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IMPACT OF SUPERCRITICAL REACTION MEDIUM WITH DIFFERENT TYPES OF SOLVENTS

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different types of solvents***

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*“Para ser grande, sê inteiro: nada
Teu exagera ou exclui.
Sê todo em cada coisa. Põe quanto és
No mínimo que fazes.
Assim em cada lago a lua toda
Brilha, porque alta vive.”*

Ricardo Reis, in “Odes”
heteronym of Fernando Pessoa (1888-1935)

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Abstract

The methylacetylene and propadiene (MAPD) hydrogenation is a widely used chemical process to produce propylene. This reaction is performed in gas-solid or gas-liquid-solid, using a catalyst made of Pd/Al₂O₃. When new catalysts are tested for this reaction, the catalytic performance and the intrinsic reaction rates are of difficult evaluation, due to heat and mass transfer limitations. In order to bypass this problem, it is possible to add a solvent and perform hydrogenation in supercritical conditions. In these conditions, gas and liquid become a single phase, which has enhanced diffusion and mass transfer rates.

In this work, the MAPD hydrogenation is investigated at supercritical conditions. The aim of the report is to understand how the reaction is affected by different types of solvents (methane, ethane, carbon dioxide, and propylene). This study involved a set of experiments in a single string pellet reactor.

In the first part of this work, the MAPD diffusion coefficients (at infinite dilution) are determined through the use of correlations. The correlations are compared with each other to determine the most reliable.

In the second part, the experimental trials are presented. The tests were conducted at 120 bar for different temperatures, H₂/MAPD ratios, MAPD concentrations, and solvents. The goal is to understand the effect of each parameter.

It was found that the main reaction (MAPD to propylene) increases for higher temperatures, H₂/MAPD ratios, and MAPD concentrations. Adding solvents and working on the supercritical domain substantially increases the MAPD conversion at low residence time, due to higher diffusion and mass transfer coefficients. Moreover, different solvents achieve similar results when equal residence time is considered. It was concluded that mass transfer limitations outside the catalyst are negligible at 120 bar and 353.15 K.

Keywords: catalytic hydrogenation; MAPD; supercritical medium; diffusivity; solvents.

Resumo

A hidrogenação de metilacetileno e propadieno (MAPD) é um processo químico amplamente utilizado para a produção de propileno. Esta reação é realizada em gás-sólido ou gás-líquido-sólido, utilizando um catalisador de Pd/Al₂O₃. Quando novos catalisadores são testados para esta reação, é difícil avaliar o desempenho catalítico e as velocidades de reação intrínsecas, devido às limitações na transferência de calor e massa. A fim de ultrapassar este problema, é possível adicionar um solvente e realizar a hidrogenação em condições supercríticas. Nestas condições, o gás e líquido passam a ser uma só fase, que apresenta difusão e taxas de transferência de massa melhoradas.

Neste trabalho, a hidrogenação de MAPD é investigada em condições supercríticas. O relatório tem por objetivo entender como a reação é afetada por diferentes tipos de solventes (metano, etano, dióxido de carbono, e propileno). Este estudo envolveu um conjunto de experiências num reator de fila única com *pellets*.

Na primeira parte deste trabalho, os coeficientes de difusão do MAPD (a diluição infinita) são determinados através do uso de correlações. Estas são comparadas entre si para determinar qual a mais fiável.

Na segunda parte, são apresentados os ensaios experimentais. Os testes foram realizados a 120 bar para diferentes temperaturas, rácios de H₂/MAPD, concentrações de MAPD, e solventes. O objectivo é compreender o efeito de cada parâmetro.

Verificou-se que a reação principal (produção de propileno a partir de MAPD) aumenta para temperaturas, razões H₂/MAPD, e concentrações de MAPD mais elevadas. Adicionar solventes e trabalhar em meio supercrítico aumenta substancialmente a conversão de MAPD a baixos tempos de residência, devido aos maiores coeficientes de difusão e de transferência de massa. Além disso, diferentes solventes obtêm resultados semelhantes para iguais tempos de residência. Pode concluir-se que as limitações de transferência de massa fora do catalisador são negligenciáveis a 120 bar e 353.15 K.

Palavras-chave: hidrogenação catalítica; MAPD; meio supercrítico; difusividade; solventes.

Declaration of Honour

I hereby declare on my honour that I personally prepared the present academic work, and also that I have used no resources other than those declared.




(Bruno Filipe Pinto de Sousa)

Porto, 13 July 2015

Declaration of Confidentiality

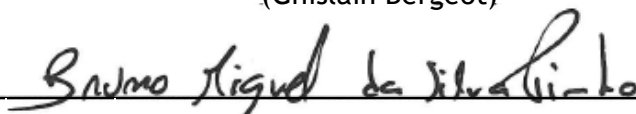
I hereby declare that the results presented in this report are confidential and cannot be published without the IFPen author's approval.



(Bruno Filipe Pinto de Sousa)



(Ghislain Bergeot)



(Bruno Miguel da Silva Pinho)

Porto, 13 July 2015

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Notation and Glossary

Equation Variables

$a, b,$ c, d	Rough Hard-spheres parameters	
D	Diffusion coefficient	$\text{m}^2\cdot\text{s}^{-1}$
D_{21}	Infinite dilution diffusion coefficient	$\text{m}^2\cdot\text{s}^{-1}$
$D_{21,mix}$	Diffusion coefficient of concentrated mixtures	$\text{m}^2\cdot\text{s}^{-1}$
d_p	Catalyst diameter	m
E_D	Mixture-dependent parameter	$\text{mol}\cdot\text{K}$
F	Molar flow rate	$\text{mol}\cdot\text{h}^{-1}$
F_{11}	Rough Hard-spheres self-diffusion factor	
F_{21}	Rough Hard-spheres correction factor	
$g(\sigma)$	Radial distribution function at contact	
K	Constant of molecular interaction	
k_B	Boltzmann constant	$\text{m}^2\cdot\text{kg}\cdot\text{s}^{-2}\cdot\text{K}^{-1}$
K_{LS}	Mass transfer coefficient	$\text{m}\cdot\text{s}^{-1}$
k_{21}, l_{21}	Intermolecular interaction parameters	
M	Molecular weight	$\text{g}\cdot\text{mol}^{-1}$
m	Weight of a molecule	kg
m_c	Mass of catalyst	kg
m_{21}	Unlike weight	kg
n_1	Solvent number density	cm^{-3}
P	Pressure	bar
p_1, p_2	Reynolds number constants	
Q_m	Hourly mass flow rate	$\text{kg}\cdot\text{h}^{-1}$
Q_V	Hourly volumetric flow rate	$\text{m}^3\cdot\text{h}^{-1}$
r	Distance between molecules	m
r_2	Solute hydrodynamic radius	m
Re	Reynolds number	
R_g	Universal gas constant	$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
Sc	Schmidt number	
Sh	Sherwood Number	
T	Temperature	K
V	Molar volume	$\text{cm}^3\cdot\text{mol}^{-1}$
v	Fluid velocity	$\text{m}\cdot\text{s}^{-1}$
V_b	Volume at boiling point temperature	$\text{cm}^3\cdot\text{mol}^{-1}$
V_d	Atomic diffusion volume	$\text{cm}^3\cdot\text{mol}^{-1}$
$V_{reactor}$	Reactor volume	m^3
X	Molar conversion	
x	Molar fraction	

Greek Letters

α	Adjustable parameter in modified hydrodynamic equation	
β	Exponential term in modified hydrodynamic equation	
ε	Energy parameter	$\text{m}^2 \cdot \text{kg} \cdot \text{s}^{-2}$
ε_L	Porosity	
η	Macroscopic viscosity	$\text{Pa} \cdot \text{s}$
μ	Viscosity	$\text{Pa} \cdot \text{s}$
ρ	Density	$\text{kg} \cdot \text{m}^{-3}$
σ	Particle size parameter	m
τ	Residence time	h^{-1}
φ	Effective RHS packing fraction	

Indices

A, B	Superscript - infinitely diluted binary mixture A and B
ET	Superscript - Enskog-Throne equation
LJ	Superscript - Lennard-Jones equation
LJ'	Superscript - Modified Lennard-Jones parameters
0	Superscript - Low-pressure conditions
*	Superscript - Reduced variable
c	Subscript - Property at critical point
i, j	Subscript - molecular species
ij	Subscript - Property of particle i in particle j
mix	Subscript - Property of the mixture
1	Subscript - Solvent
2	Subscript - Solute
21	Subscript - Property of a solute in a solvent at infinite dilution

Acronym List

AARD	Average Absolute Relative Deviations
EHS	Effective hard-sphere diameter
HS	Hard Spheres
LB	Lorentz-Berthelot
LHSV	Liquid hourly space velocity
LJ	Lennard-Jones
LSM	Liu-Silva-Macedo
MA	Methylacetylene
PD	Propadiene
SCF	Supercritical Fluid
SW	Square-Well
THF	Tetrahydrofuran
WHSV	Weight hourly space velocity
ZLWS	Zhou-Lu-Wang-Shi

1 Introduction

Many chemical processes involve the catalytic hydrogenation of a compound. In these processes, hydrogen is mixed with a substrate and both are sent to a catalytic reactor. The catalysts are either homogeneous or heterogeneous. Palladium based catalysts are commonly chosen for reactions in heterogeneous catalysis. They are particularly good in the hydrogenation of alkynes to the corresponding olefins, due to their high activity and selectivity (Wang and Froment, 2005). But many types of catalysts can be used, all depending on the substrate involved. At the same time, hydrogenations can be performed in different kinds of reactors. In general, tubular fixed-bed reactors are a good choice, as they have good mass and heat transfer properties (Baiker, 1999).

Hydrogenation can be done in gas-phase or gas-liquid-phases (Bertuccio A. and Vetter G., 2001). In the first case, substrate and hydrogen are very well mixed (same physical state) and large amounts of reactant can be available near the catalyst. Good mass transfer characteristics lead to higher reaction rates. Unfortunately, it can only be used if volatile molecules are concerned. Otherwise, very high temperatures are needed to keep the substrate gaseous. Moreover, hydrogenation reactions are normally exothermic, and gases have poor heat-transport properties. Therefore, low substrate concentration near the catalyst is needed to limit reaction rate and temperature increase. This is not a problem for gas-liquid reaction, as liquids conduct heat very well. Additionally, the vaporization of part of the reactant limits temperature increase. However, other problems arise, mainly related to the low solubility of hydrogen in these systems. As a result, very small concentration of hydrogen is present near the catalyst. So, even if the catalyst is very active, the reaction rate will be low. In these cases, reaction is therefore controlled by diffusion (Baiker, 1999; Bertuccio A. and Vetter G., 2001). On the other hand, catalyst deactivation is slower than in gas-phase, as liquids can more easily remove undesired compounds from the surface of the catalyst. This reduces operating costs and increases the catalyst life (Baiker, 1999; Wu and Li, 2011).

Heat and mass transfer resistances in hydrogenation processes make catalytic screening difficult, as these have to be accounted in the calculations. Operating conditions have to be changed (Figure 1) to perform catalytic screening in a medium where reaction is the controlling step. The particular properties of supercritical fluids might be exactly what is necessary to achieve this objective. In this domain, mass transfer coefficients are enhanced due to increased diffusivity.

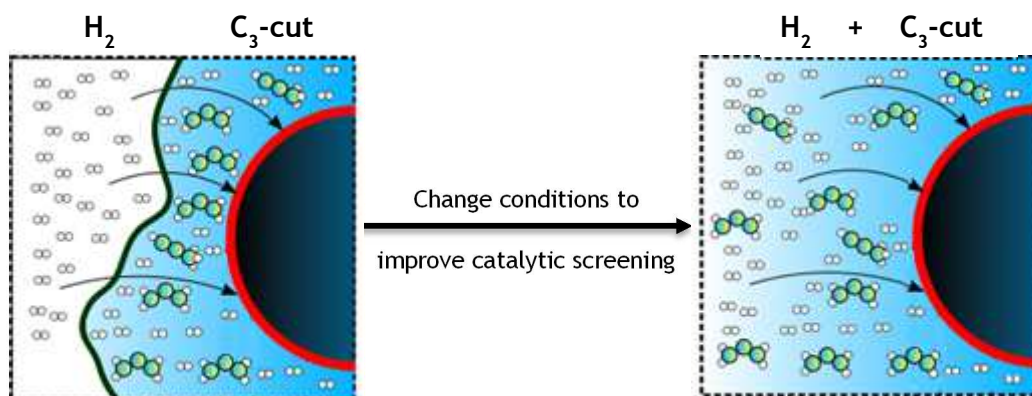


Figure 1 - Schematic representation of the MAPD catalytic hydrogenation reaction in conditions where external mass transfer resistances are present (a) and when they are absent (b). Adapted from Pinho (2014).

1.1 Enterprise Presentation

IFP Energies nouvelles (IFPEN) is a public research and training player. It has an international scope, covering the fields of energy, transport and environment. From research to industry, technological innovation is central to all its activities.

As part of the public-interest mission with which it has been tasked by the public authorities, IFPEN focuses on:

- providing solutions to take up the challenges facing society in terms of energy and the climate, promoting the emergence of a sustainable energy mix;
- creating wealth and jobs by supporting French and European economic activity, and the competitiveness of related industrial sectors.

Its programs are hinged around 5 complementary, inextricably-linked strategic priorities:

- renewable energies: producing fuels, chemical intermediates and energy from renewable sources,
- eco-friendly production: producing energy while mitigating the environmental footprint,
- innovative transport: developing fuel-efficient, environmentally-friendly transport,
- eco-efficient processes: producing environmentally-friendly fuels and chemical intermediates from fossil resources,
- sustainable resources: providing environmentally-friendly technologies and pushing back the current boundaries of oil and gas reserves.

An integral part of IFPEN, its graduate engineering school prepares future generations to take up these challenges.

1.2 Work Contributions

The present thesis is part of a project which PhD student Bruno Pinho is currently developing: “Specific properties of supercritical fluids for fast and exothermic reactive systems”.

The main objective of this work is to study the catalytic hydrogenation reaction of methylacetylene and propadiene in supercritical conditions. This will be achieved by adding different solvents to the mixture, which may affect the reaction differently. We will try to determine if performing reactions in supercritical conditions is a viable alternative to access reaction rates, which are usually disguised by mass and heat transfer limitations.

1.3 Outline of the Thesis

This dissertation is organized in six chapters, including Introduction.

- In Chapter 2, three subchapters make up the state of the art. It starts with a small description of the MAPD catalytic hydrogenation, followed by some important properties of supercritical fluids and their possible applications. The third subchapter describes existing theories for predicting diffusion coefficients. All topics are vital to fully understand the objectives of this work.
- Chapter 3 describes the methodology employed in the present work. It involves the study of available correlations for predicting diffusion coefficients and the performance of experimental trials at different operating conditions.
- In Chapter 4, predicted diffusion coefficients obtained through different correlations are compared. The best correlation is selected, and its results are used to explain the behavior observed in the experimental results.
- In Chapter 5, experimental data is presented and compared against one another. The objective is to understand how different parameters affect the reaction. It is mainly focused on the effect of solvents in supercritical conditions.
- Lastly, conclusions based on the obtained results are presented on Chapter 6. Difficulties and future work are discussed.

2 Context and State of the Art

2.1 Catalytic Hydrogenation of MAPD

C₃-cuts (cuts rich in propylene) usually come from naphtha-processing plants. This cut is not pure, having more than 90 % propylene and up to 6 % methylacetylene and propadiene. The exact composition is always dependent on the feed and on the conditions of the cracking process (Wang and Froment, 2005). MA and PD have the same molar weight and very alike properties, such as boiling point, or density (National Institute of Standards and Technology, 2011). For this reason methylacetylene and propadiene are often referred to as if they were a single compound, MAPD.

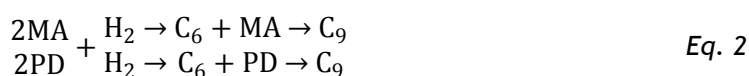
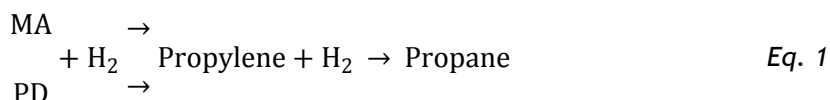
Propylene is a very useful chemical, especially for its application in polymer science. For polymerization of propylene to occur at the required extent, concentration of MAPD in the C₃-cut has to be almost inexistent (Wang and Froment, 2005). In order to remove these 'contaminants', selective hydrogenation of MAPD over a catalyst is usually the approach taken (Wu and Li, 2011). This method has also the advantage of increasing the propylene content in the stream, as MAPD hydrogenates to propylene.

Hydrogenation processes are associated with one big disadvantage. Unless catalyst selectivity for the desired reagent is 100 %, formation of by-products also occurs. When C₃-cut is concerned, side reactions lead to production of propane and oligomers. Propane results from further hydrogenation of propylene, while oligomers are formed by combination of (at least) two MA or PD molecules with molecular hydrogen. Oligomers, usually called green oils, are formed due to the existence of two types of active sites in the catalyst: metal sites, which promote hydrogenation reactions, and acid sites, which catalyzes oligomerization of the olefins (Wang and Froment, 2005). An alternative to bypass this situation might be related with the creation of new catalysts. As an example, Marshall et al. (2005) tested two palladium/carbon catalyst for the hydrogenation of MAPD. In one of these, formation of propane was not noticed, nor oligomerization reactions.

Many factors are involved when hydrogenation reactions are concerned. Operation conditions such as H₂/MAPD ratio or temperature influence selectivity (Wang and Froment, 2005). Process parameters like space velocity change conversions in the reactor (Wu and Li, 2011). In contrast, higher MAPD conversions, which are related with longer process times, give rise to higher contents of deactivating agents (Wang and Froment, 2005). Thus, factors that may alter the process should be studied thoroughly, in order to better tune the reaction.

2.1.1 Reaction scheme

The hydrogenation of MAPD has been a subject of many research in the latest years (Brandão et al., 2007; Fajardo et al., 1996; Kennedy et al., 2004; Samimi et al., 2015; Yu et al., 2012). In particular, the precise reaction schemes (production of propylene, propane, and oligomers) for the process are yet to be fully understood. So far, it appears that the simplest scheme possible correctly describes the process (Wang and Froment, 2005), and therefore will be considered. It can be presented as the following.



It is very difficult to describe the hydrogenation of MAPD through a rate expression. This is mainly due to the large number of possible reactions and difficulties in observing accurate chemical rates, as mass transfer limitations are present in the reactor and in the catalyst. Still, some authors (Kennedy et al., 2004; Wang and Froment, 2005; Wu and Li, 2011) have tried different models to describe the process. These included Langmuir-Hinshelwood and Hougen-Watson models for liquid-phase reaction, whereas empirical laws were mainly used for gas-phase.

By default, the molar conversion, X , of each species, i , at the end of the process may be given by

$$X_i = \frac{F_{i,inlet} - F_{i,outlet}}{F_{i,inlet}} \quad \text{Eq. 3}$$

where F ($\text{mol}\cdot\text{h}^{-1}$) is the molar flow rate.

The way conversion is described, it means that if a species is consumed, conversion should present a positive value. The contrary will happen if a species is produced.

2.1.2 Classical conditions for the MAPD catalytic hydrogenation

Hydrogenations can be performed in gas or gas-liquid phase. Both are used in the industry, as each has its own strengths. The conditions at which the reactions are performed are a function of many parameters that cannot be forgotten. For example, it is known that high pressures improve concentration in gas-phase. If pressure increases too much, substrate turns to liquid and a two-phase system is created. High temperature can also be of great importance, as

reaction rate may be increased. However, low-weight substrates evaporate when temperatures are high enough, dislocating the equilibrium.

When the hydrogenation of MAPD is performed with the C₃-cut in gas-phase, temperature and pressure range from 300 to 350 K and from 2.4 to 2.6 bar, respectively (Wu and Li, 2011). In general, gas-liquid conditions vary between 333 to 363 K and 16 to 20 bar (Wang and Froment, 2005).

2.2 Supercritical Medium

The term ‘supercritical’, when applied to pure fluids, refers to a compound that is above its critical temperature (T_c) and pressure (P_c). For every fluid in equilibrium, there is a set of thermodynamic conditions at which liquid and gas phases cannot be distinguished. Those conditions are referred as the critical point. Densities for liquid and gas phases become the same when the critical point is reached, thereby destroying the interphase between gas and liquid (Burgener, 2005). If temperature and/or pressure are increased above that point, the fluid is said to be in the supercritical domain (Wu et al., 1991). As it might be expected, the critical point of a mixture is dependent on its composition. If chemical reactions are implied, the critical point will constantly change (Ke et al., 2001). When continuous fixed bed reactors are used, this property changes along the length of the reactor.

Because gas and liquid phases are indistinguishable, the fluid as a whole acquires special properties. The fluid properties are now between those of liquids and gases. An order of magnitude of some important physical properties can be seen in Table 1.

Table 1 - Comparison of physical properties of gases, liquids, and supercritical fluids near critical point. Data taken from Burgener (2005).

Physical property	Gas phase ($T = 298 \text{ K}, 1 \text{ bar}$)	Supercritical fluid (T_c, P_c)	Liquid phase ($T = 298 \text{ K}, 1 \text{ bar}$)
Density / $\text{kg}\cdot\text{m}^{-3}$	0.6 - 2	200 - 500	600 - 1600
Viscosity / $\mu\text{Pa}\cdot\text{s}$	10 - 300	10 - 30	200 - 3000
Diffusion coefficient / $10^6 \text{ m}^2\cdot\text{s}^{-1}$	10 - 40	0.07	0.0002-0.002
Thermal conductivity / $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$	0.01	0.01 - 0.1	0.1

The combination of liquid and gas properties gives supercritical fluids great power in terms of mass transfer. Density is generally closer to those of liquids, which offer good dissolution power. On the other hand, these fluids appear to behave similarly to gases in terms of both diffusivity and viscosity, which enhances transport phenomena (Baiker, 1999). At the same time, SCFs are highly compressible, especially near the critical point. Due to their high compressibility, properties may change greatly with small adjustments in pressure and/or temperature. This provides a good way of tuning operation conditions (Wu et al., 1991).

Because critical properties change with mixture composition, solvents are often used in supercritical processes. By choosing the right solvent, usually with lower critical pressure and temperature, the mixture critical point is displaced towards the milder properties of the solvent. Thereby, less severe conditions are necessary (Burgener, 2005).

Processes can take advantage of SCFs physical properties. By making small changes in pressure or temperature, selectivity and reaction extent can be controlled. Other possible use involves controlling the solubility of a species, which will simplify separation processes. Moreover, supercritical processes are very much related with 'green chemistry', because supercritical solvents might replace toxic solvents (like benzene). The two main supercritical fluids used with this objective are carbon dioxide and water. And many other advantages may be present in between, such as easier recycling of solvent, better dissolution of big solutes, increased catalyst life-time, or less time-consuming equipment cleaning operations (Perrut, 2000). However, due to the necessity of high pressures and/or temperatures, supercritical processes are usually more expensive than traditional methods. In addition to this, equipment will be more robust to support the operatory conditions and higher amounts of maintenance are necessary for security reasons (Perrut, 2000). Thus, the actual cost of using supercritical fluids has to be seen in a far-reaching manner. In a publication by Perrut (2000), some factors that might influence the final cost of using supercritical fluids are described.

Supercritical fluids have been applied in many different processes. So far, they appear to be a good alternative against the more traditional methods.

2.2.1 Supercritical fluids and their uses

Supercritical fluid technology is spreading fast throughout the world. Most processes involving SCFs are related with separation and extraction of chemicals (Wu et al., 1991), but they are also used as a reaction medium. The fluid can actually participate in the reaction, or merely act as a solvent for the reactants, products, and/or catalysts (Subramaniam and McHugh, 1986). In this last case, the solute molecular weight is generally bigger than the solvent's (Baiker, 1999).

SCFs are now applied in industrial processes involving oxidation, hydrogenation, polymerization, nitration, and many others (Burgener, 2005). These processes have a wide range of possible applications, from coffee decaffeination to oil recovery. Several good reviews provide a general understanding of possible applications (Subramaniam and McHugh, 1986; Baiker, 1999; Ramírez et al., 2002).

2.2.2 Catalytic hydrogenation in the supercritical domain

Performing catalytic hydrogenations with supercritical fluids can be advantageous when compared to traditional processes, as reaction conditions can be varied independently to obtain better operating conditions (Ramírez et al., 2002). These variables were studied by Hitzler et al. (1998) in several different hydrogenation reactions. It includes temperature, pressure, hydrogen/substrate ratio, type of catalyst, among others. When catalytic hydrogenation is performed in the supercritical domain, mass and heat transport resistances between gas and liquid are eliminated, as the mixture becomes homogeneous. As a result, hydrogen, which is almost insoluble in organic liquids, may be completely miscible in supercritical fluids. Concentration of hydrogen increases near the catalyst particle, which has been linked with higher reaction rates (Ramírez et al., 2002). Van den Hark, Sander and Härröd (2001) have actually reported reaction rates of about 1000 times higher when the hydrogenation of fatty esters in propane was done in the supercritical domain.

Solvents are widely used in hydrogenation reactions. Carbon dioxide is mostly used, but small alkanes, like ethane or propane, have been able to obtain equal or better results (Baiker, 1999). As long as the solvent should not influence the reaction, it can be used. Though, one must choose the solvent wisely, as some of these may allow good conversion of substrate, but with higher production of side products. If side products involve high molecular weight compounds, like oligomers, the catalyst may lose its activity very quickly. If the right solvent is used, it is possible to disable or largely reduce the production of byproducts (Ramírez et al., 2002). Solvents are also useful in maintaining the temperature of the reactor (Bertuccio A. and Vetter G., 2001).

Like other supercritical processes, catalytic hydrogenation is often expensive (severe operating conditions and robust equipment). However, separation processes become easier, which can balance costs.

2.2.3 Mass transfer coefficient

There are many ways of perceiving the mass transfer enhancement when supercritical fluids are used. The easiest way is by considering the Sherwood number, Sh . This dimensionless number relates mass transfer with diffusion.

$$Sh = \frac{K_{LS} \times d_p}{D} \quad \text{Eq. 4}$$

where K_{LS} ($\text{m}\cdot\text{s}^{-1}$) is the mass transfer coefficient, d_p (m) is the diameter, and D ($\text{m}^2\cdot\text{s}^{-1}$) is the diffusion coefficient.

The Sherwood number can also be determined through a combination of Reynolds and Schmidt numbers.

$$Sh = 2 + p_1 Re^{p_2} Sc^{1/3} \quad \text{Eq. 5}$$

$$Re = \frac{\rho d_p v}{\mu} \quad \text{Eq. 6}$$

$$Sc = \frac{\mu}{\rho D} \quad \text{Eq. 7}$$

where ρ ($\text{kg}\cdot\text{m}^{-3}$) is the density, μ ($\text{Pa}\cdot\text{s}$) is the viscosity, and v ($\text{m}\cdot\text{s}^{-1}$) is the fluid velocity. p_1 and p_2 are constants.

Therefore, $K_{LS} \propto D^{2/3}$ by explicitly presenting all variables. And as showed before, diffusion coefficients are greatly increased in the supercritical domain.

2.2.4 Determination of reaction rates with supercritical fluids

The intrinsic reaction rate of a chemical reaction can be determined if transport resistances are negligible when performing kinetic experiments (Perego and Peratello, 1999). Temperature and concentration gradients can happen between different phases in the reactor, but also between or inside the catalyst particles. The presence of gradients makes the determination of the chemical reaction rate more difficult. Even in liquid-solid processes, where temperature gradients are not important, concentration gradients are still of concern.

In a concise but informative review, Perego and Peratello (1999) mention tests that can be performed in order to check for the presence of interphase limitations. One of those tests involves performing several experiments with increasing reactant flow rate and catalyst volume, but with the same liquid hourly space velocity (LHSV). This parameter can be defined as the volume of reactant feed per volume of catalyst, per unit time. If the conversion achieved between tests (all or some) is the same, there are no limitations present inside the reactor (Bertuccio A. and Vetter G., 2001). If no limitations are present, it should be possible for one to determine the true activation energy for a given reaction.

Considering that resistances should be almost absent in the supercritical domain, the determination of reaction rates is yet another possible use of these fluids.

2.3 Diffusivity in Supercritical Media

Understanding the catalyst performance is not always a straightforward activity, since several phenomena (e.g. mass transfer) and assumptions have to be taken into account (e.g. gas-liquid coefficient which follows a correlation). This situation becomes more problematic when dealing with heterogeneous catalysis with a highly active phase. Mass transfer rates have an important role in understanding the reactions, since these are often limited by external and interphase mass transfer. To avoid gas-liquid mass transfer, reactions can be carried out in a homogeneous medium. By this way, the mass transfer rate is only controlled by liquid-solid resistances, which can be estimated if diffusion coefficients are known.

According to literature, the diffusion coefficient is related with three main solute parameters: size, shape, and polarity (Medina, 2012). Bigger solutes tend to diffuse slower, whereas linear or non-polar molecules diffuse faster. Size and shape are connected to molar and mass volumes. Polarity impacts viscosity. The exact value of diffusivity can also be greatly influenced by adding a solvent. Apart from the solute characteristics, temperature and pressure have an important role in diffusion. It is known that diffusion increases with increasing temperature, and it decreases with increasing pressure (Medina, 2012; Silva and Macedo, 1998). Both properties are, therefore, inversely related.

The goal of this subchapter is to investigate how the diffusion of a species is affected in the supercritical state. This will be done by studying correlations for diffusivity in high-pressure conditions (~120 bar, 303.15 K and 353.15 K).

2.3.1 Experimental determination

When dealing with supercritical fluids, it is essential to have reliable diffusion coefficients to better understand the impact in mass transfer. Diffusion coefficients can be obtained through several routes, such as chromatographic peak broadening method (developed by Taylor (1953) and Aris (1956)). This is the most widely used method for measuring diffusion coefficients (Olesik and Woodruff, 1991; Silva and Macedo, 1998; Pizarro et al., 2009). It consists on injecting a tracer in a solvent. The fluids then flow through a capillary column and the response is monitored at the outlet. This signal is afterwards related with diffusion. More details can be found in literature (Eaton et al., 1995; Funazukuri et al., 2004; Lin and Tavlarides, 2010). However, such method has been proved to be unsuitable for polar compounds, as they tend to adsorb onto the column wall, causing substantial peak tailing (Madras et al., 1996). In order to bypass this problem, Funazukuri et al. (2000; 2004) used another technique named chromatographic impulse response, which was able to obtain better results for the referred substances. Other methods for determining the diffusion coefficients, though not so commonly

used, include the modified Taylor method, the solid dissolution rate measuring, the capillary evaporation, the nuclear magnetic resonance method, the radioactive tracer response, and the light scattering method (Funazukuri et al., 2004; Medina, 2012).

2.3.2 Diffusion correlations

Most of the experimental methods to determine diffusion coefficients involve a large set of experiments and are expensive and time consuming (Zhou et al., 2000; Zhu et al., 2002; Shi and Lu, 2010). This task is even more challenging if multicomponent mixtures are concerned. A feasible alternative is to determine diffusion coefficients using empirical correlations. In literature, there are a wide number of correlations available. Normally, when the data is inexistent for a studied mixture, a correlation that fits well a close mixture is adopted. This is the case for methylacetylene (MA) and propadiene (PD). As far as known, there are no experimental data available for supercritical or subcritical conditions for those components.

The correlations used to estimate diffusion coefficients of pure fluids and mixtures are based in many concepts. Some of those include free volumes, viscosity of solutes/solvents (Funazukuri et al., 2006), or even residual entropy (Vaz et al., 2012). A recurring problem among different correlations is their specificity to a given solvent or their limited application range in terms of temperature and pressure (He et al., 1998). Therefore, it is important to study different correlations, in order to gain confidence in the values obtained.

Correlations can be subdivided into three main groups: **A.** Hydrodynamic Theory of Stokes-Einstein, **B.** Enskog-Thorne Hard-Spheres Theory and **C.** Other correlations (Medina, 2012). The last group is called “Other correlations” because it does not fit inside any of the other two theories. The first theory relates viscosity with diffusion, while the second is an approach of free-volume (Ángel Mulero, 2008). An overview of each theory will be done before detailing some correlations of interest.

A. Hydrodynamic Theory of Stokes-Einstein

The Hydrodynamic Theory estimates infinite dilution diffusion coefficients in dense fluids, such as liquids. This theory consists in treating the solute as large spherical molecules within a solvent, whose molecules are much smaller. Thereby, the solvent can be seen as a continuous phase (Olesik and Woodruff, 1991) and the diffusion coefficients (D_{21} , Eq. 8) are controlled essentially by the macroscopic viscosity of the solvent (η_1) and the hydrodynamic radius of the solute (r_2). The resultant hydrodynamic equation can be written as

$$D_{21} = \frac{k_B T}{6\pi\eta_1 r_2} \quad \text{Eq. 8}$$

where T (K) is the temperature and k_B ($\text{m}^2\text{kg}\cdot\text{s}^{-2}\cdot\text{K}^{-1}$) is the Boltzmann constant. η_1 is given in $\text{Pa}\cdot\text{s}$, while r_2 can be expressed in m. The subscripts 1 and 2 in the diffusion coefficient D ($\text{m}^2\cdot\text{s}^{-1}$) refer to solvent and solute, respectively.

This theory was the first to give some insight about the molecular dynamics of solutes in liquids (Sharma and Yashonath, 2006). However the theory had some flaws. Due to its simplicity, it can only be applied if the solvent flow is laminar, i.e., for low Reynolds number. Moreover, the applicability of this equation is limited in supercritical fluids because of the strong dependency of fluid density (Funazukuri et al., 2008). To correct this divergence some modifications were proposed by other authors.

In a recent review, Medina (2012) found that, at high pressure, most correlations tend to overestimate the diffusion coefficient, especially those based on the hydrodynamic theory. According to Magalhães et al. (2013), hydrodynamic-based equations fail to predict diffusivities in the supercritical region due to the clustering of solute molecules. That ‘cluster’ effect is more significant at lower densities. In theory, for better estimations of diffusion in supercritical media, Hard-Spheres based correlations should be used (Medina, 2012). Still, some correlations based on the Hydrodynamic Theory are described in the Appendix 1 - Correlations based on the Hydrodynamic Theory (A)

B. Enskog-Thorne Hard-Spheres Theory

The Hard-Spheres (HS) Theory was first conceptualized by Enskog, and later further improved by Thorne. This theory considers solute molecules as if they were hard spheres that interact with each other. Enskog considered that molecular diameters are as important as interparticle distance, especially at high pressure. This means that the probability of collisions in a fluid depends on the number of near particles, but also on their size (σ) (Magalhães et al., 2011a). For binary diffusion at infinite dilution, the scaling to high pressure is achieved by dividing the diffusion coefficient at low-pressure (D_{21}^0) by the radial distribution function at contact, $g(\sigma_{21})$ (see Eq. 9). This function depends on the HS packing fraction of the solvent, and sometimes on the solute-solvent diameter ratio. While D_{21}^0 is always obtained through the rigorous kinetic theory of Boltzmann, several radial distribution functions have been used (Carnahan-Starling, Mansoori,...).

$$D_{21}^{ET} = \frac{D_{21}^0}{g(\sigma_{21})} \quad \text{Eq. 9}$$

where D_{21} ($\text{m}^2\cdot\text{s}^{-1}$) refers to diffusion of a solute (2) in a solvent (1) at infinite dilution, and the superscript *ET* denotes the Enskog-Thorne equation. The kinetic theory of Boltzmann applied to binary mixtures is then expressed by

$$D_{21}^0 = \frac{3}{8n_1\sigma_{21}^2} \sqrt{\frac{k_B T}{\pi m_{21}}} \quad \text{Eq. 10}$$

where n_1 (m^{-3}) is the solvent number density, k_B ($\text{m}^2\cdot\text{kg}\cdot\text{s}^{-2}\cdot\text{K}^{-1}$) is the Boltzmann constant, and T (K) is the absolute temperature. σ_{21} (m) and m_{21} (kg) are the size and weight of the unlike molecules, respectively. The latest variable can be determined by an average of molecular weights.

$$m_{21} = \frac{2m_1m_2}{m_1 + m_2} \quad \text{Eq. 11}$$

Hard-Spheres are normally used as the first approximation to a physical “problem”. For a more realistic model, an effective diameter can be coupled. It takes into account the repulsive potential of molecules (Vaz et al., 2012). The effective hard-sphere diameter (EHSD) can be determined through several expressions. These are dependent on the theory applied to calculate the thermodynamic properties (Matyushov and Schmid, 1996). The effective diameter is always temperature-dependent, although in some expressions density is also considered. In a broad study performed by Silva et al. (1998a), it has been shown that temperature has clearly a greater impact in the effective diameter than density. Since the different expressions available for the calculation of the effective diameter provide similar results, it is advised the use of a correlation that is just temperature dependent.

In Eq. 10, molecules are assumed to be smooth spheres that collide without rotating, which is not accurate. As density increases these interactions become more important. This fact makes the equation inappropriate over a large range of density. Therefore, to account for the loss of momentum in a collision between molecules a coupling factor has to be accounted (Olesik and Woodruff, 1991; Magalhães et al., 2011a). Through molecular simulations, it was determined the need of a correction factor (F_{21}) that is dependent on both solute and solvent. The correct equation is usually referred to as Rough Hard-Spheres. It is defined as:

$$D_{21} = \frac{3}{8n_1\sigma_{21}^2} \sqrt{\frac{k_B T}{2\pi m_{21}}} \left(\frac{F_{21}}{g(\sigma)} \right) \quad \text{Eq. 12}$$

In order to compensate the deviations introduced by repulsive and attractive interactions between molecules, an extra term has to be added. In general, an exponential term centered on the Lennard-Jones (LJ) potential model or Square-Well (SW) fluids is used (Zhu et al., 2002).

The SW model consists of viewing a molecule as a sphere with a rigid diameter. The molecule is surrounded by an attractive shell of strength ε that affects other molecules in an extent of $K\sigma$. The value of K is generally taken as 1.5. On the other hand, the LJ model possesses both repulsive and the inverse sixth power London forces. This model assumes that molecules become somehow ‘softened’, i.e. contrary to the SW model these molecules do not have an impenetrable shell (Liu et al., 1996). The Lennard-Jones potential is used frequently because it is capable of representing the attraction and repulsion among molecules very simply. Known as the Lennard-Jones (12-6) Potential, this function is given by

$$u(r_{ij}) = 4\varepsilon_{ij}^{LJ} \left\{ \left(\frac{\sigma_{ij}^{LJ}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}^{LJ}}{r_{ij}} \right)^6 \right\} \quad \text{Eq. 13}$$

where u ($\text{m}^2 \cdot \text{kg} \cdot \text{s}^{-2}$) is the intermolecular potential, ε^{LJ} ($\text{m}^2 \cdot \text{kg} \cdot \text{s}^{-2}$) is the Lennard-Jones energy parameter (value for low energy collisions), σ^{LJ} (m) is the Lennard-Jones size parameter (the length at which the interaction energy becomes zero), r (m) is the distance between molecules, and i and j subscripts represent particles i and j , respectively (Iwai et al., 1997). Both energy and size parameters for unlike molecules can be determined if there are data for pure fluids (σ_n^{LJ} and ε_n^{LJ} , where n can be molecule i or j). This is done by the application of combining rules. Due to the importance of these rules in the Hard-Spheres model, this subject will be discussed separately in another subchapter.

Modifications to the Hard-Spheres theory can be made by just following different interpretations of the parameters that interact in a fluid. This model is very robust, as it takes into consideration a fair amount of interactions that may occur between molecules. The simple assumption of molecules as spheres with defined volume permitted the construction of many correlations. Some are described in Appendix 2 and will be used to estimate diffusion coefficients of MAPD in several solvents.

C. Other correlations

The last group is reserved for correlations that do not fit into any of the other two theories. These are not used often, as they can only deliver rough predictions of diffusion coefficients. As an example, the equation developed by Zhou et al. (2000) relates critical temperature T_c (K) and pressure P_c (MPa) with the infinite dilution diffusion coefficient, D_{21} (Eq. 14).

$$D_{21} = 6.58 \times 10^{-8} \left(\frac{T_c}{P_c} \right)^{-0.3471} \quad \text{Eq. 14}$$

The construction of this correlation was supposedly based on the hydrodynamic equation. However, Zhou et al. correlation considers critical properties, whereas the Hydrodynamic

Theory involves solvent viscosities. It is possible to say that both expressions are alike, but they follow completely different approaches. This type of correlations do not have theoretical ground, and this fact can make them rather inaccurate, especially for a wide range of systems.

2.3.3 Tested correlations for diffusivity estimation

There are many correlations available for predicting diffusion coefficients. Some are more suitable for gas, liquid, or supercritical fluids. Others can be used within large ranges of conditions, but may have a higher average error. It was decided to study some correlations more thoroughly, either because they represent well one of the models described, or because good predictions are obtained by using them. Four correlations that do not require specific mixture parameters were chosen: Wilke-Chang (1955), Fuller et al. (1966), He-Yu (1998), and Liu-Silva-Macedo (1997); as well as four correlations that do: the Hydrodynamic Equation of Evans et al. (1979), Magalhães et al. (2013), and Lito et al. (2013).

Average absolute relative deviations (AARD %) for the chosen correlations are presented in Table 2. The errors were retrieved from different sources, and sometimes more than one source was considered for the same correlation. Because, actually, Magalhães et al. (2013) tested different simple two-parameter correlations instead of just one, an interval of errors is given.

Table 2 - Average absolute relative deviation for Hydrodynamic and Hard-Spheres theories based correlations. Data was retrieved from several publications. ¹Funazukuri et al. (2008); ²Medina (2012); ³Lito et al. (2013); ⁴Magalhães et al. (2013); ⁵Fuller et al. (1966); ⁶He and Yu (1997); ⁷Liu et al. (1997).

Correlation	Based Model	Systems / Data points used	AARD %
Hydrodynamic Equation (1979)	Hydrodynamic Theory	12 / 1006	6.2 ¹
Wilke-Chang (1995)	Hydrodynamic Theory	40 / 600 487 / 8293	10.3 ² 26.5 ³
Magalhães et al. (2013)	Hydrodynamic Theory	539 / 8219	2.78-3.05 ⁴
Fuller et al. (1966)	Hard-Spheres Theory	--- / 340	7.4 ⁵
He-Yu (1998)	Hard-Spheres Theory	40 / 600 113 / 1332	6.6 ² 7.3 ⁶
Liu-Silva-Macedo (1997)	Hard-Spheres Theory	77 / 1033 487 / 8293	14.77 ⁷ 3.6 ³
Lito et al. (2013)	Hard-Spheres Theory	487 / 8293	2.74 ³

As it can be seen, error can be as big as 26.5 %, or as small as 2.74 %. However, the average error depends very much of the amount of experimental data points used in its development.

2.3.4 Mixing rules for concentrated mixtures

The previously mentioned correlations are able to predict diffusion coefficients, but mainly in diluted systems. To correlate the diffusion coefficient of a concentrated mixture with the individual tracer diffusion coefficients of the concerned substances, mixing rules, such as Darken or Vignes rules, can be used (Lito et al., 2013). The Darken rule is usually used when molecules are of similar morphology and non-polar. Otherwise, Vignes rules is more suitable (Medvedev and Shapiro, 2004). The rules to calculate mixture diffusion coefficients ($D_{21,mix}$) are given by

$$D_{21,mix}^{Darken} = x_1^A D_{21}^A + x_1^B D_{21}^B \quad Eq. 15$$

$$D_{21,mix}^{Vignes} = (D_{21}^A)^{x_1^A} (D_{21}^B)^{x_1^B} \quad Eq. 16$$

where x is the molar fraction, and D_{21} (with any suitable units) is the infinite dilution diffusion coefficient of solute 2 in solvent 1. The subscripts A and B refer to different infinitely diluted binary mixtures.

The rules can, therefore, predict binary diffusion coefficients if the solvent (1) in mixture A is the solute (2) in mixture B , and vice-versa. Basically, the infinite dilution diffusion coefficients of both compounds in one another are necessary. More interesting are ternary mixtures. In this case, it is necessary to have tracer diffusion coefficients of a solute in two different solvents.

2.3.5 Energy and size potential parameters

One big problem concerning pairs of parameters is that their values diverge among authors. This can be due to different experimental procedures. As a result, it is difficult to decide which parameters could result in better diffusivity predictions. The same problem has been encountered by many authors. For instance, Zhou et al. (2000) compared three different sets of potential parameters for carbon dioxide with the available diffusion data. Each pair of values was determined by different methods. The parameters of Iwai et al. (1997), which were obtained by fitting the Pressure-Volume-Temperature properties of carbon dioxide, showed the best agreement with the experimental data. The other two sets also provided fair agreement, but tend to underestimate the diffusion coefficient of CO_2 . Different pairs of parameters can also be a result of modifications in the potential model. As an example, Vrabec et al. (2001) determined size and energy parameters for several substances through molecular simulations. The group considering a two-center Lennard-Jones plus pointquadrupole (for further

explanation on this model, please see cited work). Their parameters were then used to estimate some thermodynamic properties, and good results were achieved. The average errors were very small, which means the set of values are very good.

The best way to understand which energy and size parameters should be used is by trying pairs of values that look promising. Sometimes they can be very different, but lead to similar results.

2.4 Conclusions

Both gas and gas-liquid reactions have their own advantages and drawbacks. It would be interesting if the benefits of each process could be coupled, so mass transfer would not be limited. This would make possible to understand the catalytic performance, as reaction rates would not be hindered by external limitations. That can be achieved by performing the reaction in the supercritical domain.

The discovery of the supercritical domain and of its properties has brought many new possibilities. From extraction processes, to catalytic reaction, or improvement of catalyst life, supercritical fluids may be used to improve existing processes, or even enable others. This is mainly due to their properties between a gas and a liquid, which favors mass transfer. When applied to hydrogenation reactions, extremely high reaction rates may be achieved. Even though supercritical processes bring many advantages, it is always necessary to verify if the alternative is profitable.

Knowing the diffusion coefficients of a solute in a mixture is of fundamental importance in many industrial processes, especially for those involving reaction. There are many techniques to experimentally determine these coefficients, or one can also estimate them by using the many available correlations. However, their employment is not a straightforward task, as some can only be used in certain ranges of physical properties. Correlations are mainly based on the Hydrodynamic Theory or on the Hard-Spheres Theory. When the objective is estimating infinite diluted diffusion coefficients in the supercritical domain, the second group of correlations may achieve better results. These are normally very robust, involving several parameters like the Lennard-Jones potential parameters. Afterwards, it is possible using mixing rules to adapt predictions into more concentrated media.

Some practical correlations were studied in this chapter and will be used to determine MAPD diffusion coefficients in specific solvents. This will provide some insight about how much mass transfer can be improved if solvents and supercritical conditions are used in the MAPD hydrogenation reaction.

3 Methodology

The purpose of this work is to study the impact of solvents in the MAPD catalytic hydrogenation. This reaction will be executed in the supercritical domain. As explained earlier, mass transfer is improved in this medium, which is mainly related with better diffusion coefficients. These can be estimated when experimental data is not available. If diffusion coefficients are known, mass transfer limitations will be (or not) expect beforehand.

The first part of this work will involve the study of some correlations for the prediction of MAPD diffusion coefficients at infinite dilution. Their results will be compared with each other, in order to decide which correlation provides the best predictions. Afterwards, the chosen correlation will be used to estimate the MAPD diffusion coefficient in mixtures with solvents (mixing rules). The objective is to estimate the possible impact of each solvent in the reaction behavior.

Several experimental tests will be performed in a pilot fixed-bed reactor, all of which at high-pressure. In some of these experiments, solvents will be added at different proportions. In relation to the experiments without solvent, some factors that influence mass transfer and reaction rate will be studied - weight hourly space velocity (explained in Chapter 5), temperature, and H_2 /MAPD ratio. Then, different solvents will be added to the load and hydrogen, which will take the mixture to the supercritical domain.

It is expected that reactions with and without solvent may present very different MAPD conversions, due to the specific properties of supercritical fluids. If this situation is perceived, the predicted diffusion coefficients for mixtures with and without solvent can be used to explain the results.

4 Diffusivity

4.1 Evaluation of correlations

Diffusion coefficients will be obtained through the use of correlations. This option was selected since diffusion data for MAPD are not available in literature (Zhu et al., 2002; Medvedev and Shapiro, 2004; Magalhães et al., 2013). The correlations were only applied to the MAPD, because it is the most interesting reactant to study.

In relation to the correlations studied, only those that have variables easily quantified were accounted. Within these, only the most suitable to supercritical fluids were studied in detail. They should provide diffusion coefficients with value at the full range of physical phases, namely gas, supercritical and liquid ($D_{\text{gas}} > D_{\text{supercritical}} > D_{\text{liquid}}$). Four correlations were chosen to predict diffusion coefficients: He-Yu, Liu-Silva-Macedo (LSM), Fuller et al. and Wilke-Chang. He-Yu and LSM correlations are able to predict tracer diffusion coefficients in supercritical conditions and, at the same time, their average error is among the best available (Medina, 2012). Fuller and Wilke-Chang correlations are only adapted to predict tracer diffusion coefficients in gas and liquid phases, respectively. Even knowing that they are not suitable to the supercritical region, they will still be used to study gas and liquid diffusivities. It is expected that these two correlations will be able to set the boundaries for the real diffusion coefficients.

In this subchapter, the strategy followed include four steps:

1. verify the correlations for a literature experimental case (to avoid mistakes and gain confidence);
2. compare different correlations for different solvents and select which one provides better results in the supercritical domain;
3. compare the solvent effect with the previously selected correlation;
4. determine diffusion coefficients for concentrated mixtures.

4.1.1 Validation of correlations

Before establishing the most suitable correlation, their formulation should be verified for a literature case in order to gain confidence. The Fuller et al., Wilke-Chang, and He-Yu correlations have a straightforward formulation. Due to their parametric simplicity they will not be verified. On the other hand, the LSM equation involves a several amount of parameters and should be carefully analyzed. Therefore the best literature practices were applied.

A mixture of tetrahydrofuran (THF) in supercritical carbon dioxide was chosen to verify the LSM correlation (Silva and Macedo, 1998). This publication was chosen because it offers experimental data and also data for pure substances to be used in the correlation. In their work, a comparison was made between the estimated values and the experimental data. To verify their results, new calculations are going to be made. The Lennard-Jones parameters and mixing rules proposed by the authors were used, in order to be coherent. According to them, the AARD (%) is close to 14.87 %. Hence, estimations were performed with the LSM correlation in the same conditions, and an equal AARD was obtained (14.78 %). In Figure 2, the difference between experimental and predicted data values is shown for illustrative purposes. Experimental data was obtained at different temperatures and pressures.

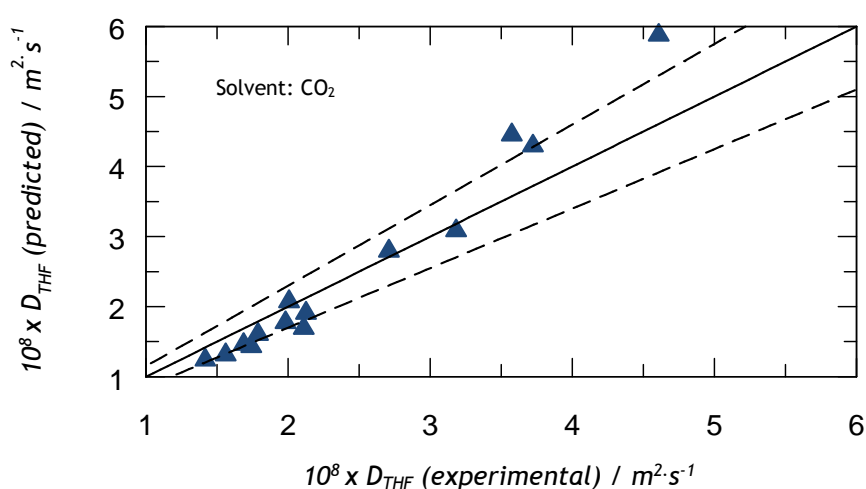


Figure 2 - Deviation between experimental data and estimated values for the diffusion of THF in supercritical CO_2 . The dashed line represents a deviation of 15 %.

After verifying that Liu et al. correlation is mistake free for the experimental data tested, the next step is to compare the different correlations and select the best suitable one.

4.1.2 Comparison between different correlations

To compare the proposed correlations, similar conditions and fluid properties (parameters) were studied. In Table 3, all data necessary for prediction calculations are listed, except for viscosity and density. Those were retrieved from National Institute of Standards and Technology (2011). The values were obtained from the authors publications, whenever possible. For the present correlations, methylacetylene and propadiene were considered as a single fluid, having average properties. It should be a fair assumption, since both species have very close physical properties.

Table 3 - Fluid data to be used in the chosen correlations. Information gather in ¹National Institute of Standards and Technology (2011); ²database of Pro II V9.2 software; ³Sastri et al. (1996); ⁴Fuller et al. (1966); ⁵Liu et al. (1996). *Properties V_d and V are both the molar volume, but the tables used for their estimation were not the same. **Estimated through Eq. 32. ***Estimated through Eq. 31.

Property	MAPD	Propylene	Methane	Ethane	CO ₂
¹ M , g/mol	40.07	42.08	16.04	30.07	44.01
¹ T_c , K	398.12	365.57	190.56	305.33	304.13
¹ P_c , bar	53.87	46.65	45.99	48.72	73.77
² V_c , cm ³	163.00	188.40	99.00	145.50	94.00
³ V^* , cm ³ /mol	59.32	63.00	---	---	---
⁴ V_d^* , cm ³ /mol	57.42	61.38	---	---	---
⁵ σ_{LJ} , Å	4.391**	4.473**	3.585	4.176	3.262
⁵ ϵ_{LJ}/k_B , K	316.10***	290.26***	167.15	213.08	500.71

The correlations were compared by determining tracer diffusion coefficients of MAPD for four solvents: methane, ethane, carbon dioxide and propylene. The first step requires deciding which correlation is the best to describe the diffusional behavior.

Figure 3 (a-d) illustrate the estimated diffusion coefficients of MAPD in each solvent, at different temperatures. The results are presented at constant pressure of 120 bar, where it is possible to see the relative impact of each solvent. In all cases, diffusion should be slower when propylene is used (bigger molecule). In contrast, when using methane as solvent, it is more likely to have the greatest impact in diffusion.

Liquid state — | Supercritical domain —·—

120 bar

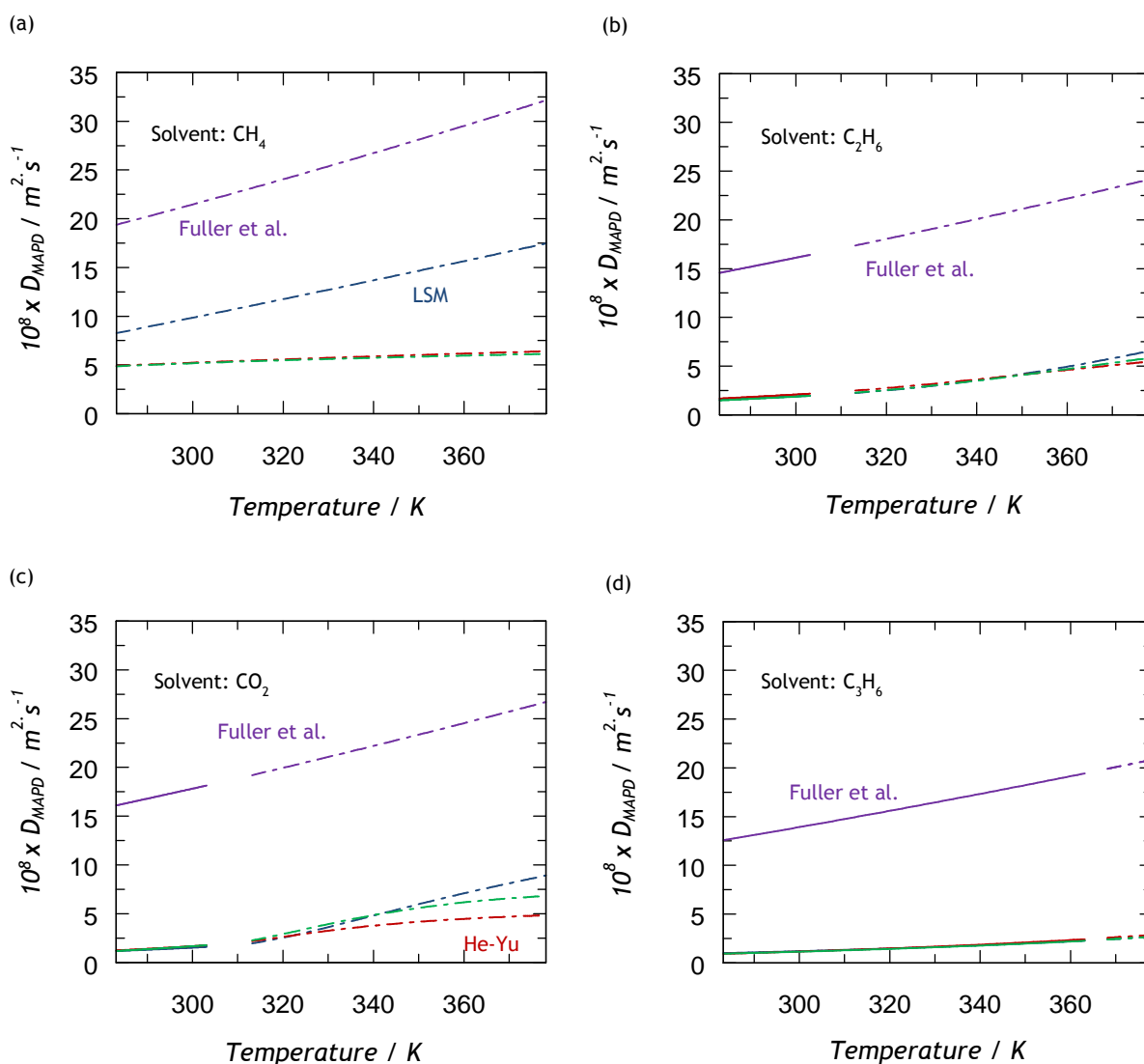


Figure 3 - Diffusivity of MAPD in (a) methane, (b) ethane, (c) carbon dioxide, and (d) propylene at constant pressure of 120 bar. Range of temperatures between 283.15 and 373.15 K. (blue) Liu-Silva-Macedo (1997); (red) He-Yu (1998); (green) Wilke-Chang (1955); (purple) Fuller et al. (1966).

Solvents used in supercritical processes are usually small molecules. Solute and solvent should have different sizes for diffusion to increase. Since propylene and MAPD have both 3 carbon molecules, no substantial differences from the MAPD self-diffusion are expected. Diffusion coefficients for CO₂ and ethane are similar in all range, with carbon dioxide being slightly higher.

Fuller et al. correlation greatly overestimates the diffusion coefficients of MAPD for all solvents. This result was expected, because the correlation is meant to be used with gases, which has a higher diffusional power than liquids. If any other correlations had given higher or even similar

results, we could assume that that correlation would be unrealistic for our case. Wilke-Chang's obtains similar results to those of LSM, except for methane. The values obtained from He-Yu correlation are also similar to those of Wilke-Chang correlation (in the considered range). The only exception occurs for CO₂, where the estimates are lower than those of other correlations.

Considering these results and what is known about each correlation, some conclusions can be summarized.

- Fuller et al. can be discarded because predictions using this correlation are completely different from the values of the other correlations;
- Good predictive ability was expected when using He-Yu equation for carbon dioxide as solvent (Lin and Tavlarides, 2010). Since results differ among all correlations tested, that conclusion cannot be confirmed. For other substances the free volume is often negative, which goes against its physical meaning (a volume must be positive or null);
- Liu-Silva-Macedo correlation is based on physical meaningful properties;
- Wilke-Chang correlation has high deviation (see Table 2), even when used with liquids.

Due to these reasons, it is believed that the LSM correlation is more reliable than He-Yu's. Therefore, the subsequent analysis will be entirely made with the results obtained through Liu-Silva-Macedo expression.

4.1.3 LSM correlation results

Figure 4 (a) compiles the MAPD tracer diffusion coefficients at constant pressure (120 bar) for all concerned solvents. The effect of each one is clearly visible. Diffusivity is significantly increased for both ethane and carbon dioxide after their critical point (pure point - dealing with infinitely diluted MAPD) is passed and when the supercritical state is established (a few degrees after critical temperature). This fact provides more confidence on the predictive ability of Liu-Silva-Macedo correlation to estimate diffusion coefficients in the supercritical domain, as literature expected an increase in diffusion in the supercritical domain.

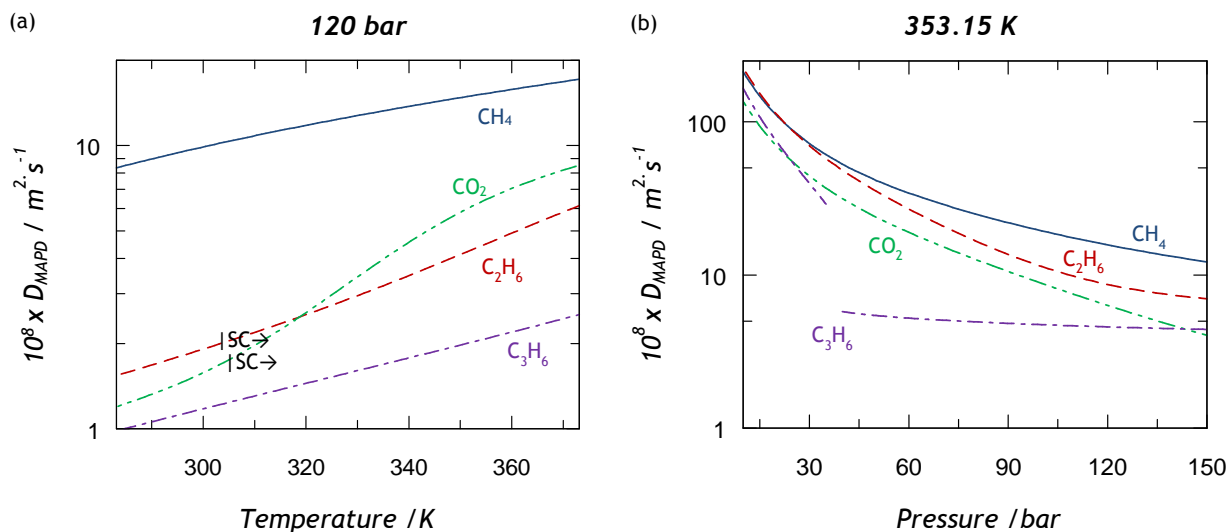


Figure 4 - Predicted diffusion coefficients for MAPD in (blue) methane, (red) ethane, (green) carbon dioxide, and (purple) propylene at (a) constant pressure of 120 bar and (b) constant temperature of 353.15 K. (SC - Supercritical state)

In Figure 4 (b), the diffusion coefficients were obtained at 353.15 K for different pressures (10 to 150 bar). We can see that small increases in pressure have a major effect at low pressure values. At high pressure, the decrease is not significant. The bigger variations at low pressure are due to changes in solvent density (see Table 1). Solute density does not change significantly to influence diffusion. MAPD is always in liquid state in the range explored.

From highest to lowest predicted diffusion, we can organize the solvents by: Methane > Carbon Dioxide > Ethane > Propylene.

Some estimations at 303.15 K were also performed to quantify the effect of temperature on the diffusion coefficient (Figure 5). Only methane was considered, since the effect is recurrent for the other solvents. The only exception is propylene, whose values are somewhat the same (see Table 1 for propylene critical temperature). According to the results seen in Figure 5, passing from 303.15 K to 353.15 K can increase diffusivity by almost 1.5 times, on average. In some processes, this improvement can be crucial, even though it may imply higher costs.

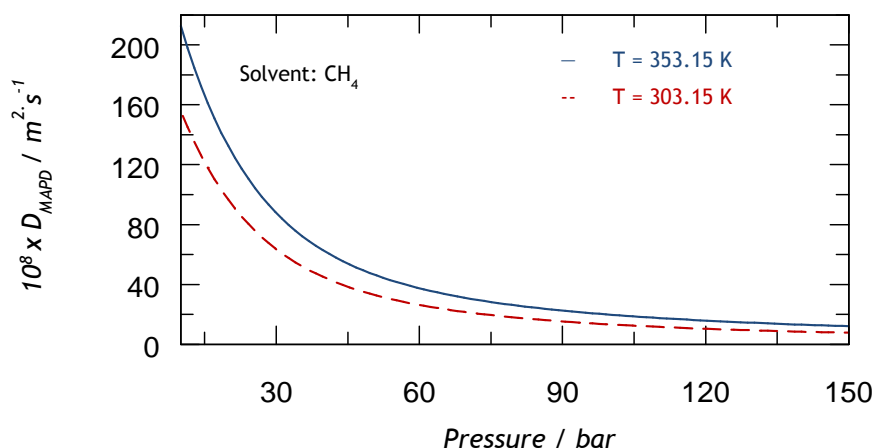


Figure 5 - Diffusion coefficients of MAPD in supercritical methane at constant temperature. (-) 353.15 K; (--) 303.15 K.

A comparison between diffusion coefficients in the considered conditions can be seen in Table 4. It is possible to obtain a relative gain in terms of diffusion by simply dividing two diffusion coefficients (of different solvents) with one another. Presently, a relative gain was determined against the diffusion coefficient of propylene, since this solvent is the one which offers lower diffusion coefficients for MAPD.

Table 4 - Diffusion coefficients of methane, ethane, carbon dioxide, and propylene at 120 bar and 303.15 or 353.15 K, according to the LSM correlation. A comparison between diffusion in propylene and in other solvents is made through a relative gain.

Conditions	Diffusion coefficients ($\text{m}^2\cdot\text{s}^{-1}$)			
	Methane	Ethane	Carbon Dioxide	Propylene
$T = 303.15 \text{ K};$ $P = 120 \text{ bar}$ (Relative gain)	1.01×10^{-7} (8.3)	1.96×10^{-8} (1.6)	1.60×10^{-8} (1.3)	1.22×10^{-8} (1.00)
$T = 353.15 \text{ K};$ $P = 120 \text{ bar}$ (Relative gain)	1.49×10^{-7} (7.3)	4.31×10^{-8} (2.1)	6.42×10^{-8} (3.1)	2.04×10^{-8} (1.00)

4.1.4 Diffusivity in mixtures

As previously referred in Chapter 2.3, it is possible to use rules such as those of Darken and Vignes to estimate diffusion coefficients for real mixtures. Therefore, an attempt was made by application of these rules. Since propylene and propane are very similar molecules and the amount of propylene is much higher (96 % against 2.2 % in the feed used in this work), it was

considered that propane is not present in the mixture. This way, only diffusion coefficients of MAPD in propylene and in the other solvents are needed for the calculations.

The diffusion coefficients for the concerned mixtures are displayed in Figure 6. The calculations were performed considering the tracer diffusion coefficients at 120 bar and 353.15 K. As expected, both rules provide different results. This is due to Darken rule (a) being linear, while Vignes (b) rule is exponential. The values given by these two rules are only equal when solvent fraction is 0.0 or 1.0. Here, diffusion coefficients are those predicted for diluted MAPD in propylene and diluted MAPD in other solvents, respectively. Darken rule considers that diffusivity increases proportionally with the amount of solvent. With Vignes rule, the effect of solvent is mainly felt after its amount reaches 50 % in the mixture.

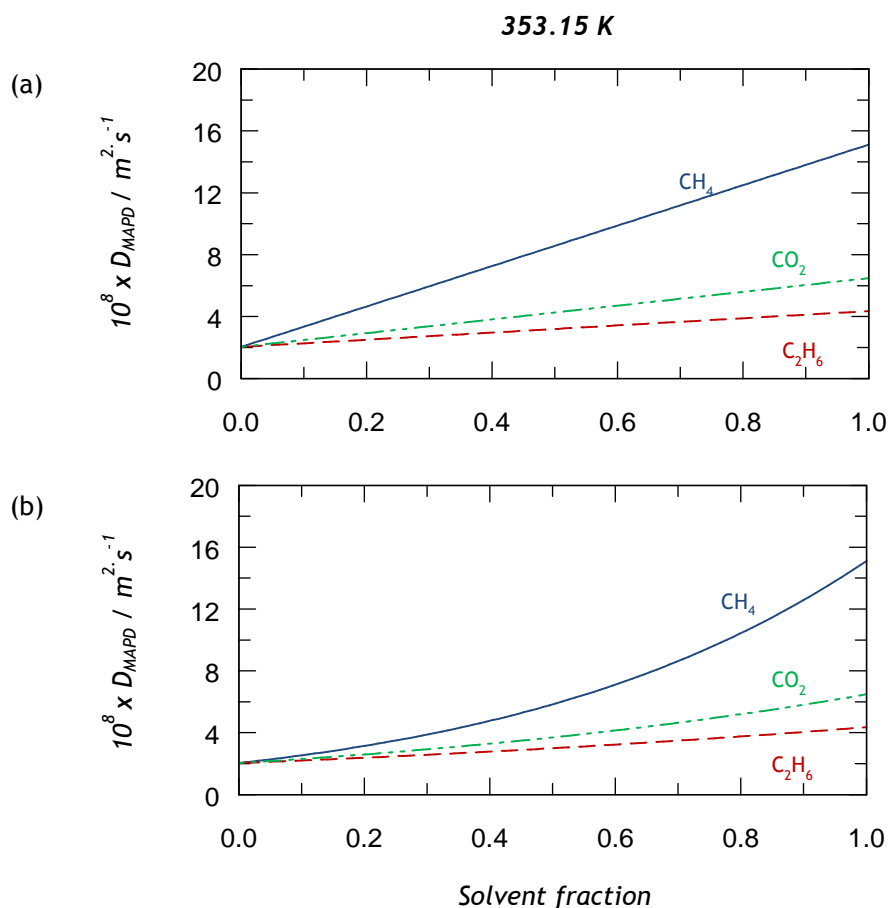


Figure 6 - Predicted diffusion coefficients for a mixture of MAPD in propylene and solvent, at 120 bar and 353.15 K, using (a) Darken and (b) Vignes rules. (blue) methane; (red) ethane; (green) carbon dioxide.

None of these rules consider phase change and are rough approximations to real diffusion coefficients. When higher amounts of solvent are used the mixture passes to the supercritical domain, where diffusion is greatly improved. This means that after adding a certain amount of solvent, diffusivity will start increase faster with equal increments of solvent. Therefore, it was

decided that the Vignes rule will be the one considered, since it better approximates the described behavior.

4.1.5 Conclusions

Several correlations to estimate infinite dilution diffusion coefficients were tested in this chapter. Liu-Silva-Macedo correlation appears to give good predictions for the tested conditions (constant pressure of 120 bar, or constant temperature of 353.15 K) and is based in physical meaningful parameters. Results with this correlation predict that MAPD will have higher diffusion coefficients in methane, followed by carbon dioxide and ethane. It was decided that Vignes rule will be used to estimate diffusion coefficients for mixtures of MAPD in propylene and another solvent.

In the next chapter, experimental results of MAPD hydrogenation will be presented. The predictions performed in the chapter should help explain these results.

5 Experimental Data

To achieve supercritical domain, solvents are often used because (i) they moderate experimental conditions and (ii) they improve mass transfer coefficients, due to changes in diffusion coefficients (Chapter 4). For this reason, two solvents were chosen: methane and ethane. These fluids are alkanes with low molecular weight, probably having great potential as solvents for supercritical operations (Baiker, 1999). Carbon dioxide will not be considered, even though similar diffusion coefficients to those of ethane were obtained.

An experimental work has been done by Pinho et al. (2014) to determine the mixture critical points (working conditions) for the solvents mentioned above. The authors determined that the tests could be performed at 120 bar and 353.15 K, with a molar fraction of solvent above 60 %, for ethane, and 30 %, for methane.

The main objectives of the experimental trials are to understand:

1. WHSV effects in high-pressure (liquid state) (information acquired in Pinho, 2014);
2. WHSV and temperature effects;
3. H₂/MAPD ratio effects;
4. the solvent effect (liquid mixture and supercritical mixture).

In continuous flow reactors, contact time between the fluid and the catalyst can be defined as the hourly mass flow rate of liquid substrate (Q_m) over the catalyst (of mass m_c) present in the reactor.

$$WHSV = \frac{Q_m}{m_c} \quad \text{Eq. 17}$$

where $WHSV$ (h⁻¹) is the weight hourly space velocity. Q_m and m_c are given in kg·h⁻¹ and kg, respectively. This parameter can be seen as the inverse of residence time, $1/\tau$.

5.1 Setup and procedure

The experimental tests were performed in a pilot installation. A schematic representation of the primary equipment is showed in Figure 7.

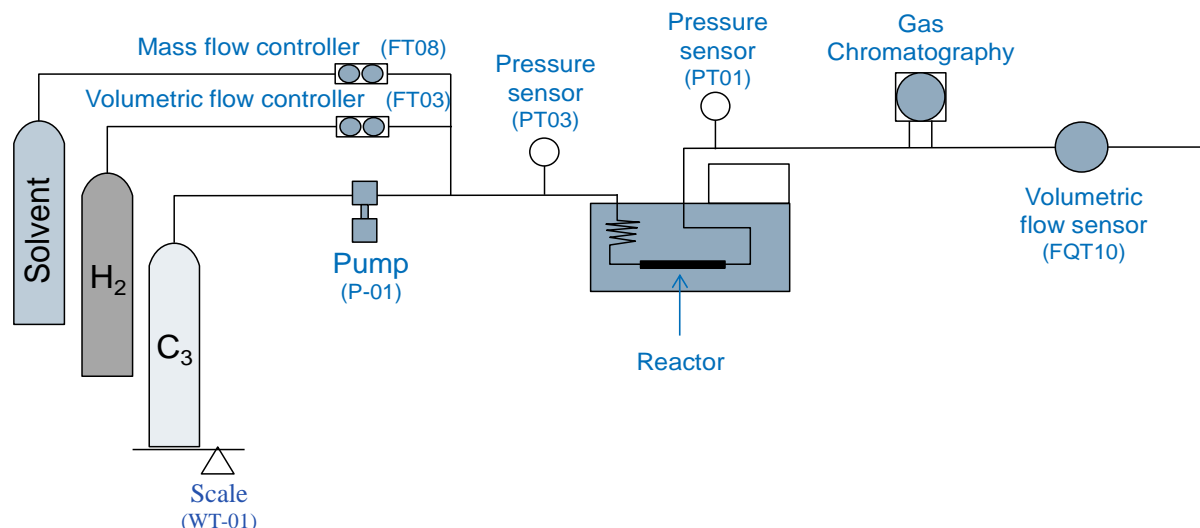


Figure 7 - Schematic representation of the pilot installation primary equipment (Pinho, 2014).

The reaction is conducted in a 1.40 mL single string pellet reactor (a continuous flow reactor), which has 30 % random pack organization. The reactor is submerged in a thermostatic bath for temperature control. Two pressure sensors placed immediately before (PT03) and after (PT01) the reactor make sure the pressure inside remains constant. A schematic representation of the reactor is given in Figure 8.

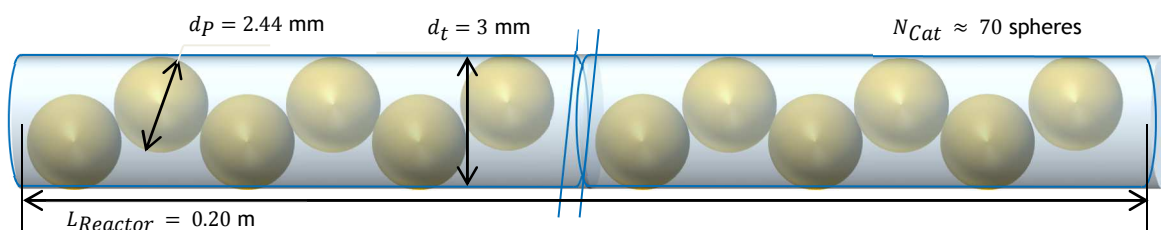


Figure 8 - Schematic representation of the pilot reactor used in the experiments (Pinho, 2014).

Feedstock is pumped to the reactor by using a piston pump (P-01). A scale (WT-01) is laid under the bottle with feedstock, in order to know the mass spent during each trial. A line of hydrogen is directly connected to the installation, and its flow is measured by a thermal mass flow controller (FT03). As for the solvent, it is compressed by a compressor (not represented in the picture) before reaching the plant. Its flow is controlled by a Coriolis mass flow controller (FT08).

After reacting, the fluid passed through a drum (FQT10) in order to measure its flow. A fluid sample is sent to a chromatograph to be analyzed, while the remaining goes into a waste line. Before starting the experiments, a load sample is also analyzed in the chromatograph.

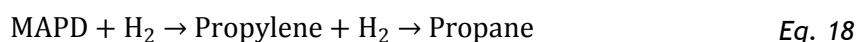
Succintly, the procedure involves 6 steps:

1. Analyze load (several analysis may be done);
2. Define temperature and pressure settings;
3. Define load, hydrogen, and solvent flows;
4. Analyze mixture from the reactor (several analysis may be done);
5. Stop load and solvent feeds;
6. Decompress the reactor, while maintaining hydrogen flowing. It will clean the catalyst for the next day.

Each procedure takes (on average) between 2-4 hours to be completed, as the reactor needs to reach steady state before the analysis can be accounted.

5.2 Experimental Results

In this section, the results obtained during the internship are presented. It is important to note that oligomerization (parasite reaction) could not be taken into account in the analysis. Therefore, a simplified reaction scheme was considered.



The tests performed in the installation can be divided into three groups: high-pressure (tests without solvent), supercritical (tests with methane or ethane as solvent), and diluted load (tests with propylene as solvent). Five parameters (see Table 5) were individually changed in each test, in order to understand their effect in the reaction. Moreover, parameters were equally changed between groups of testes, to allow their comparison. All parameters and their tested values are listed in Table 5, as well as the feedstock composition.

Table 5 - Experimental parameters and their values for the set of tests at high-pressure, in supercritical conditions, and with diluted load, as well as the feedstock composition for all tests.

Set of tests	Temperature (K)	Pressure (bar)	H ₂ /MAPD molar ratio	WHSV (h ⁻¹)	Solvent
High-pressure	303.15; 353.15	120	1; 2; 4	200; 400; 800	None
Supercritical	353.15	120	1; 2; 4	200; 400; 800	Methane; Ethane
Diluted load	353.15	120	1; 2; 4	200; 400; 800	Propylene

Feedstock composition: 96.01 % Propylene (11943 mol·m⁻³); 2.23 % Propane (227 mol·m⁻³); 1.63 % MAPD (203 mol·m⁻³); traces of Methane and Ethane.

In the next subchapters, we will study the effects of WHSV and H_2 /MAPD ratio in conventional liquid conditions for two different temperatures. Afterwards, the effect of adding a solvent (including load dilution) will be studied.

5.2.1 Effect of WHSV

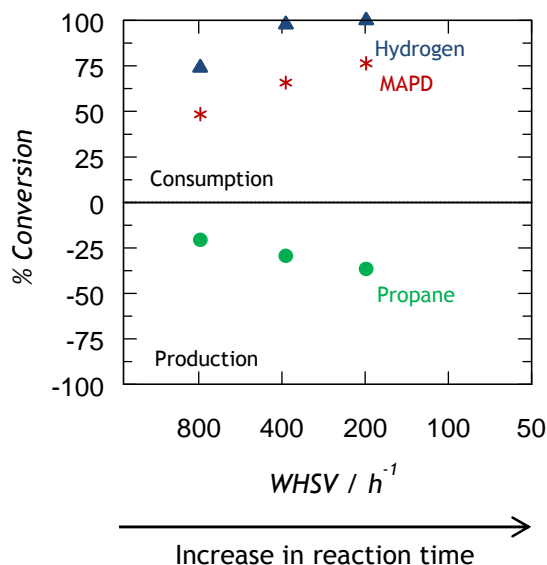
Conditions: 120 bar, 303.15 K, 1 H_2 /MAPD ration and 0.6 kg of catalyst W.

a) Observations

Regarding Figure 9, the hydrogen is totally consumed when WHSV is lower than 800 h^{-1} . In relation to propylene, it is stable in Figure 9 (b) for the full WHSV range studied. However, low WHSV (below 800 h^{-1}) favors propane production. This seems directly proportional to the MAPD consumption.

Reaction conversion

(a)



(b)

Liquid phase / 303.15 K

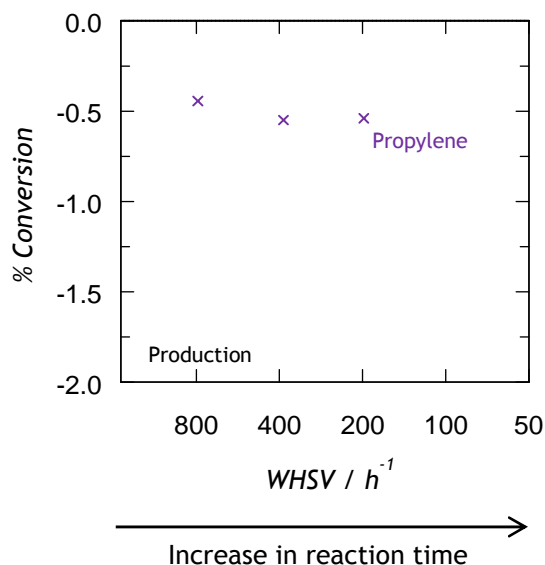


Figure 9 - Conversion of the species present in the load, at 303.15 K, 120 bar and 1 H_2 /MAPD ratio. (\blacktriangle) Hydrogen; ($*$) MAPD; (\bullet) Propane; (\times) Propylene. Note: The X-axis is presented in semi logarithmic scale to simplify data interpretation.

b) Conclusions

At the tested conditions, MAPD conversion drops from around 76 % (200 h^{-1}) to 48 % (800 h^{-1}). Simultaneously, propane production decreases from 36 % (200 h^{-1}) to 21 % (800 h^{-1}). Hydrogen being totally consumed may suggest that there is enough residence time to perform the

reaction. With the present results it is not clear if the reaction at high-pressure conditions is limited by WHSV, by liquid-solid mass transfer, or by the lack of H₂.

5.2.2 Effects of WHSV and temperature

Conditions: 120 bar, 1 H₂/MAPD ration and 0.6 kg of catalyst W.

a) Observations

Results at 120 bar evaluated at temperatures of 303.15 and 353.15 K are shown in Figure 10.

The main difference between the results at different temperatures is related to the MAPD conversion (Figure 10 (a)). At 200 h⁻¹, the conversions are similar. It appears that MAPD conversion is limited to a maximum value for the temperatures chosen (conversion is around 76 % for 200 h⁻¹). From 400 to 800 h⁻¹, MAPD is more converted at 353 K (highest temperature studied).

Hydrogen (Figure 10 (b)) at 303.15 and 353.15 K is totally consumed below 800 h⁻¹. Despite the temperature increase, the amount of propane formed is similar for the two temperatures at all WHSV studied (Figure 10 (c)). So, propylene production is increased at higher temperature without increasing the propane content (Figure 10 (d)).

Reaction conversion

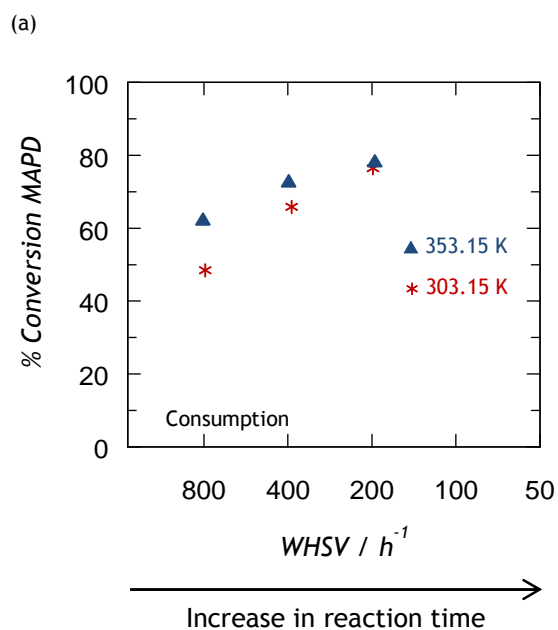
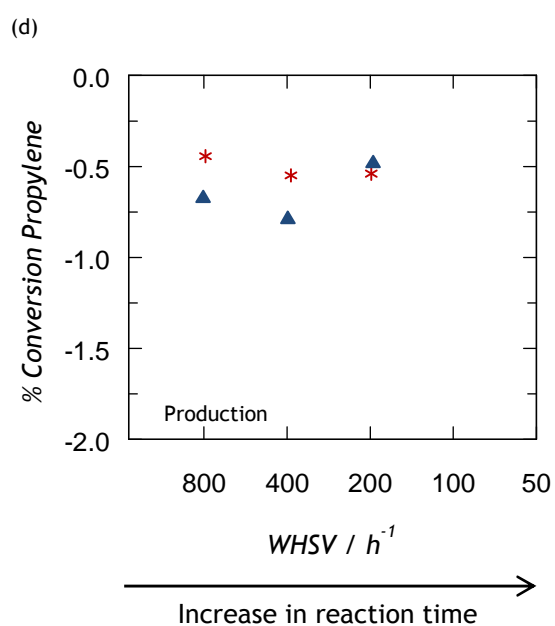
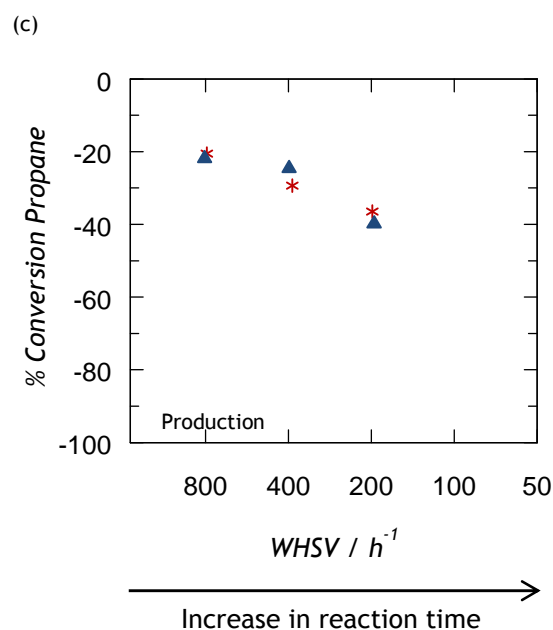
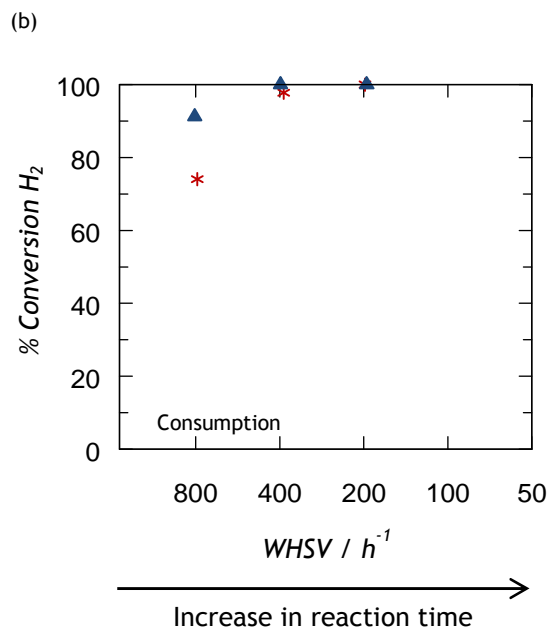
Liquid phase / 1 H₂/MAPD ratio

Figure 10 - Conversion of the species present in the load at (▲) 353.15 K and (*) 303.15 K. Pressure set at 120 bar and 1 H₂/MAPD ratio. Note: The X-axis is presented in semi logarithmic scale to simplify the data interpretation.

b) Conclusions

The results can be linked with an increase of the reaction rate (exponential constant in the Arrhenius equation). But it is still not clear if the system is limited by WHSV, by mass transfer, or by the lack of hydrogen, as propane also consumes H₂. Even knowing that diffusivities for

both MAPD (Figures 3 (a) Chapter 0) and hydrogen in propylene are higher with increasing temperatures, it is not possible to obtain further conclusions.

Regarding 200 h^{-1} , between 303.15 and 353.15 K, decreasing WHSV (extending the residence time) is not advantageous, as MAPD conversion appears to have reached a maximum. As a final remark for this study, one can conclude that higher temperatures favor the intended reaction.

5.2.3 H_2 /MAPD ratio and WHSV effects

Although temperature affects the reaction outcome, the total hydrogen present in the reactor is also an important parameter to study, since it might help identifying the zones where the reaction rate has slowed down. To understand how H_2 /MAPD ratio affects the reaction, several experiments were performed. The H_2 /MAPD (molar) ratio was evaluated at 1, 2, and 4.

Conditions: 120 bar, 353.15 K, and 0.6 kg of catalyst W.

a) Observations

The conversion of MAPD rises when increasing the H_2 /MAPD ratio, regardless of the WHSV used. For instance, at 200 h^{-1} and 4 H_2 /MAPD ratio, the MAPD conversion is 92.4 %, which is greater than the 76 % achieved at ratio of 1. Having a higher MAPD conversion leads to higher amounts of propane produced. At 200 h^{-1} and 4 H_2 /MAPD ratio, the propane content at the outlet increased by 223 %. At 800 h^{-1} , where the amount of MAPD converted was lower, the increase in propane content was 168 %. This outcome is also reflected in the propylene conversion.

Reaction conversion

Liquid phase / 353.15 K

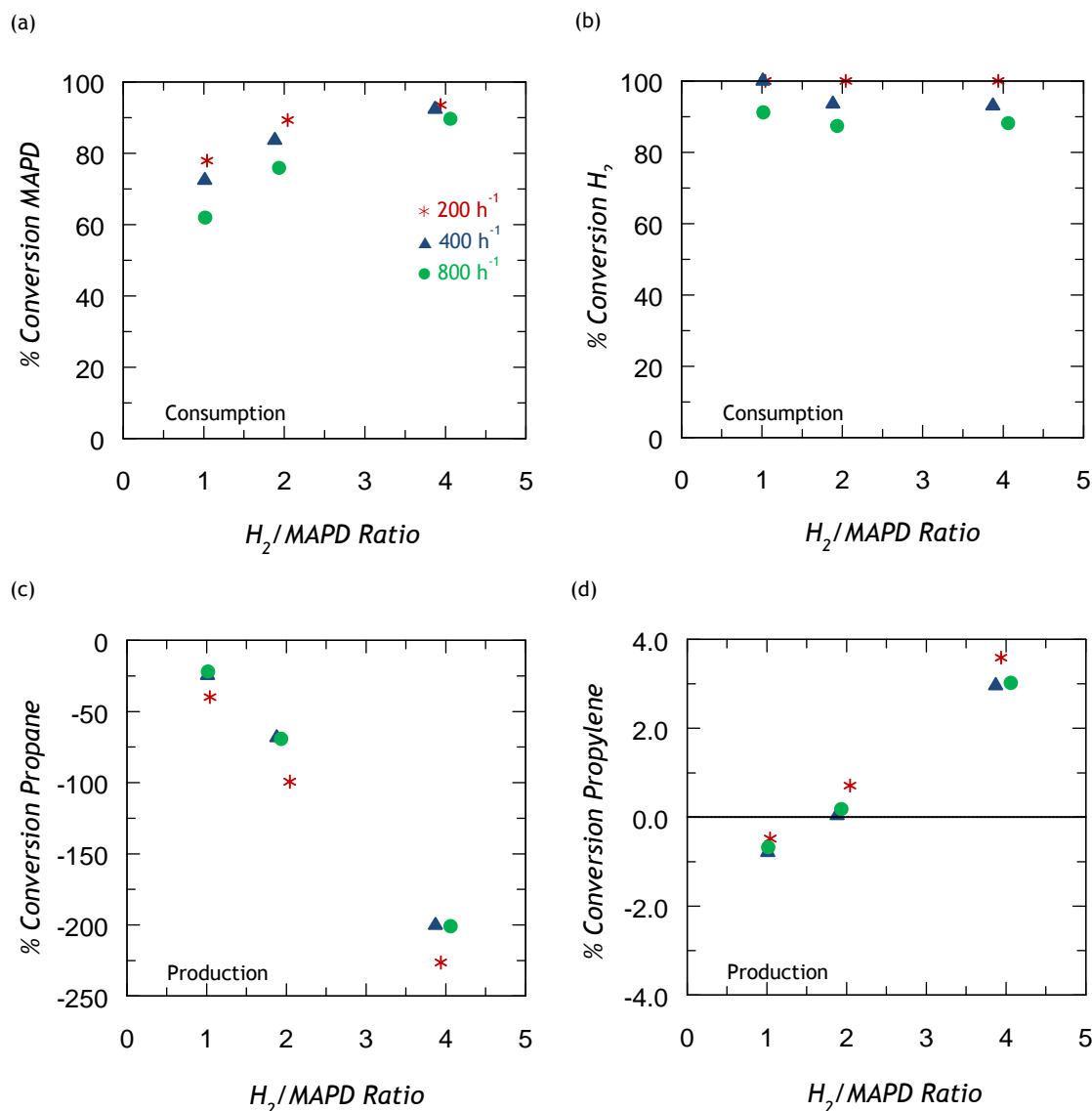


Figure 11 - Conversion of (a) MAPD, (b) hydrogen, (c) propane, and (d) propylene at different H_2/MAPD ratios. Trials were performed at 120 bar and WHSV of (*) 200 h^{-1} , (▲) 400 h^{-1} and (●) 800 h^{-1} .

b) Conclusions

Since the conversions have the same trend lines for the WHSV studied, we might say that mass transfer may remain constant when changing H_2/MAPD . Looking carefully at 800 h^{-1} and 200 h^{-1} , all the conversions at 800 h^{-1} are inferior to 200 h^{-1} . This might be related to not enough contact time. If so, it means reaction is not the limited phenomenon. Conversion limitations are significant after 400 h^{-1} , therefore the (total) reaction rate should be obtained at around 600 h^{-1} .

5.2.4 Solvent effect

Better results in terms of mass transfer are expected when adding a solvent, due to the increase of mixture diffusivity (LSM correlation and mixing rules). Diffusion coefficients for a mixture can be predicted if Darken or Vignes mixing rules are considered (Lito et al., 2013). This was previously detailed on Chapter 2.3. In the present study, the Vignes mixing rule will be used (more adapted to the system). Supercritical experiments were performed with two solvents, methane or ethane.

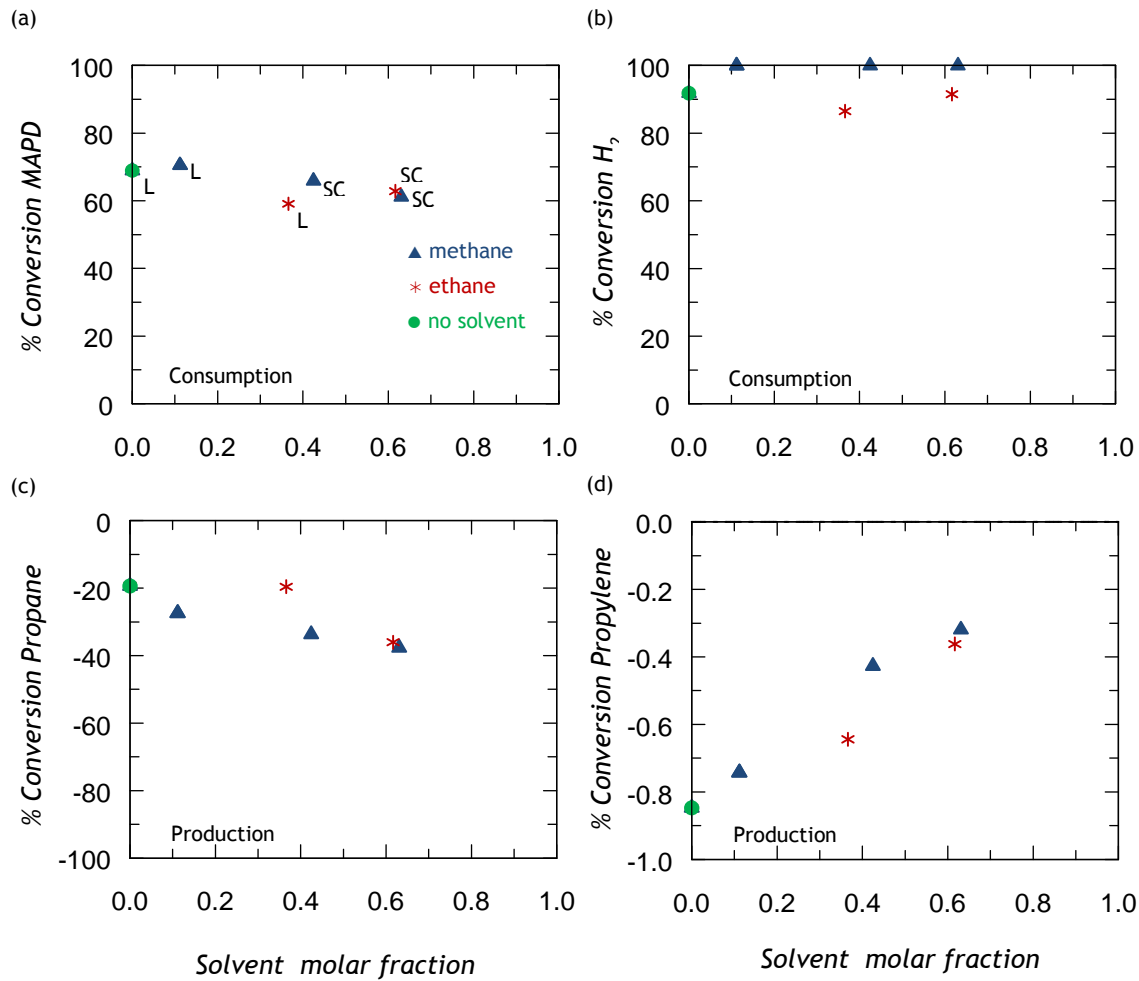
Conditions: 120 bar, 353.15 K, 1 H₂/MAPD ration and 0.6 kg of catalyst W.

a) Observations

Figure 12 (a-d) shows the conversions when different quantities of supercritical solvent are added. Higher fractions of solvent in the load appear to reduce the MAPD conversion. When 60 % of solvent is added, methane and ethane lead to equal results. At these conditions, the mixtures are both in the supercritical domain (where mass transfer is improved). All the hydrogen available is consumed when methane is used, but 11 % remains unreacted for ethane.

When 60 % (molar base) of methane or ethane is added to the mixture, propane increases about 40 %. This might be a result of MAPD dilution. As a result, propylene tends to be converted to propane (less propylene formed).

Reaction conversion



Mass transfer (MAPD)

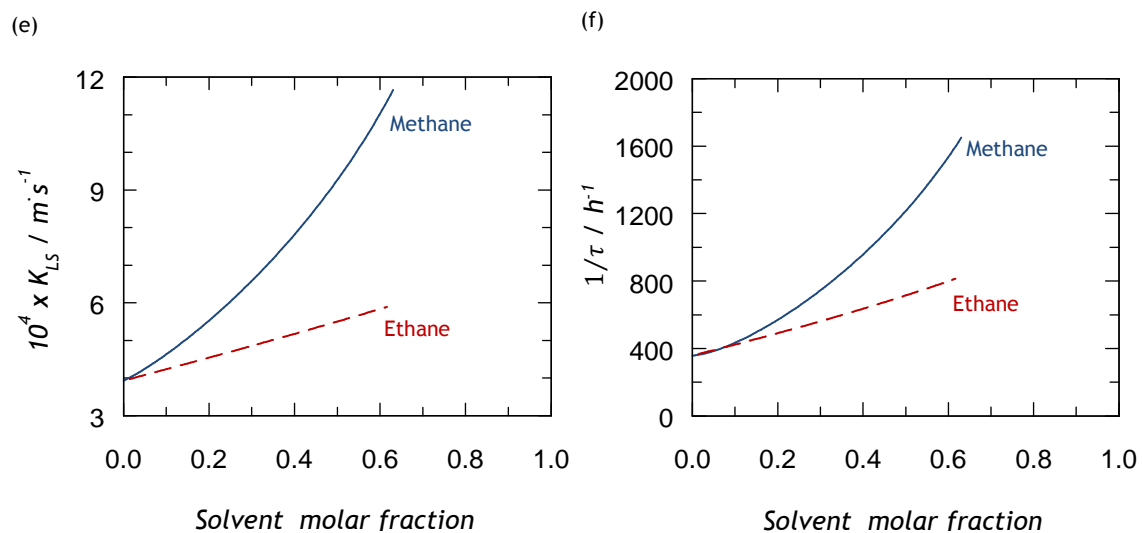


Figure 12 - Conversion of (a) MAPD, (b) hydrogen, (c) propane, and (d) propylene, at 353.15 K, 120 bar and 1 H₂/MAPD ratio. (▲) Methane; (*) Ethane; (●) No solvent. (e) MAPD mass transfer coefficient and (f) inverse of residence time for the mixture in (-) Methane (--) and Ethane.

b) Conclusions

So far, it appears that the use of supercritical solvents does not enhance reaction rate. But the previous analysis ignored that the molar concentration of MAPD and residence time (or WHSV) change with the solvents (Figure 12 (f)). Therefore, the effect of higher diffusivity and mass transfer is disguised (Figure 12 (e)).

Regarding Figure 12 (f), the inverse of residence time ($1/\tau$, in h^{-1}) is very different for high molar concentration of methane and ethane. It was decided that results should be compared for similar MAPD concentration ($\text{mol}\cdot\text{m}^{-3}$) at a given flow rate. A new expression for the residence time, which is related with concentration, is obtained when the mixture volumetric flow ($Q_{V,mixture}$) is divided by the reactor volume ($V_{reactor}$), which has a porosity (ε_L) of 0.55.

$$\frac{1}{\tau} = \frac{Q_{V,mixture}}{V_{reactor}\varepsilon_L} \quad \text{Eq. 19}$$

where $Q_{V,mixture}$ and $V_{reactor}$ are given, respectively, in $\text{m}^3\cdot\text{h}^{-1}$ and m^3 .

To gather trustworthy conclusions about the solvents effect, supercritical results will be compared to those in high-pressure conditions with similar concentration.

5.2.5 Supercritical vs. high-pressure conditions

H_2/MAPD ratios of 1 and 2 will be compared. By this way, we will try to understand the influence of H_2/MAPD and supercritical fluids. From all the data points evaluated, only the ones with a inv. of time residence of $\sim 900 \text{ h}^{-1}$ were chosen, which will be represented as a function of MAPD (molar) concentration in the reactor conditions, $C_{MAPD,R}$.

Conditions: 120 bar, 353.15 K, $\sim 900 \text{ h}^{-1}$, and 0.6 kg of catalyst W.

a) Observations

MAPD: For the data points without solvent, from 173 to $40 \text{ mol}\cdot\text{h}^{-1}$ the MAPD conversion decreases 35 %. That value is even greater (50 %) if 2 H_2/MAPD ratio is considered. At low concentrations, different H_2/MAPD ratios appear to have no significant impact in the MAPD conversion. When solvents are used, the MAPD conversion is similar for methane and ethane, if equal H_2/MAPD ratios are considered.

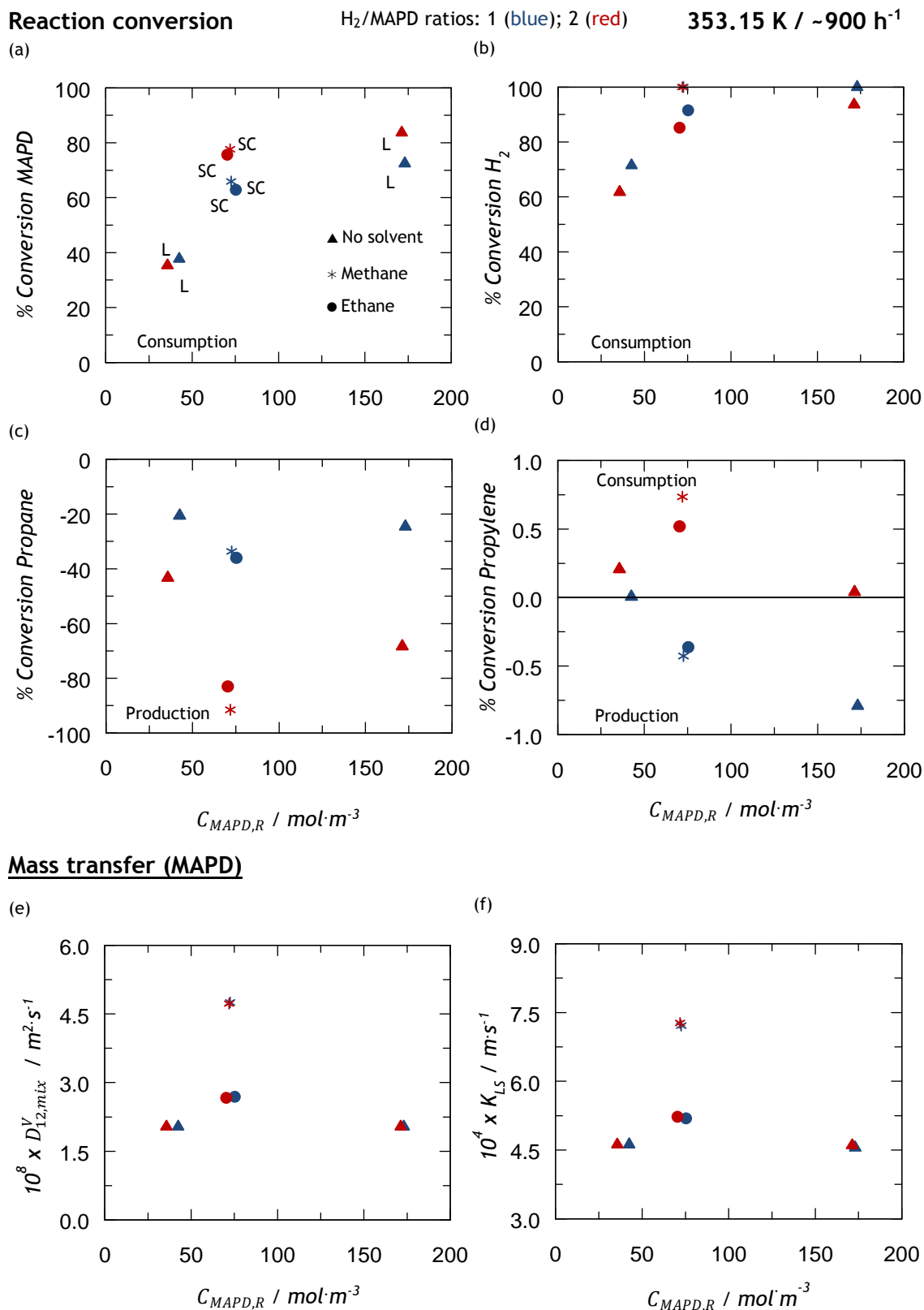


Figure 13 - Conversion of (a) MAPD, (b) hydrogen, (c) propane, and (d) propylene, at 353.15 K and 120 bar, having $H_2/$ MAPD ratio of (blue) 1 and (red) 2. (e) MAPD diffusion coefficients and (f) MAPD mass transfer coefficient. (▲) No solvent; (*) Methane; (●) Ethane.

Hydrogen: When no solvent is used, the consumption of hydrogen decreases significantly for low MAPD concentration (around $40 \text{ mol}\cdot\text{h}^{-1}$). For methane, the hydrogen is always totally consumed. For ethane, some hydrogen is still available at the end of the reaction, which may be related to smaller diffusion coefficients when compared to methane.

b) Conclusions

This approach uncovers information that were hidden when using solvent molar percentage. Three main conclusions can now be stated:

- Concentration of MAPD in the mixture defines the extent of the reaction. High hydrogen/MAPD ratios are better to be used if MAPD is present at high concentrations.
- Same conversions were obtained for different supercritical mixtures with methane or ethane. Since both mixtures have different mass transfer coefficients, we may say that the reaction has no mass transfer limitation in the zone studied (in terms of residence time and MAPD concentration).
- Hydrogen consumption is different when methane or ethane are used. However, MAPD conversion is similar. This situation may be related with the uncertainty of H_2 determination at the outlet (gas chromatography).

5.2.6 Comparison between high-pressure (liquid) and supercritical (methane as solvent)

To test the reliability of the previous conclusions, we can use the data points for which the inv. of residence time was $\sim 1700 \text{ h}^{-1}$. These are only available for methane, without solvent, and diluted load. Only experimental data at H_2/MAPD ratios of 1 and 4 will be showed.

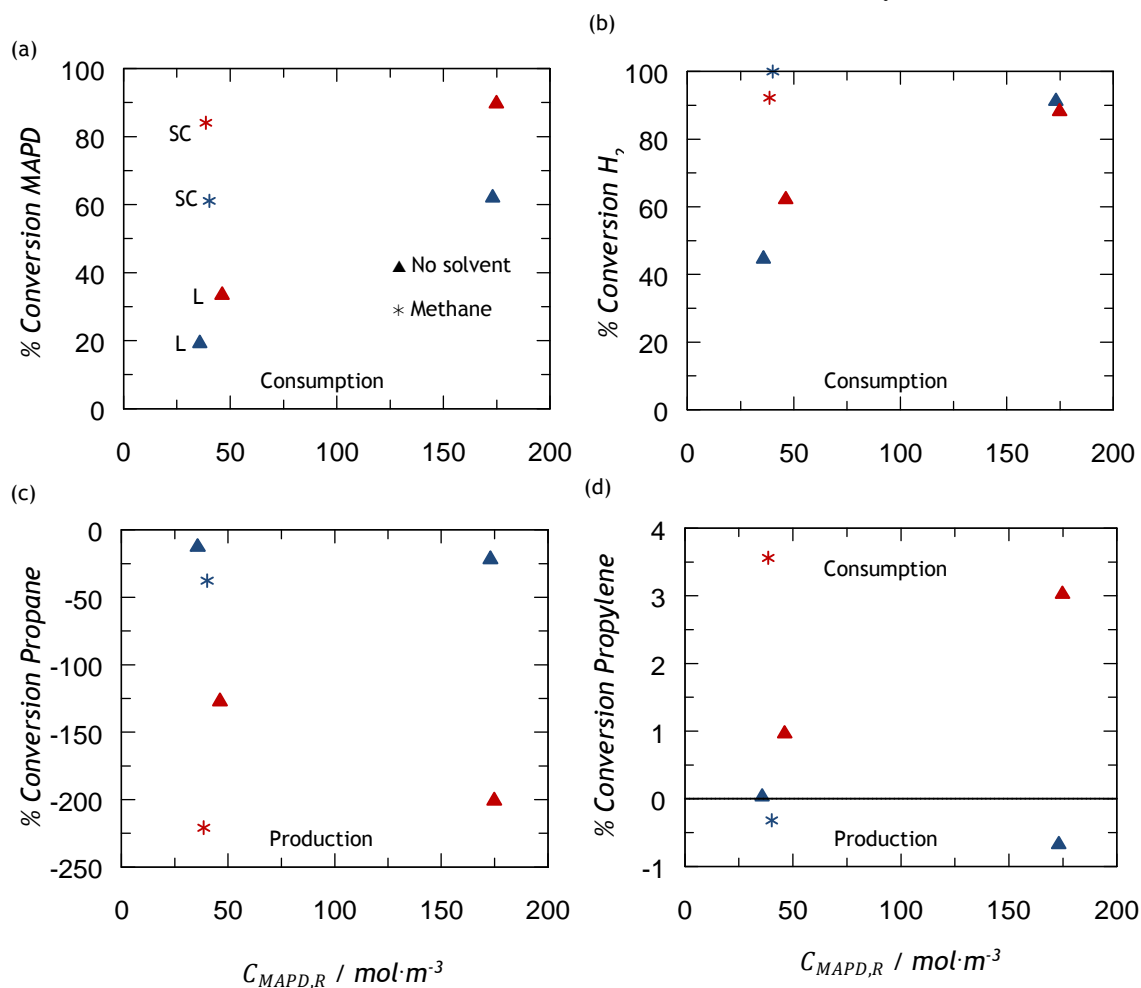
Conditions: 120 bar, 353.15 K, $\sim 1700 \text{ h}^{-1}$, and 0.6 kg of catalyst W.

a) Observations

It has been seen in Figure 13 that when solvents are not used and the MAPD concentration is low, 1 and 2 H_2/MAPD ratios lead to similar results. In Figure 14, we can see that if 4 H_2/MAPD ratio is used instead, some differences are visible. When methane is used, a small increase in the MAPD conversion is also observed for 4 H_2/MAPD ratio.

Using higher H_2/MAPD ratio leads to higher conversions for solvent and no solvent mixtures. For mixtures with solvent, hydrogen is totally consumed, excepting for 4 H_2/MAPD ratio ($>92\%$). It is possible that the 8 % are not accounted and are related with oligomers formation. Nevertheless, much is used to produce propane (increase of 221 % for 4 H_2/MAPD). As a result, the propylene starts to be greatly converted (for 4 H_2/MAPD). For mixtures without methane, similar behavior is observed.

Reaction conversion

H₂/MAPD ratios: 1 (blue); 4 (red)353.15 K / ~1700 h⁻¹

Mass transfer (MAPD)

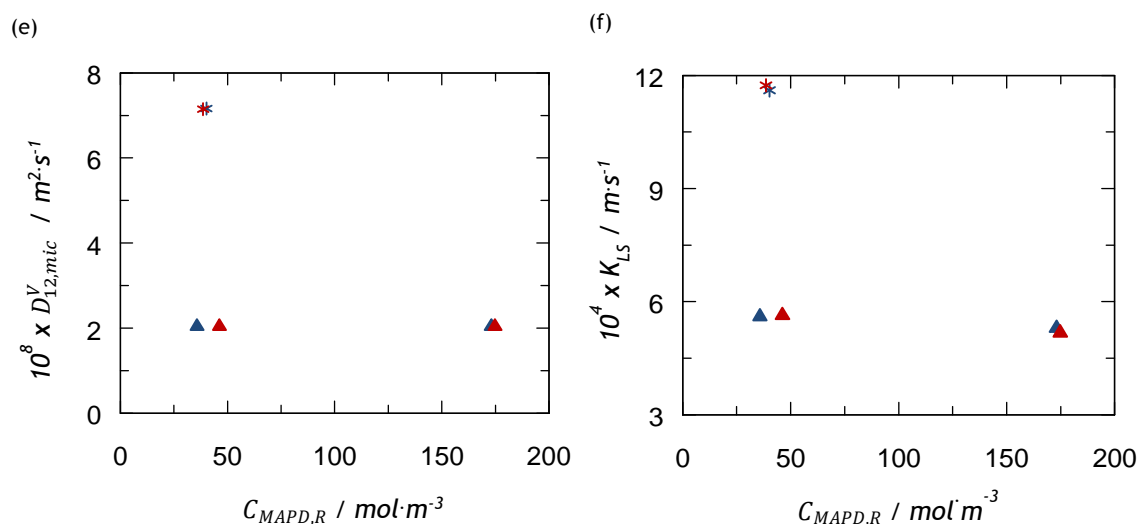


Figure 14 - Conversion of (a) MAPD, (b) hydrogen, (c) propane, and (d) propylene, at 353.15 K and 120 bar, with H₂/MAPD ratio of (blue) 1 and (red) 4. (e) MAPD diffusion coefficients and (f) MAPD mass transfer coefficient. (▲) No solvent; (*) Methane.

When solvents are not used, the reaction at 1 H₂/MAPD ratio leads to poor MAPD conversion (~20 %). As a result, propane is not largely produced, but neither is propylene. With methane, conversions of 61 % are obtained. Propane and propylene conversions are also increased. These results might be connected with mass transfer rate.

b) Conclusions

From Figure 14 some important conclusions can be made:

- The MAPD conversion is higher in supercritical conditions than in high-pressure conditions. This is related to greater diffusion (Figure 14 (e)) and liquid-solid mass transfer coefficients (Figure 14 (f)).
- High conversions were achieved at around 1700 h⁻¹ (inverse of residence time) and 4 H₂/MAPD ratio. It seems that the reaction is not limited by residence time. For the same conditions, it seems that the reaction does not have mass transfer limitations, because the hydrogen is fully converted (4 H₂/MAPD ratio).
- There is clear advantage in using supercritical conditions in comparison with high-pressure conditions. In high-pressure conditions (for 353.15 K), the total reaction rate can be found near 555 h⁻¹ (600 h⁻¹ if WHSV is considered) (see Chapter 5.2.3). In supercritical conditions (for 353.15 K), the total reaction rate is found above 1700 h⁻¹ (higher values are expected).

6 Conclusions

It is a challenge to perform and understand reaction results in fast reactions, due to mass transfer limitations. Adding a solvent and carry out reactions in supercritical medium can suppress those limitations. That way, reaction rates are close to intrinsic kinetics, which simplifies and improves catalytic screening.

Liquid-solid mass transfer resistances are negligible when using supercritical fluids due to higher diffusion coefficients. These were predicted by using Liu-Silva-Macedo correlation. It was concluded that when a solvent is added (methane, ethane or carbon dioxide) the diffusivity is higher (up to 8 times) than that observed without a solvent.

Several experimental trials were performed at different operating conditions. The results showed that the MAPD hydrogenation increases with higher temperature, H_2 /MAPD ratio and the MAPD concentration. It was also found that when using supercritical fluids, the MAPD conversion is unaffected at low residence time, which is a result of higher diffusion and mass transfer coefficients. Moreover, the total reaction rate in supercritical conditions is higher than in high pressure conditions (visible limitations at $>1700\text{ h}^{-1}$ vs $\sim 555\text{ h}^{-1}$).

When comparing solvents, methane and ethane achieved similar results at equal inverse of residence time and reactant concentrations, even though they have different diffusion coefficients. It can be concluded that mass transfer limitations outside the catalyst are negligible. The supercritical conditions may be applied in the future for catalytic screening.

6.1 Accomplishments

The purpose of the internship was to study the impact of the supercritical medium in the MAPD (catalytic) hydrogenation. Several tests were performed to verify the effect of different parameters in the reaction's outcome. Based on the conclusions, we may say that supercritical fluids may be used to carry out catalytic screening.

6.2 Limitations and future work

Performing experimental trials in the pilot unit was an easy task. The installation worked in a semi-automated mode. However, the main challenge was the short time available to test the solvent carbon dioxide. Other challenges included:

- The piston pumps used to feed the load to the reactor that were constantly having their check valves damaged. Since this problem was normally realized halfway through the tests, several trials had to be repeated. The type of pump chosen was probably not suitable to work with light hydrocarbons.

- The first industrial feedstock used (C₃-cut) that was contaminated lead to conversions which were substancially lower than expected by Pinho (2014). As a result, an entire month of experimental trials could not be accounted and had to be redone.

The chromatograph was not programmed to analyze oligomers, even though it could detect (but not specify) them. This means that hydrogen was not fully accounted in the mass balance, resulting in some deviations. For future experiments, it is advised that all species are accounted by the chromatograph.

Diffusivity was studied as thoroughly as possible by using different correlations. However, diffusion is a complex subject and requires a long time to be fully understood.

6.3 Final appreciation

Few students are able to work in a pilot installation before finishing their courses. Even more difficult is doing this kind of work in a renowned company such as IFPen, where high standards are always expected. Being able to gain professional experience by doing very interesting experimental work was a very rewarding experience, especially considering that good results were obtained during the internship. I hope the knowladge acquired can be further used in the future.

7 References

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Appendices

Appendix 1 - Correlations based on the Hydrodynamic Theory (A)

Three different correlations were chosen to represent this theory.

1.1. Modified hydrodynamic equation (1979)

In order to increase the range of application of the Stokes-Einstein hydrodynamic equation, a simple modification can be performed: the addition of an exponential term (β) to solvent viscosity and viewing $\frac{k_B}{6\pi r_2}$ as an adjustable parameter (α). This possibility was first acknowledged by Evans et al. (1979). The equation has, therefore, two parameters that are dependent on the mixture. When $\beta = -1$, the correlation becomes the Stokes-Einstein equation. The parameters are determined by fitting experimental data.

$$D_{21} = \alpha T \eta_1^\beta \quad \text{Eq. 20}$$

where T (K) is the temperature and η_1 (Pa·s) is the solvent viscosity. The subscripts 2 and 1 refer to solute and solvent, respectively.

This equation provides good results for binary systems, but it can also be applied to self-diffusion with equal outcome (Funazukuri et al., 2008).

1.2. Wilke-Chang (1955) correlation

Wilke-Chang (1955) correlation is another modified Stokes-Einstein equation, but its development was purely empirical. It is one of the most used to describe diffusion for nonionic species in liquids at dilute concentrations (Louis J. Thibodeaux and Donald Mackay, 2010). The equation is written as:

$$D_{21} = 7.4 \times 10^{-8} \frac{T \sqrt{\gamma M_1}}{\eta_1 V_{2b}^{0.6}} \quad \text{Eq. 21}$$

where D_{21} ($\text{m}^2 \cdot \text{s}^{-1}$) is the diluted diffusion coefficient of a solute (2) in a solvent (1), T (K) is the absolute temperature, M_1 ($\text{g} \cdot \text{mol}^{-1}$) is the solvent molecular weight, η_1 (cP) is the solvent viscosity, and V_{2b} ($\text{cm}^3 \cdot \text{mol}^{-1}$) is the solute molar volume at its normal boiling temperature. γ is a dimensionless (association) factor, being 1 for unassociated solvents, such as linear alkanes.

If V_b data are not available, it is possible to predict them by group contribution method (Sastri et al., 1996).

This hydrodynamic-based correlation is used with great ease since it is able to determine diffusion coefficients with sufficient accuracy for a huge range of solutes (Olesik and Woodruff, 1991). However, according to Lin and Tavlarides (2010) for some mixtures the average relative deviations are quite important. One way for the correlation to provide better results would be by varying the association factor.

1.3. Magalhães et al. (2013) correlations

In a recent work, Magalhães et al. (2013) tested simple two-parameter correlations, from which four were based in the Hydrodynamic Theory. They all achieved great accuracy even for prediction purposes (global AARD was lower than 4.46 % in all cases). Although, experimental data has to exist in order to regress the parameters of those equation.

Appendix 2 - Correlations based on the Hard-Spheres Theory (B)

Four different correlations were chosen to represent this theory.

2.1. Fuller et al. (1966) correlation

Fuller et al. (1966) developed a semi-empirical correlation for the diffusion in binary systems where the solvent is in the gaseous phase. The correlation is based on the average molar volumes of solute and solvent. It is mainly used when Lennard-Jones parameters are not available or when their values are questionable (Bruce E. Logan, 1999). Fuller's correlation is given by

$$D_{21} = \frac{T^{1.75} \times 10^{-3}}{P (V_{2,d}^{1/3} + V_{1,d}^{1/3})^2} \left(\frac{1}{M_2} + \frac{1}{M_1} \right)^{1/2} \quad \text{Eq. 22}$$

where D_{21} ($\text{cm}^2 \cdot \text{s}^{-1}$) is the binary diffusion coefficient, T (K) is the absolute temperature, P (atm) is the pressure, $V_{i,d}$ ($\text{cm}^3 \cdot \text{mol}^{-1}$) is the atomic diffusion volume, and M_i ($\text{g} \cdot \text{mol}^{-1}$) is the molecular weight. The coefficients 1 and 2 refer to solvent and solute, respectively, whereas the subscript d denotes diffusion. (The atomic diffusion volume is essentially the molar volume. Though, it will be treated as something different in order to be coherent with the author's work).

The information required to use this correlation are easily gathered. If the atomic diffusion volume (ADV) of a compound is not available, one can estimate it through the volume contribution of each atom that composes the molecule. In this work, all the considered hydrocarbons have only a certain number of carbon and hydrogen atoms in their constitution, whereas carbon dioxide has oxygen instead of hydrogen. According to Fuller et al. (1966) tabulated values, the volumes of hydrogen, carbon, and oxygen are 1.98, 16.5, and 5.48, respectively. As an example, the ADV of propylene ($V_{propene,d}$) is given by

$$V_{propene,d} = 3 \times 16.5 + 6 \times 1.98 = 61.38 \text{ cm}^3 \quad \text{Eq. 23}$$

The atomic diffusion volume for all the substances that will be considered are given in Table A. 1.

Table A. 1 - Atomic diffusion Volumes for the compounds considered in this work. *Methylacetylene and Propadiene are different species, but have exactly the same atoms in their constitution. Therefore, they can be view as a pseudo-compound.

Compound	# of C atoms	# of H atoms	# of O atoms	ADV (cm ³ ·mol ⁻¹)
Carbon Dioxide	1	0	2	27.46
Methane	1	4	0	24.42
Ethane	2	6	0	44.88
Propylene	3	6	0	61.38
MAPD*	3	4	0	57.42

This equation is very simple and fairly accurate (according to the authors, the average error is 8.96 %) and it has the advantage of being able to be used in a wide range of temperature and pressure (Fuller et al. 1966).

2.2. He-Yu (1998) correlation

In the 1950s, Cohen and Turnbull studied the molecular motion in dense liquids and glasses. They came up with a theory that described diffusion as occurring when a molecule is able to move into a void with a size greater than a critical volume, V_c . Voids would be formed during the redistribution of free volume within solvent. Inspired by the work of Cohen and Turnbull, He and coworkers (He, 1997; He and Yu, 1997; He et al., 1998; He, 1998; He and Yu, 1998) developed correlations that approached the theories of free volumes and Hard-Spheres.

The first proposed equation (He, 1997; He and Yu, 1997) successfully predicted tracer diffusion coefficients for liquid and solid solutes in supercritical solvents. 107 systems and 1167 data points were considered, achieving an average deviation of 7.5 %. In the following year (He et al., 1998), the group made small modifications to their correlation. Comparable results for the same conditions were achieved. They used experimental data of 105 binary systems with 1146 data points, and the average deviation was 7.4 %. Afterwards, He (1998) stated that the reason why most correlations fail to predict diffusion coefficients in a large range of conditions was probably because the effect of solvent density had been neglected. Hence, the author combined his previous correlation with an exponential term that accounted for the effect of density. Although the new equation had a bigger AARD %, the database used for its development was more extended (113 binary systems with 1332 data points, deviation of 8.2 %).

He and Yu (1998) finally came up with another correlation for the estimation of tracer diffusion coefficients. The group assumed the following:

- the close-packet molar volume depends only on the solvent properties, since the amount of solute is very small;
- The effect of temperature is neglected when estimating molecular diameters

After analyzing the available experimental data, they concluded that the correlation would be influenced mostly by the properties of the solvent. The new equation, known as He-Yu correlation, is given by

$$D_{21} = A \times 10^{-9} \sqrt{\frac{T}{M_2}} \exp\left(-\frac{0.3887V_{c_1}}{V_1 - 0.23V_{c_1}}\right) \quad \text{Eq. 24}$$

where A is a parameter that depends of the solvent , T (K) is the temperature, M_2 ($\text{g}\cdot\text{mol}^{-1}$) is the solute molecular weight, V_{c_1} (cm^3) is the solvent critical volume, and V_1 ($\text{cm}^3\cdot\text{mol}^{-1}$) is the solvent molar volume. The parameter A is calculated through

$$A = 14.882 + 5.908k + 2.0821k^2 \quad \text{Eq. 25}$$

$$k = \frac{T_{c_1} V_{c_1}}{1000M_1} \quad \text{Eq. 26}$$

where M_1 ($\text{g}\cdot\text{mol}^{-1}$) and T_{c_1} (K) are the molecular weight and critical temperature of the solvent, respectively.

The solvent molar volume may be determined by the following expression.

$$V_1 = \frac{1000M_1}{\rho_1} \quad \text{Eq. 27}$$

where ρ_1 ($\text{g}\cdot\text{cm}^{-3}$) is the solvent density.

When applied to the experimental data (113 binary systems with 1332 data points), the correlation was able to predict the tracer diffusion coefficients in supercritical and high-temperature liquid solvents with an AARD % of only 7.3 %. At the same time, it covered a large range of solvent temperature ($0.70 \leq T_{r_1} \leq 1.78$) and density ($0.22 \leq \rho_{r_1} \leq 2.62$), as well as wide range of solute molecular weight ($58.1 \leq M_2 \leq 885.4$).

Lin and Tavlarides (2010) verified the effectiveness of He-Yu correlation. Due to the reduced density range (minimum value), the duo believed the equation should only be used for estimations in the supercritical region.

More than a decade later, Shi and Lu (2010) modified the He-Yu equation by incorporating the solute density with the purpose of improving the accuracy when high-density solutes are concerned. The AARD of the new equation is 6.55 % (better than the He-Yu's), even though they used more data points. However, the prediction ability of He-Yu equation is higher when the solute molar mass is smaller than 100 g·mol⁻¹. So, in general, the new equation does not bring a significant improvement (Zhu et al., 2002). That is the reason why He-Yu correlation was chosen instead.

2.3. Liu et al. (1998) correlation

The equation of Liu-Silva-Macedo (LSM) is based on Hard-spheres and on the Lennard-Jones potential. Initially, the group developed an equation for the estimation of self-diffusion coefficients in dense fluids (Liu et al., 1996). The simple substitution of self-property parameters for mixture parameters made their equation suitable for predicting tracer diffusion coefficients in dense gases and liquids (Liu et al., 1997). These would be determined through simple combining rules. In order to improve the combining rules, correction parameters were introduced separately for each one. They improved the AARD % significantly, but it can only be applied if experimental data for pure substances is available. The modified equation without the correction parameters was not able to predict diffusion coefficients in the supercritical domain with good accuracy (16.88 % deviation). For the same conditions, the two corrected equation have deviations of 7.16 and 7.17 %, respectively.

In another work, Silva et al. (1998a) made reference to the attractive forces that have an important role at low temperatures. In order to account the refer forces in their correlation, an effective diameter was coupled. The following equation was used.

$$\sigma_{21}^{eff} = 2^{1/6} \sigma_{21}^{LJ} \left[1 + \sqrt{\frac{1.3229T}{\frac{\epsilon_{21}^{LJ}}{k_B}}} \right]^{-1/6} \quad Eq. 28$$

where σ_{21}^{LJ} (cm) is the Lennard-Jones size parameter, and ϵ_{21}^{LJ} (K) is the Lennard-Jones energy parameter. T (K) is the temperature, k_B (m²·kg·s⁻²·K⁻¹) is the Boltzmann constant, and the superscript *eff* denotes effective diameter.

After this last improvement, Liu-Silva-Macedo equation for prediction of tracer diffusion coefficients (D_{21}) in dense fluids was completed (Eq. 29). The correlation has two parameters, σ_{21}^{LJ} and ϵ_{21}^{LJ} .

$$D_{21} = \frac{k_B T}{\left(\frac{8}{3}\right) n_1 (\sigma_{21}^{eff})^2 (\pi m_{21} k_B T)^{1/2}} \exp \left[-\frac{0.75 n_1^*}{1.2588 - n_1^*} - \frac{0.27862}{T_{21}^*} \right] \quad \text{Eq. 29}$$

where n_1 (cm^{-3}) is the solvent number density of solvent. m_{21} (g) and T_{21}^* are the unlike weight and the reduced temperature of the mixture, respectively. The first is given by Eq. 11, while the second can be estimated through

$$T_{21}^* = \frac{T k_B}{\varepsilon_{21}^{LJ}} \quad \text{Eq. 30}$$

For validating their correlation, 2514 data points were used. The Lennard-Jones parameters cited in their work (Liu et al., 1996) are optimized values.

In another work, Silva et al., (1998b) points out that their previous equation could not represent with ease the diffusion coefficients if molecules were polar or non-spherical. In order for the correlation to account for this substances, the group decided to introduce two parameters. These should be determined by regression of experimental data. In the same work, the group studied the possibility of creating generalized correlations for the estimation of LJ parameters. It was already known that the diffusion coefficient was more sensitive to diameter than to energy. Therefore, it was decided that the later would be given by a simple corresponding states equation:

$$\frac{\varepsilon_i^{LJ}}{k_B} = 0.794 T_c \quad \text{Eq. 31}$$

where T_c (K) is the critical temperature and i is the molecular species.

When the goal is to estimate thermodynamic properties of mixtures, the approach that is used the most concerns the one fluid approximation. This idea consists of combining the individual properties of components in a mixture into pseudo-properties that define the system as a whole (a pseudo-fluid). Of course, several one fluid approximations may be used. It is assumed that the pseudo-fluid will follow the Corresponding States Principle. This principle was first identified by van der Waals, who during his investigation noticed that the thermodynamic properties of different fluids could be expressed by the exact same set of expressions, as long as the aforementioned are scaled, i.e., if expressions are presented in terms of reduced properties (Galliéro et al., 2006).

As for the LJ diameter, the team managed to relate its value with the critical properties of compounds (Eq. 32).

$$\sigma_i^{LJ} = \left[0,17791 + 11,779 \left(\frac{T_c}{P_c} \right) - 0,049029 \left(\frac{T_c}{P_c} \right)^2 \right]^{1/3} \quad \text{Eq. 32}$$

where P_c (bar) is the critical pressure of compound i .

2.4. Lito et al. (2013) correlation

Based on the Rough Hard-Spheres model and the work of Liu and coworkers, Magalhães et al. (2011a; 2011b) developed a new correlation for the prediction of tracer diffusivities. The first step was to develop a new expression for the Rough Hard-Spheres correction factor, F_{21} (the subscript '21' indicates a correction factor for the diffusion of a solute (2) in a solvent (1)). Through the use of a statistical software, the group was able to present an improved correction factor, given by

$$F_{21} = \frac{F_{11} + n_1^{*1.7} [a \ln(\sigma_2^{LJ}/\sigma_1^{LJ}) + b \ln^2(\sigma_2^{LJ}/\sigma_1^{LJ}) + c \ln^2(m_2/m_1)]}{1 + n_1^{*3.0} [d \ln(\sigma_2^{LJ}/\sigma_1^{LJ})]^2} \quad \text{Eq. 33}$$

where n_1^* is the solvent reduced number density, m (kg) is the molecular mass, σ^{LJ} (m) is the Lennard-Jones diameter, F_{11} is the self-diffusion factor, and a , b , c , and d are parameters. The parameters can be calculated through the following expressions:

$$\begin{cases} a = -1.676382n_1^* + 1.638561 \\ b = -8.516830n_1^* + 8.631536 \\ c = -1.3203472n_1^* + 1.351067 \\ d = -5.062546n_1^* + 5.409662 \end{cases} \quad \text{Eq. 34}$$

$$F_{11} = 1 + 0.94605n_1^{*1.5} + 1.4022n_1^{*3} - 5.6898n_1^{*5} + 2.6626n_1^{*7} \quad \text{Eq. 35}$$

For the radial distribution function, the group decided to use the expression of Mansoori et al. (1971), for its simplicity.

$$g(\sigma_{21}) = \frac{1}{(1 - \varphi_1)^3} \left(1 - \varphi_1 + \frac{2\varphi_1}{1 + \sigma_2^{LJ}/\sigma_1^{LJ}} \right) \left(1 - \varphi_1 + \frac{\varphi_1}{1 + \sigma_2^{LJ}/\sigma_1^{LJ}} \right) \quad \text{Eq. 36}$$

$$\varphi_1 = \frac{\pi}{6} n_1^* \quad \text{Eq. 37}$$

Lastly, an exponential factor with a fitting parameter was selected and added to the Rough Hard-Spheres model to account for the attractive forces (see Eq. 38). The unlike LJ parameters are determined through the LB combining rules. The formulae for estimating LJ parameters and the EHSD, as well as for calculating the unlike mass of the system (m_{21}) are those used by Liu et al. (the molecular diameters σ^{LJ} presented on Eq. 36 and Eq. 37 are, in fact, the effective diameters. The reduced number density is also calculated using the effective diameter).

In order for the correlation to be applied to real fluids, Lito et al. (2013) decided that the solvent size parameter should be seen as a fitting parameter, instead of taking its real value. Therefore, the resultant correlation for tracer diffusion coefficients is given by Eq. 38. It had two fitting parameters, σ_1^{LJ} and E_D , and it can be used with all kinds of mixtures.

$$D_{21} = \frac{3}{8n_1\sigma_{21}^2} \sqrt{\frac{k_B T}{2\pi m_{21}}} \left(\frac{F}{g(\sigma)}\right) \times \exp\left(-\frac{E_D}{R_g T}\right) \quad \text{Eq. 38}$$

where R_g ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$) is the universal gas constant, E_D ($\text{J}\cdot\text{mol}^{-1}$) is a parameter related to the mixture, n_1 (m^{-3}) is the solvent number density, k_B ($\text{m}^2\cdot\text{kg}\cdot\text{s}^{-2}\cdot\text{K}^{-1}$) is the Boltzmann constant, and T (K) is the absolute temperature.

The parameters of the correlation have to be fitted to experimental data. The group used 8293 data points (487 systems), which resulted in an AARD of only 2.74 %, according to the authors. This correlation offers excellent accuracy, especially if one considers the existence of only two parameters.

When potential parameters are not available, the authors suggest the using Eq. 32 (LSM correlation) to predict the molecular size. For the molecular energy, Eq. 39 is recommended.

$$\frac{\varepsilon_i^{LJ}}{k_B} = 0,774T_c \quad \text{Eq. 39}$$

Appendix 3 - Combining rules for potential parameters

Combining rules are used to estimate properties of mixtures, through the knowledge of those properties for pure fluids. In order to determine the Lennard-Jones parameters of unlike molecules, many rules have been proposed to this day. The ones usually used by default were developed by Lorentz (1881) and Berthelot (1898), therefore known as Lorentz-Berthelot (LB) rules. The unlike size parameter of a binary mixture (σ_{21}^{LJ}) is given by the arithmetic mean of pure fluid size parameters (σ_1^{LJ} and σ_2^{LJ}). On the other hand, the unlike energy size parameter of a binary mixture (ε_{21}^{LJ}) is given by the geometric mean of pure fluid energy parameters (ε_1^{LJ} and ε_2^{LJ}).

$$\sigma_{21}^{LJ} = \frac{\sigma_1^{LJ} + \sigma_2^{LJ}}{2} \quad \text{Eq. 40}$$

$$\varepsilon_{21}^{LJ} = (\varepsilon_1^{LJ} \times \varepsilon_2^{LJ})^{1/2} \quad \text{Eq. 41}$$

where all parameters are given in any set of coherent units.

The LB combining rules are both simple and accurate for the majority of cases (Schnabel et al., 2007). For that reason, they are used most of the time. Recently, Galliéro et al. (2006) studied the effect of the size and energy parameters of a mixture, when employed in the estimation of viscosity. They tested several empirical combining rules (basically, different expressions to calculate averages) in order to test the sensibility of the van der Waals one-fluid approximation. The team determined that all rules lead to negligible deviations. In the following year, Schnabel et al. (2007) tested the predictive power of eleven robust combining rules. The group's objective was to predict three different properties of fluids (vapor pressure, bubble density, and dew point composition), which can be related with the size and energy parameters. Their study showed that all sets of parameters were not able to correctly predict the properties intended. By defining a certain target area through computer simulations, the group found that the LB combining rule was the one closest to that area, even though the values were mostly underestimated.

It is true that the Lorentz-Berthelot rules may comprise some error. For that reason, some studies have been performed in order to improve this set of rules. For instance, by using molecular dynamics simulations, Iwai et al. (1997) determined the energy and size parameters for naphthalene and 2-naphthol in supercritical carbon dioxide. The LB combining rules were selected, to which they added intermolecular interaction parameters, l_{21} and k_{21} .

$$\sigma_{21}^{LJ'} = (1 - l_{21}) \left(\frac{\sigma_1^{LJ} + \sigma_2^{LJ}}{2} \right) \quad \text{Eq. 42}$$

$$\varepsilon_{21}^{LJ'} = (1 - k_{21}) (\varepsilon_1^{LJ} \times \varepsilon_2^{LJ})^{1/2} \quad \text{Eq. 43}$$

where the parameters l_{21} and k_{21} are between 0 and 1. The superscript LJ' refers to modified Lennard-Jones parameters

The objective was to account the interaction between different molecules. Their simulations showed that the use of these parameters would not have a major impact on the estimation of diffusion coefficients for the referred solutes, albeit they would improve the results. According to White (2000), it is usual that the attractive (related to energy) and the repulsive (related to size) interaction parameters follow inverse paths when correction factors are used. If $(1 - l_{21})$ is bigger than 1, $(1 - k_{21})$ will be lower than 1. This makes sense, because smaller molecules should attract each other with higher intensity. Therefore, the effect that the introduction of parameters could have had is cancelled out.

Using Iwai's results along with the size and energy parameters for several other compounds available in the literature, Zhou et al. (2000) estimated the infinite dilution diffusion coefficients for the aforementioned solutes in supercritical carbon dioxide. Through molecular dynamics simulations, the group applied both the LB combining rules and a set of empirical rules developed by them (ZLWS combining rules). By comparing with experimental data, Zhou et al. concluded that the ZLWS predicted more precisely than the LB combining rule. Moreover, the latest lead to systematically lower diffusion values. It was also concluded that one can obtain better results if size parameters are determined through the LB rule and the energy parameter is adjusted. This statement corroborates the conclusions of White (2000).

In an recent extensive work, Haslam et al. (2008) generalized the Hudson and McCoubrey combining rules by deriving several expressions for different kinds of molecules (small, large, polar, non-polar,...), which considered not only the standard Lennard-Jones intermolecular potential, but also more complicated intermolecular potentials with additional terms. The group then compared the resultant combining rules with the available experimental data. They found out, among other things, that even though the more complex combining rules achieved better results, the enhancement was not interesting enough for one to use them in binary mixtures of n-alkanes, in spite of the Lorentz-Berthelot rules, especially if the alkanes are of similar size. Therefore, it can be anticipated that an alkane-alkene mixture should lead to similar conclusions.

To assume that one set of combining rules is better than another is debatable, as it was clearly shown. However, most authors believe that the Lorentz-Berthelot rules provide sufficient

accuracy to be applied as a first approximation. They can also be applied if rigorous values are not strictly necessary. For other situations, it is important to try different combining rules, so as to find out one which best suits the purpose. Nevertheless, the best way to create robust mixture parameters, no matter what they are related to, is through experimental data.

Appendix 4 - Effect of different sets of potential parameters

The LSM equation uses Lennard-Jones parameters on their correlation. The parameters, were obtained from the group's previous works. However, different sets of parameters from other authors could also reveal themselves as accurate. For prediction purposes in this work, parameters of Liu et al. were used. However, a comparison against the parameters of other authors was made, so as to understand their influence in the final results.

There are many sets of parameters in the literature. It was decided that the reported experimental parameters of Lito et al. (2013), Vrabec et al. (2001), Iwai et al. (1997) and Yu and Gao (2000) would be used for comparison (Table A. 2). Since Lito et al. suggests equations for predicting potential parameters (see Eq. 32 and Eq. 39), those were used to estimate the sets for which the group provide no experimental data (propylene, propadiene, and methylacetylene). For the other cases, when data was not available, the parameters of Liu et al. (experimental or predicted) were chosen.

Table A. 2 - Compilation of Lennard-Jones parameters used in the present work. Include data of Liu et al. (1997), Lito et al. (2013), Vabrec et al. (2001), Iwai et al. (1997), and Yu and Gao (1999). *Estimated using Eq. 32. **Estimated using Eq. 33. ***Estimated using Eq. 40.

Species	Authors				
	LSM	Lito et al.	Vabrec et al.	Iwai et al.	Yu-Gao
	$\sigma_{LJ}, \text{Å} / \varepsilon_{LJ}/k_B, \text{K}$				
H ₂	5.941 /	5.941 /			
	3.45x10 ⁻³	3.45x10 ⁻³	---	---	---
CH ₄	3,585 /	3,585 /	3.728 /		3.570 /
	167.15	167.15	148.55	---	140.38
C ₂ H ₆	4.176 /	4.176 /	3.490 /		3.609 /
	213.08	213.08	136.99	---	155.36
C ₃ H ₆	*4.473 /	*4.473 /	3.817 /		
	290.26	*281.95	150.78	---	---
H ₂ CCCH ₂	*4.438 /	*4.438 /	3.637 /		
	312.72	*304.84	170.52	---	---
HCCCH ₃	*4.343 /	*4.343 /	3.546 /		
	319.49	*311.84	186.43	---	---
CO ₂	3,262 /	3,262 /	2.985 /	3.720 /	
	500,71	500,71	133.22	236.1	---

The comparison for all solvents is shown in Figure 15. In all cases, it is shown that using Vrabec et al. parameters result in overestimated diffusion coefficients, when compared to the other sets of parameters. Apart from ethane that has higher diffusivity if Yu and Gao parameters are used, for methane and propylene the results are almost the same. When Iwai et al. parameters are used for carbon dioxide, diffusion coefficients are similar to those of LSM. Finally, and as expected, results with Liu et al. parameters and Lito et al. parameters are also almost overlaid.

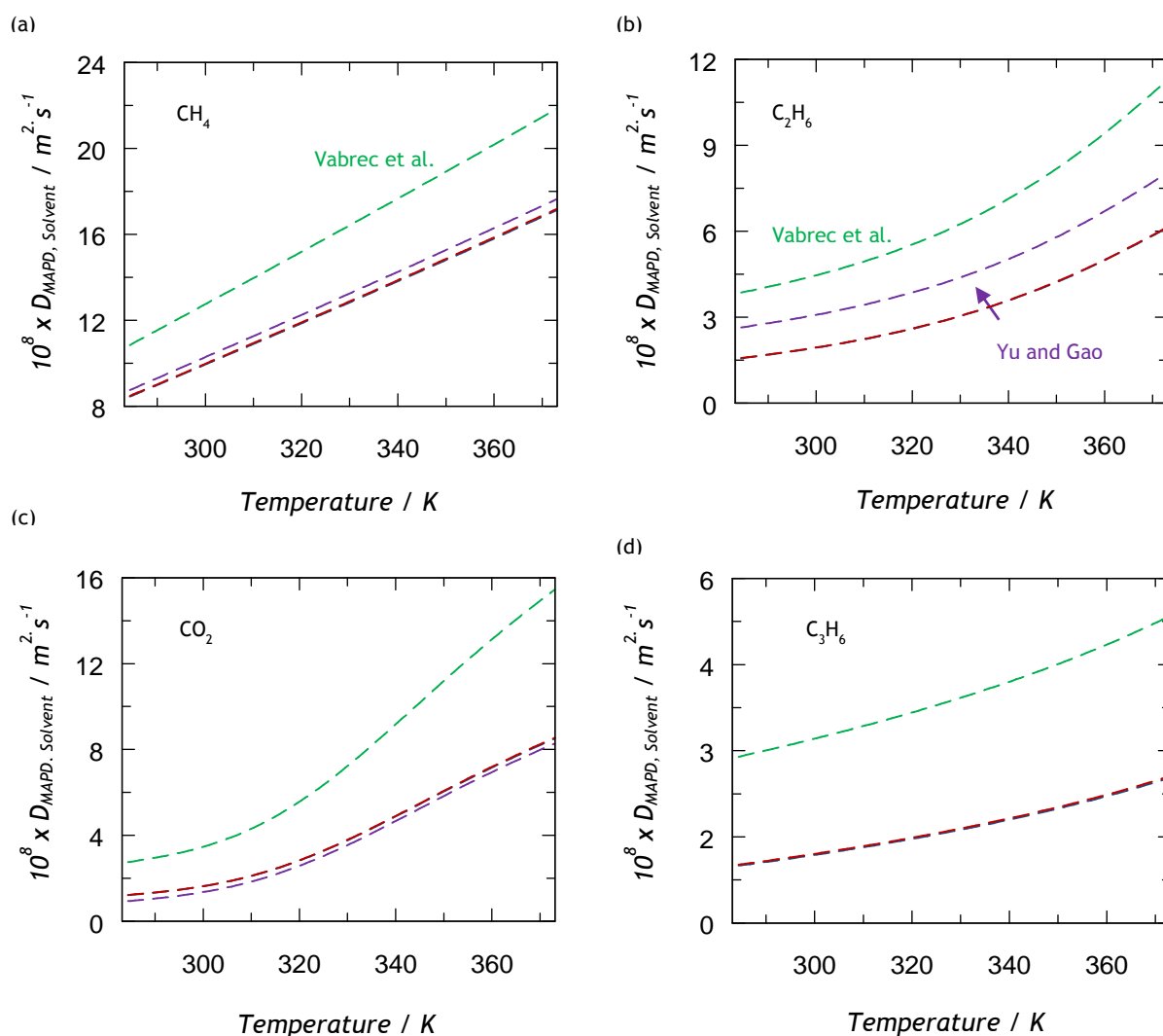


Figure 15 - Predicted diffusion coefficients for MAPD in methane (a), ethane (b), carbon dioxide (c), and propylene (d), at 120 bar. Different sets of Lennard-Jones parameters were used with the LSM correlation. (--) Liu et al. (1997); (--) Lito et al. (2013); (--) Vrabec et al. (2001); (--) Iwai et al. (1997) in (c) and (--) Yu and Gao (2000) in (a), (b), and (d).

This study has clearly shown that very different sets of parameters may lead to similar, or completely different results. The fact that parameters of LSM were used along with Yu-Gao and Iwai et al. parameters may have disguised the effect the different author's parameters could

have brought to the final results (as size and energy parameters are averaged). Performing a previous study about the existing sets of parameters should always be performed, in order to obtain the best results for the intended property(ies).

It would also be possible to test different combining rules for the parameters, rather than those recommended by the authors of the correlation. However, that would result in a modified LSM correlation, which is not the objective of this work. Moreover, it has been explained earlier that different combining rules have minor effects in the prediction of properties, such as diffusivity.

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