial \tau} \bigg|_{\sigma} = \frac{\partial \psi_i}{\partial \tau} \bigg|_{\sigma^+} + \frac{\partial \psi_i}{\partial \sigma^+} \bigg|_{\tau} \left( \frac{\sigma^+}{\sigma^+} \frac{\partial \sigma^+}{\partial \tau} \right) \bigg|_{\sigma} \]  

(G2.8)