Identification, conversion and reactivity of diolefins in thermally cracked naphtha

By

Nidia Yohana Páez Cárdenas

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Abstract

Bitumen extracted from Canadian oil-sands has a high viscosity, which limits its transportation. Field upgrading has become an option to overcome that limitation, without having to dilute the bitumen. During the field upgrading of bitumen, solvent deasphalting in combination with thermal cracking (visbreaking) can be used to produce a material ready to be transported for refining. In the thermal cracking process, mono-olefins and diolefins are generated especially in the light fractions. In many cases the olefin content exceeds the Canadian pipeline specification of <1% as 1-decene equivalent, required to have a product suitable for pipeline transportation. The usual treatment is hydrogenation, however, that treatment is not an option for a field upgrader facility due to the cost of H_2 production and the size of the facility.

Diolefins and especially conjugated diolefins are very reactive at high temperatures. They are capable of undergoing addition reactions to form molecules of high molecular weight better known as gums, that later could form coke. In previous research a non-conventional aromatic alkylation process was proposed to treat mono-olefins, but the conversion of diolefins at high temperatures contributed to catalyst deactivation by fouling. Therefore a hydrogen-free and low temperature alternative was sought to eliminate the diolefins.

Three objectives were set in order to solve that problem: (1) to identify diolefins thermally cracked naphtha, (2) to explore alternative low temperature treatments for diolefins conversion and (3) to

stablish a reactivity sequence of representative olefinic and diolefinic species present in cracked naphtha. The approach taken to develop the research involved three steps that corresponded to each objective.

The identification of diolefins in thermally cracked naphtha was done by means of the gas chromatography-mass spectrometry (GC-MS) coupled with two chemical reactions: hydrogenation and Diels-Alder cycloaddition. This work was done in collaboration with Alberta Innovates Future Technologies (AITF), which analyzed the same sample using gas chromatography with vacuum ultra violet detector (GC-VUV). There was matrix interference due to the variety of compounds present in the naphtha. Four compounds were identified as diolefins, all of them with a conjugated structure: *trans*- 1,3-pentadiene, *cis*-1,3-pentadiene, 2-methyl-1,3-pentadiene and a cyclic diolefin of 7 carbons, possibly 5,5-dimethyl-1,3-cyclopentadiene. Five diolefins were identified by GC-VUV, two conjugated, two isolated and one cumulated: 2,3-dimethyl-1,3-butadiene, 3-methyl-1,3-pentadiene, *trans*-1,4-hexadiene, 1,7-octadiene and tetramethylallene.

The low temperature treatment reactions explored were hydration and Diels-Alder cycloaddition. Hydration was first attempted on a model compound at 110°C, 3 MPa and using four acid catalysts: sulfuric acid in aqueous solution, solid phosphoric acid, Siral-5 and H-ZSM-5. The model compound used was 2,5-dimethyl-2,4-hexadiene. The expected alcohol products of the water addition were not seen, instead a mixture of cracking, oxygenate and addition products was formed. The compounds present in the mixture were: *trans*-1,3-pentadiene, 1,5-hexadiene, 1,3-hexadiene, 1,3-cycloheptadiene, 2,5-dimethyl-2,4-hexadiene and cyclopentene and benzene as

impurities. Conjugated and isolated linear diolefins underwent double bond and *cis-trans* isomerization. The disubstituted conjugated diolefin 2,5-dimethyl-2,4-hexadiene was converted into a cyclic ether.

In the case of the Diels-Alder cycloaddition, the anticipated cyclohexene derivatives, were formed at the conditions of 60°C and using 10 and 15% of $AlCl_3$ as catalyst. The reaction was done using model compounds and a mixture of diolefins with two dienophiles: 3-buten-2-ol and methyl vinyl ketone (MVK). In the case of the model compounds, stereoisomers of 2,4-hexadiene were used, the diolefin *trans-trans*-2,4-hexadiene was the most reactive towards the dienophile. The mixture of diolefins was formed by 2,3-dimetyl-1,3-butadiene, 1,3-hexadiene, *cis*-3-methyl- 1,3-pentadiene, *trans*-3-methyl-1,3-pentadiene, 1,3-cycloheptadiene and 2,5-dimethyl-2,4-hexadiene. The diolefins of open chain were more prone to the cycloaddition, showing higher conversions than the cyclic diolefin. Similar to the reaction using model compounds, when the model mixture was used, the compounds with the *trans* configuration were more reactive.

To stablish a reactivity sequence, hydrogenation was used as test reaction using Pt/C as catalyst. Eight compounds with different structure, but olefinic nature were selected. The order in reactivity found in this work from the most reactive to the least was: 1,4-pentadiene > 1-hexene > *trans*-1,3-pentadiene > 1-methylcyclohexene > 3-methyl-1,3-pentadiene > cyclohexene > 1,3-cylclohexadiene > vinylcyclopentane. According to the results, compounds with linear structure were more reactive, and the presence of branches or a cycle in the molecules decreased their reactivity for hydrogenation.

Dedication

To my parents, Carlos and Elvia and my sister, Claudia. You were not here physically but I could feel your presence in every supporting word. I love you.

"Cuando crezcas, descubrirás que ya defendiste mentiras, te engañaste a ti mismo o sufriste por tonterías. Si eres un buen guerrero, no te culparás por ello, pero tampoco dejarás que tus errores se repitan."

(Pablo Neruda)

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I want to give special thanks to my supervisor, Dr. Arno De Klerk. Thanks for your time and your guidance during the development of this project; your patience and willingness to help in every step of the process made the difference in its culmination. I take advantage of this opportunity to express my sincere gratitude for the opportunity you gave me; besides the academic challenge, which is extremely important to me, this experience helped me to grow in a personal level.

I would like to thank my lab co-workers. Thanks to all the people that had a word of encouragement when the stress could be seen in my face; those words helped me to keep going. Special thanks to Natalia, a fellow grad student, but more than that my friend; thank you for giving me your advice when I asked for it, for enriching the discussion by thinking differently and simply for being there along the way.

To my friend, Yoshinori Casas, I think I would have never come here without that last push you gave me to make the final decision. Thank you.

To my friends back home, Colombia. It has been wonderful to keep in touch. Thank you for being happy for me and encouraging me to continue. Special mention to Yu and Collazos, I remember a call from both of you in a very stressful and disappointing day, you both made me laugh and I treasure that.

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CHAPTER 1 – INTRODUCTION

1. Background

Bitumen from the Canadian oil sands is produced in large amounts and is characterized by the higher viscosity and higher density than that of conventional oil.[1] With a high viscosity, the fluidity of the material is poor and the transport to the market is a more difficult task. A process is required to reduce the viscosity of the Bitumen to make it suitable for transportation.

The present study deals with the partial upgrading process developed by Nexen Energy UCL (Figure 1.1). The bitumen is treated to separate it from salt, water, solids and the asphaltene fraction is precipitated in a solvent deasphalting unit (asphaltenes are a group of really big molecules that contribute to the high viscosity of the oil); the product obtained is called deasphalted oil (DAO). The DAO is upgraded to decrease the oil viscosity in a thermal cracking (visbreaking) process.

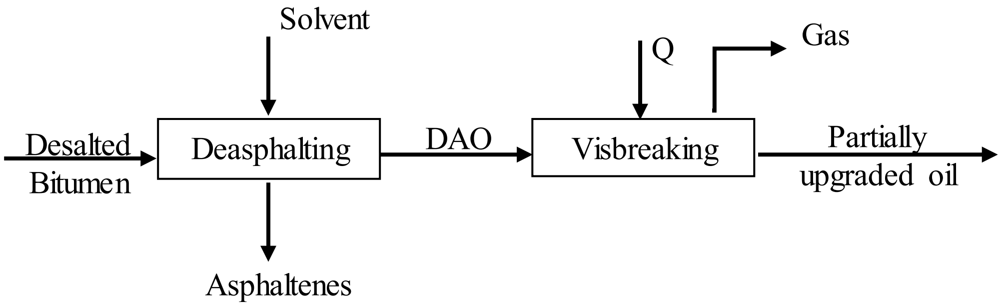


Figure 1. 1. Simplified process flow diagram of a partial upgrading process.

Among the thermal cracking technologies, visbreaking receives special attention in the context of the problem, because it is a mild thermal process. Due to the low severity conditions that characterize it (short residence times and low operating pressure),[2] it is well suited for partial upgrading. During the thermal cracking of DAO a fractionation unit is placed after the visbreaking unit to separate the compounds into streams according to their boiling point range.

Thermal cracking results in the formation of unsaturated and polyunsaturated (diolefins) compounds, found particularly in light boiling fractions, e.g. naphtha fraction.[3] Olefins and diolefins are formed through free radical hydrogen disproportionation reactions.[4] In many cases the concentration of mono-olefins and diolefins together exceeds the Canadian pipeline specification of < 1 wt% as 1-decene equivalent set by the Canadian Association for Petroleum Producers. This is not unique to thermal cracking of bitumen, but a general outcome of thermal cracking processes.[5]

Dealing with olefins in thermally cracked fractions coming from field upgrading facilities requires a conversion pathway that does not require hydrogenation. As mentioned earlier the size of a field upgrading facility is small and the cost associated with hydrogen production make hydrogenation an unsuitable method for partial upgrading processes. For such purposes, a nonconventional aromatic alkylation reaction was developed employing acid catalysis. It was found that despite the basic nature of nitrogen containing compounds present in the mixture, an acid catalyst can be used to alkylate aromatic compounds with olefins, hence forming a non-olefinic product.[6]

The findings were applied to an industrial sample (i.e. thermally cracked naphtha sample coming from a field upgrading facility), but while doing so the catalyst was inhibited by the interaction of the active sites with the basic molecules in the feed, but also deactivated due to carbonaceous deposits formed on the catalyst. Diolefins are deleterious even in units using homogeneous catalysts. It is known that if diolefins are present in great proportions in aliphatic alkylation feedstocks, the life of the acid catalyst is compromised due to diolefin polymers and mono-olefin co-polymers dissolved in the catalyst.[7] There is evidence showing that diolefins give an unstable product capable to initiate addition reactions from which molecules with higher molecular weight are formed.[8] Based on those findings it was hypothesised that conversion of diolefins at high temperature could have been the reason for the observed catalyst fouling behavior.

The presence of diolefins affects not only the treatment of mono-olefins, but also represents a problem for the stability of the cracked naphtha during storage, especially due to conjugated diolefins known for their high reactivity. Diolefins are known for reacting with oxygen to produce hydroperoxides and initiate free radical chain reactions.[9,10] Low temperature free radical addition reaction creates bigger structures forming gums that after precipitation cause the clogging of pipelines. If they make their way to the refinery they will most likely be present under high temperature processes and the outcome of that could be the formation of coke causing the fouling of catalysts or the obstruction in equipment due to gum formation. Having those polyunsaturated molecules become an issue that needs to be addressed, not only to meet pipelining specifications, but also to avoid problems in subsequent processes.

The topic investigated is the identification and treatment of diolefins in light boiling fractions. There were constraining factors imposed by the intended implementation. Two specific aspects that were considered in this work: (1) in dealing with diolefins to avoid the consequences mentioned earlier a low temperature and hydrogen-free strategy is required, (2) to find an adequate treatment, defining the kind of diolefins present must be done beforehand. The light boiling fraction of thermal cracking is a complex mixture of hydrocarbons and hence the identification of diolefins is anticipated to be difficult.

2. Objectives and scope of work

2.1 Objectives

I. The first stage of the present work aimed to develop a strategy for the characterization of diolefins in complex mixtures. The individual diolefins present in a thermally cracked naphtha sample, coming from an industrial cracking facility, had to be identified.

II. Low temperature strategies for converting diolefins without the use of hydrogen were evaluated. The selection of the alternative strategies for reduction of diolefins was based on the characterization of diolefins present in cracked naphtha.

III. The reactivity sequence of representative olefinic and diolefinic species in thermally cracked naphtha was determined. The purpose was to guide future work. Although hydrogenation is not considered for partial upgrading, it was useful as test reaction to evaluate the reactivity sequence of the different olefins.

2.2 Scope and outline of the thesis

The literature of thermally cracked products was consulted, paying especial attention to the formation of unsaturated compounds, their chemical characteristics and main identification techniques available (Chapter 2). Gas chromatography coupled with mass spectrometry (GCMS) in combination with reactions and derivatizations were used in order to characterize diolefins in an industrial sample coming from a thermal cracking process. Results from analysis performed by an external laboratory on the same sample using gas chromatography coupled with a vacuum ultraviolet detector (GC-VUV) were also reported and interpreted (Chapter 3). Hydration, was presented as one possible strategy to decrease the content of diolefins (Chapter 4). It does not involve the use of hydrogen, can be carried out at low temperatures and uses an abundant reagent, water. Another strategy to reduce the diolefins content in naphtha was based on the conjugated nature of some of the diolefins present; the Diels-Alder reaction was investigated (Chapter 5). Tests were conducted in a batch reactor, using model compounds and model mixtures and different acid catalysts (homogeneous and heterogeneous). The study was concluded by determining the reactivity sequence of selected olefins and diolefins found in the cracked naphtha (Chapter 6). The purpose of this work was to help guide future research. Conclusions and suggestions for future work were presented in Chapter 7.

References

(1) Speight, J. G. *Heavy Oil Production Processes*; Gulf professional publishing: Oxford, 2013.

(2) Speight, J. G. *Heavy and Extra-heavy Oil Upgrading Technologies*; Gulf professional publishing: Oxford, 2013.

(3) Speight, J. G. *Fouling in Refineries*; Gulf professional publishing: Amsterdam, 2015.

(4) Rahimi, P. M.; Chen, J.; Brecher, L.; DeBruijn, T. Hydrotreating of liquid products from Cold Lake bitumen obtained in the write process. In *ACS Division of Fuel Chemistry, Preprints*; 2004; Vol. 49, pp 75–76.

(5) Raseev, S. *Thermal and catalytic processess in petroleum Refining*; Marcel Dekker: New York, 2003.

(6) Yuhan, X. Acid Catalyzed Aromatic Alkylation in the Presence of Nitrogen Bases MSc thesis, University of Alberta, Edmonton, AB, Canada, 2012.

(7) Anderson, J.; McAllister, S. H.; Derr, E. L.; Peterson, W. H. Diolefins in Alkylation Feedstocks. *Ind. Eng. Chem.* **1948**, *40* (12), 2295–2301.

(8) Gray, M. R.; McCaffrey, W. C. Role of chain reactions and olefin formation in cracking, hydroconversion, and coking of petroleum and bitumen fractions. *Energy and Fuels* **2002**, *16* (3), 756–766.

(9) Pereira, R. C. C.; Pasa, V. M. D. Effect of mono-olefins and diolefins on the stability of automotive gasoline. *Fuel* **2006**, *85* (12-13), 1860–1865.

(10) Von Zanier, a.; Jäckle, H. W. Thermal-oxidative stability of motor gasolines. *Erdoel Erdgas Kohle* **2000**, *116* (3), 109–115.

CHAPTER 2 – LITERATURE REVIEW

1. Introduction

This chapter provides general background on key topics discussed in the development of this project. Some works found in the literature are cited in order to explain the concepts. The main topics reviewed are divided in three: it was of first interest to understand how olefins are formed during thermal cracking of hydrocarbon mixtures and to show what the consequences of having those compounds are. After that, a short review of the olefin identification techniques is given; for which it was found that most of the methods are more focused on the quantification of the species as a whole or the identification of group types rather than the identification of individual molecules. The last is a brief summary of the reactivity of alkenes, with special emphasis on three reactions that were of great importance during this research: hydration, hydrogenation and Diels-Alder cycloaddition.

2. General aspects of thermal cracking in partial upgrading of bitumen

Heavy crude oil extracted from oil sands (Bitumen) has a high viscosity.[1] In order to be transported to refineries meeting pipeline specifications and increase its value, it must be upgraded. The upgrading can be full or partial; the first aims for the removal of solids, water, salts and the reduction of heteroatoms in large scale facilities, almost comparable with a refinery. The partial upgrading approach controls solids, water, reduces viscosity and is carried out in a small scale close to the bitumen production site.[2] In a partial upgrading facility the reduction in viscosity can be achieved by thermal processes such as visbreaking, delayed coking and fluid coking. Visbreaking is preferred due to the low residence time and pressures involved (mild form of thermal cracking); when used in atmospheric residue upgrading the method reaches about 15% conversion to naphtha and gas oil giving also a low-viscosity residual fuel.[3] The following section show a general reaction mechanism of thermal cracking[4] and includes among other products the formation of alkenes. An explanation of why having unsaturated compounds, more specifically polyunsaturated molecules can be counterproductive is also provided.

2.1 Formation of alkenes during thermal cracking processes

Defining the reaction mechanism of thermal cracking in heavy complex mixtures is difficult, but the process is comparable to other feedstocks. Although the mechanism of of single compound light molecules does not display the same diversity of reactions, it can be considered as a "cousin" of the cracking of heavy feedstocks. The chemical transformations produced in thermal cracking processes are basically an effect of the high temperatures and involve the formation and reaction of free radical species formed due to the breakage of covalent bonds.[4] Free radicals are highly reactive species with an unpaired electron; when the free radical reacts with another molecule, the most common reaction is the transfer of hydrogen. The original molecule then becomes a free radical and will react with other species of atoms and molecules in a long series (or chain) of reactions until the process reaches the termination phase. In this phase two free radicals combine, sharing the pair of electrons and terminate free radical propagation. Radicals with a short chain (hydrogen, methyl or ethyl) are more "stable" than those with longer chain. Longer chain free radicals can continue to crack and break down into an olefin and a shorter chain radical.[5] The main steps in the free-radical chain reaction for cracking of n-alkanes are the following:

$$\begin{array}{lll}
\textit{Initiation}: & M \xrightarrow{k_1} 2R\bullet & (1) \\
\textit{Propagation}: & & \\
\quad \textit{Hydrogen abstraction} & R\bullet + M \xrightarrow{k_2} RH + M\bullet & (2) \\
\quad \beta-\textit{Scission} & M\bullet \xrightarrow{k_3} R\bullet + A & (3) \\
\textit{Termination}: & \text{Radical+Radical} \longrightarrow \text{Products} & (4)
\end{array}$$

Where M and M• are the parent alkane and parent radicals, respectively; R• and RH are lower alkyl radicals and the corresponding alkanes, respectively. A represents olefins. Free radical chain reactions are also observed in a variety of alkyl-aromatic and alkyl-cycloaromatic compounds.

2.2 Implications of alkenes in light fractions

Due to their high reactivity, olefins are not common in natural crude oil. However, in refineries they are generated by several cracking processes.[3] The concern regarding the presence of such reactive compounds has been present as early as 1920 when changes in the composition of cracked gasoline affecting its stability properties started to be known.[6]

The presence of olefins can act in detriment of two very important characteristics of a fuel: storage stability and thermal stability. Storage stability is considered as the ability of a fuel, stored over extended periods of time under ambient conditions, to remain unchanged or without appreciable deterioration. Thermal stability is the ability of a fuel to suffer relatively high-temperature stress for short periods of time, without considerable deterioration. The main changes due to stability alterations are related with aspects such as color and formation of soluble or insoluble compounds.[7] During storage at ambient temperature, diolefins especially, present in gasoline react with absorbed oxygen from the air and even with each other; the products formed are resinous, polymeric, and non-volatile materials commonly called gum.[7] Gums are highly aromatic compounds, with a molecular weight ranging from 200 to 500 g/mol.[6] The gum is insoluble in the liquid, but prior to its formation, the polymerization and oxidation of olefins renders soluble compounds.

The definition of what type of olefins contribute the most to the gum formation has not come to an agreement. As a general finding, the participation of conjugated diolefins is crucial in the gum formation, since they are considered the most unstable gasoline constituents.[8] However some researchers have stated that cyclic and branched olefins are the main gum producers.[9] Not only is the presence of individual mono-olefins or diolefins important, the interaction between those two types of alkenes has an effect on the gum formation.[7] There is also an important relationship between olefins and sulfur and oxygen atoms; research has shown that decreasing the amount of those two elements, has a negative impact in the formation of gums.[6]

In regard to its composition, the elemental analysis of gums showed that besides carbon, hydrogen and oxygen, heteroatoms such as sulfur and nitrogen are also present in the deposits. The oxygenated compounds have hydroperoxide, hydroxyl, carbonyl, ether, ester and acid groups; whereas the sulfur compounds are mainly thiothers.[10] Gums have a lot of aromatic constituents with a high degree of branching in their structure.[6] The main difference between storage stability and thermal stability is the origin of the free radicals leading to these reactions. In upgrading processes the formation of free radicals is caused by the process.

The implications of the gum formation can be seen at different stages of the fuels production; if the solid deposits are formed in the field upgrading facility, pipelines could be clogged by gum obstruction. In refining processes the implications are related with the correct functioning of the equipment, heat exchangers have been fouled by gum formation. In processes like bitumen residue conversion, the high temperatures promotes the olefins addition products that can become higher molecular weight material or coke, which is a poison for different catalysts.[11]

Formation of gums is problematic even in refineries. In the production of high octane paraffinic motor gasoline from isobutene and olefins (better known as alkylate) diolefin impurities form diolefin polymers and diolefin-mono-olefin copolymers that dissolve in the catalyst limiting its life. Concentrations as low as 2 or 3% of the olefin stream are enough to affect the alkylation process due to the acid consumption.[12] If the soluble gums made their way to the final fuel and precipitate, the performance of the vehicles is negatively affected due to the formation of deposits in the vehicle-fuel system.[8]

3. Alkenes identification

The analytical characterization of alkenes can be categorized to three different aspects: (1) the quantification of the total amount of olefinic species present in certain feed, (2) the identification of specific classes such as mono-olefins, diolefins, cyclo-olefins and the classes in between or (3) the identification of individual compounds.[13] The methodologies stablished throughout the years are diverse, but they can be divided in two categories: chemical methods and physical and instrumental methods.[14]

The first class of methods, are based on the reactivity of the carbon-carbon double bond. They encompass the addition of a reagent that will become a substituent on the carbons. Hydrogenation and halogenation are reactions usually used to measure the content of alkenes; the amount of reagent consumed indicates the degree of unsaturation in the sample. Most of the halogenation methods involve the addition of bromine, but other halogens such as iodine (iodine number) have been used to a small extent. The addition of bromine is known as bromine number titration (Br#) and is based on the ASTM D 1159-89 standard.[15] Bromine number determines the amount of bromine in grams absorbed by 100 grams of analyte. Nowadays, the method can be applied to fractions boiling up to 550°C. Among the limitations of the method are the reaction of bromide with nitrogen, sulfur and oxygen containing compounds;[13] as well as some interference due to aromatic compounds.[16]

Hydrogenation is an alternative method to halogenation. The determination involves the reaction of the unsaturated mixture with excess hydrogen under proper conditions (metal catalyst and solvent if needed) to measure manometrically or volumetrically the reacted hydrogen.[14]

Another chemical method is specific for the determination of conjugated diolefins, it does not identify the specific structure of the dienes, but allows one to find the amount of dienes present in a sample. It is known as diene value by maleic anhydride addition and is the basis of the widely known the UOP-326 method. It is an intermolecular cyclization where the maleic anhydride reacts in excess with the conjugated diolefin to produce a cyclohexene derivative. One of the disadvantages of that method is that the determination requires around 5 hours of work. The reaction lasts approximately 3 hours and after that, the maleic anhydride remaining is hydrolyzed and titrated with sodium hydroxide to know the total content of conjugated dienes; that process could take another 2 hours.[17] Besides the long analysis time, the method has interference by primary alcohols, because of their esterification with maleic anhydride.[18]

On the other hand, there are the physical and instrumental methods. Great portion of them are based on chromatographic techniques. The following is a summary of some of them:

a. High performance liquid chromatography (HPLC): it is a powerful methodology to separate hydrocarbons by group type and quantify olefins in cracked petroleum products. The method can separate olefins in light boiling point fractions, however the conventional set up gives unsatisfying results for heavier feedstocks. In that case some works report the use of HPLC with dual chromatographic columns (silica gel coated with silver nitrate and silica gel) as liquid mobile phase to separate olefins, from other type of hydrocarbons present in distillates and residues of high-boiling point.[19,20]

b. Gas chromatography-Mass spectroscopy (GC-MS): gas chromatography and mass spectroscopy have also been used separately, but the integration of those methods proved to give better results. The separation of the compounds is done by capillary columns installed in the GC; then the MS helps in the determination of the molecular weight of the compounds and provides structural information about the position and geometry of double bonds. Some of the problems with this method are related with the complexity of the matrix in the samples analyzed, usually there is coelution of peaks and in the case of low olefins concentration their identification is obscured by other compounds.[13]

c. Gas chromatography with vacuum ultra-violet detection (GC-VUV): Almost 7 years ago, a significant advance in detectors for gas chromatography was achieved, the inclusion of a non-destructive analysis by VUV detection. The detector overcomes some problems of common detection technologies such as MS. Identification of compounds in complex mixtures is improved by the deconvolution of co-eluting peaks, which makes possible the differentiation between analytes. The detector is a great tool to distinguish between isomers due to the unique absorption spectra of each molecule, usually their identification is done by separation with different specialized columns.[21]

d. Supercritical fluid chromatography and ultra violet detection (SFC-UV): is a method that works fairly similar to liquid chromatography, but uses supercritical CO_2 as mobile phase. The works done using this technique aim for the identification of conjugated dienes; the basis is the separation of diolefins from the hydrocarbon mixture by using different coatings in the column and detecting the conjugated molecules with an UV detector.[22]

e. Nuclear magnetic resonance spectroscopy (NMR): it has a short analysis time and for some time has been used for determination of gasoline composition. The approach consists in dividing the NMR spectra in sections; different hydrocarbon structures will be in different sections. Proton NMR has been used in complex materials such as bitumen; there is a method used by petroleum producers to find the total olefin content in samples and report it as mass percentage of 1-decene equivalent.[23] Two dimensional proton NMR spectroscopy has been applied in the identification of isomers of conjugated diolefins in fossil fuel liquids under the presence of higher levels of olefins and aromatic compounds.[24]

f. Infrared (IR) spectroscopy: Is a successful technique for the characterization of olefins. Internal olefins and terminal olefins with mono and di-alkyl substituents at the double bond have different IR bands, which makes feasible the distinction between the type of olefin.

g. Spectrophotometry: Colorimetric determination of conjugated diolefins[25] was achieved by reacting that type of diolefins with strong coupling agents like p-nitrobenzenediazonium salts. The reaction gives colored crystalline azo compounds that will have maximun absorption band at different wavelengths. The intensity of the maximum is linearly related to the concentration of the diolefins in certain concentration range. The experiments were done with model compounds not in complex fuel mixtures.

4. Chemistry of alkenes

The reactions undergone by molecules with carbon-carbon double bond in their structure are multiple, and the literature about them is extensive. The most common chemical transformation that alkenes participate in is based on addition reactions. In its simple form it can be said that the π bond of the carbon-carbon double bond in the alkene is comparatively weak, and the saturation of the bond by the addition of an A-B reagent is thermodynamically feasible and proceeds to give a saturated product as shown in Figure 2.1.[26] The additions most readily done are the electrophilic additions; due to the delocalization of the electron density on the double bond, the π-electron cloud is polarizable in such a way that the alkene can act as a nucleophile. Although nucleophilic attacks on the carbon-carbon double bond are also feasible.[14] Hydroboration, halogenation, halohydration, epoxidation, ozonolysis, addition of hydrogen halides, addition of molecular hydrogen or addition of water are examples of electrophilic addition reactions of alkenes.[26,27] Is not intended to discuss all of them here, only two are going to be touched on and summarized due to their use in the development of this project.

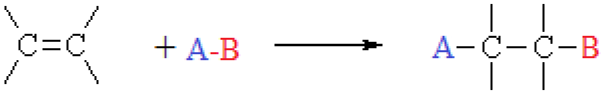


Figure 2. 1. General scheme of electrophilic addition.

The electrophilic addition reactions researched are Hydration and Hydrogenation. Other type of addition reaction, specific of conjugated diolefins is also summarized in the following sections, giving just some general and important aspects of them. Hydration was of interest due to its ability to convert diolefins and hydrogentation was of interest as reaction to measure relative reactivity of olefinic compounds.

4.1 Hydration

The addition of water to an alkene is an exothermic acid catalyzed process that gives alcohols as products and proceeds via the formation of a carbocation intermediated obtained by the protonation of the alkene. Hydration is a regioselective reaction, according to the Markovnikov's rule. H^+ adds to the less substituted carbon to form the most stable carbocation that will be substituted by the OH^- group through a nucleophilic attack, ending up at the more substituted carbon.[26] An example of the mechanism is illustrated in Figure 2.1.

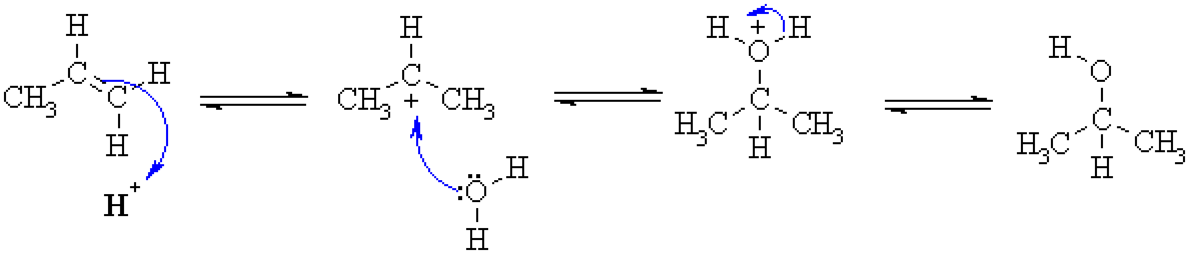


Figure 2. 2. Simplified reaction mechanism of alkenes hydration in acid media.

The most commonly used catalyst is phosphoric acid based, but mineral acids like H_2SO_4 have been used as well in hydration of olefins and research has been done using other type of acid catalyst. Y type zeolite was used as catalyst to hydrate short chain olefins (C_2-C_4), having calcium, rare-earth elements and chromium as cations.[28] Ferrierite and pentasil-type zeolites showed high activity towards olefin hydration when working at high pressure;[29] the results were comparable to those obtained using solid phosphoric acid. Several investigations have been conducted aiming for the hydration of diolefins using sulfuric acid[30] and ruthenium complexes with an acid component.[31]

In the mechanism of alkene hydration there is an equilibrium constraint. The presence of the acid allows the establishing of an equilibrium between the alcohol and the alkene, but the equilibrium favors dehydration over hydration. The equilibrium towards hydration is improved when the reaction is carried at low temperatures and water is in excess to shift the reaction toward the formation of the alcohol. Because of the equilibrium, the alcohols can be dehydrated and protonated again to give water as leaving group and the subsequent formation of a carbocation that can undergo side reactions like hydrogen and alkyl shifts. As a result the thermodynamically most stable alkene or a mixture of isomers product of double bond shift can be formed.[26]

Hydration of alkenes is an important reaction in the industry. For instance, in the production of ethanol, an alcohol widely used as solvent or starting material for other chemical products; the process involves the reaction of ethene with steam over phosphoric acid coated on silicon dioxide.[32] The temperature of the process is 300°C and the pressure is about 60 to 70 atmospheres.[33] One of the advantages of solid phosphoric acid is its ability to avoid the formation of the carbocation intermediate, promoting the direct hydration of the alkene. Iso-propanol (2-propanol) is also produced using water and propylene, similar to the formation of ethanol from ethane. The use of the reaction is not limited to the alcohol production for chemical use, ethene generated in Fischer-Tropsch refineries can be refined to ethanol, giving value to the gases produced in the refinery. [34]

The reaction is also used in the production of *tert*-butyl alcohol from 2-methylpropene; the alcohol is a raw material in the production of isobutylene, which may be used to produce methyl tertiary butyl ether, a common gasoline additive, or to produce butyl elastomers used in the production of automobile tires.[35]

4.2 Catalytic Hydrogenation

Hydrogenation is a widely used reaction, especially in the oil industry. The addition of hydrogen to oil is commonly known as hydroprocessing, that operation is done to serve different purposes. Thus, the formation of light molecules from heavy feedstocks through a free radical mechanism and further stabilization of the stream by hydrogen addition is called residue hydroconversion. The operations where heteroatoms and metals are removed are under the category of Hydrotreating and depending on the element to reduce, the process can be named: Hydrodesulphurization (HDS), Hydrodenitrogenation (HDN), Hydrodeoxygenation (HDO) and Hydrodemetallation (HDM).[36] The partial hydrogenation of alkenes can be used to saturate dienes selectively and prevent processing problems (although in practice it is not completely selective). As was mentioned earlier, the polyunsaturated compounds can form gums that have a negative impact on refining operations for reasons already explained. Is not the goal of this review to present every detail about the hydrogenation reaction and additional information will be provided in Chapter 6. The research done and importance of the reaction are such, that it would be ambitious trying to cover every detail. Instead, general aspects about the alkenes reduction are given.

To be able to reduce alkenes to alkanes, a catalyst must be present; several systems have been used and their selection depends on factors such as the activity and selectivity required. Common heterogeneous hydrogenation catalysts employ metals such as nickel, platinum, palladium, rhodium and ruthenium; other metal oxides and metal sulfides are also active as hydrogenation catalysts. A simple explanation of the mechanism involves the adsorption of both, the alkene and the molecular hydrogen on the catalyst surface, the transfer of hydrogen to the carbons forming the unsaturation (the insertion of the hydrogen is done to the same side of the double bond i.e. *syn* addition) and the subsequent desorption of the product. An example of the ethylene hydrogenation is depicted in Figure 2.3.

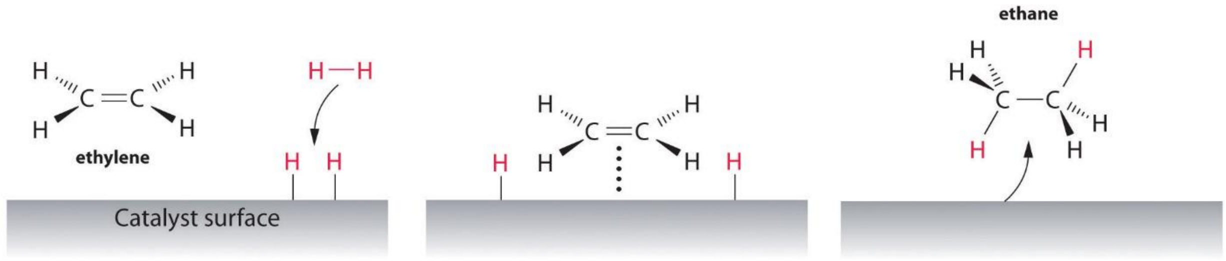


Figure 2. 3. Simplified reaction mechanism of hydrogenation.

From that, a whole field of study is derived. Different mechanisms have been proposed explaining aspects such as: how the hydrogen is adsorbed on the catalyst, how does the alkene, what is the sequence of steps to achieve the hydrogenation, what step is slower or faster. The mechanism depends not only on the catalyst but also on the alkene and a unique set of steps cannot describe accurately the hydrogenation of different types of compounds.[37]

In the past years a number of metal complexes have been used as catalysts for the homogeneous hydrogenation of carbon-carbon double bonds. In the reactions with homogeneous catalyst the hydrogen is transferred from the hydride-transition metal complex in three steps: (1) hydrogen activation, (2) substrate activation, (3) hydrogen transfer.[38]

The activity and selectivity of the reaction are determined not only by the type of catalyst used, but also by the reaction conditions such as temperature and pressure. For instance, the reaction of 1-hexene in vapor phase on Pt/Al_2O_3 at 603K showed the presence of double bond shift; the isomerization was reduced by increasing the pressure of hydrogen in the system.[37] The consumption of hydrogen takes place in hydrogenation but not during isomerization, hence a higher amount of hydrogen on the surface of the catalyst, should increase the reaction rate of hydrogenation, respect to the isomerization.[39]

As was mentioned earlier, each hydrogenation varies depending on the substrate, but in general, if a more selective reaction is wanted, lower temperatures are preferred because side reactions are less occurring.[40] The amount of catalyst used is also important; normally the catalyst to substrate ratio influences the product distribution and the reaction rate. Increasing the amount of catalyst also reduces the possibility of side reactions to occur as lower temperatures and pressures can be used, having a positive effect on the selectivity of the reaction.[40]

The hydrogenation of each functional group has its own particularities; because the group of interest here are the olefins, some specifics about their hydrogenation using heterogeneous catalysis are given. Thus, the hydrogenation of isolated double bonds is faster than any other functional group except for acetylenes and allenes. Usually in compounds with several double bonds, the reduction will take place preferentially in the least hindered bond. In general, the rate of hydrogenation of the double bond in mono-olefins decreased roughly with an increase in the number and branching of the alkyl substituents.[38] The hydrogenation of alkenes with large substituents is more difficult, because the substitution hinders the adsorption of the olefin on the catalyst decreasing the reaction rate.

Generally the *cis* isomers are preferentially hydrogenated over the *trans* conformations; a disubstituted double bond in the *cis* conformation hydrogenates faster than the *trans* isomer. The hydrogenation is stereospecific, giving products where the hydrogens are added to the same, least hindered side of the olefin. The hydrogenation of conjugated olefins gives the 1,2 or 1,4 addition products of the first mole of hydrogen.

4.3 Diels-Alder reaction[41,42]

Otto Diels and Kurt Alder were awarded with the Nobel Prize in Chemistry in 1950 for their finding and the reaction took their name. The Diels-Alder reaction is based on the stereospecific addition of a conjugated diene to the olefinic or acetylenic bond of a compound, called a dienophile; the reaction product is called an adduct. During the product formation, it goes through a cyclic transition state, reason why is described as a cycloaddition. The product is a six-membered ring, containing an alkene (cyclohexene). The Diels-Alder reaction is a very powerful reaction widely used in synthetic organic chemistry. It is particularly useful to identified conjugated diolefins. The diene may contain atoms different to carbon in its structure, but is a requirement that the double bonds are conjugated. If one or more dienophile atoms are not carbon, the reaction is called hetero-Diels-Alder reaction. Under certain conditions, the Diels-Alder reaction can become reversible, in that case it is called retro-Diels-Alder reaction.

Diene. The diene can be of varied kind, but they can be classified as: acyclic, cyclic, outer ring, inner-outer ring and across rings. The substituents affect the reactivity of the diene; electron donating groups (EDG) on the nucleophilic diene increase the reactivity, whereas electron withdrawing groups (EWG) decrease it. Examples of dienes are illustrated in Figure 2.4.

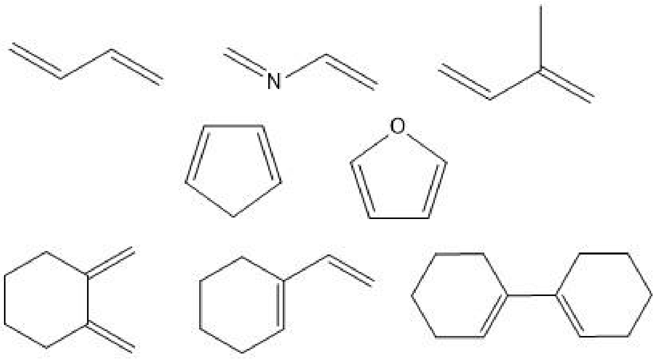


Figure 2. 4. Examples of dienes that can undergo Diels-Alder reaction.

A requirement for the diene is to be capable of acquiring the *cisoid* conformation; that is essential to have overlapping of the p-orbitals in the diene and the dienophile. In the alternative *transoid* conformation, the ends of the diene are too far to facilitate overlapping with the p-orbitals of the dienophile. Figure 2.5 exemplifies the transition state formed with both conformations and shows the highlighted differences.

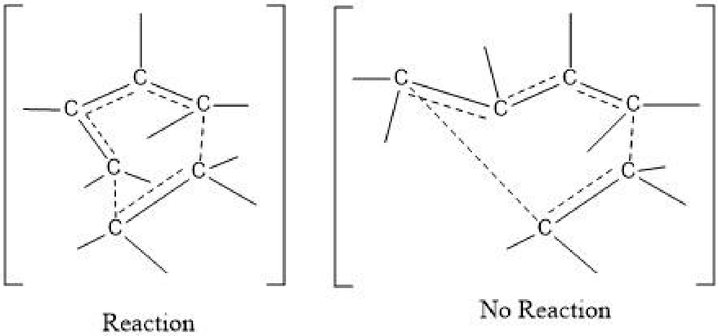


Figure 2. 5. Representation of transition state in the Diels-Alder reaction with *cisoid* and *transoid* diene conformation.

Dienophile. Normally Diels-Alder reaction is favoured by electron withdrawing groups (EWG) on the electrophilic dienophile (i.e. carbonyl, cyano, nitro, halogens). In fact, if more than one EWG is conjugated to the double or triple bond of the dienophile a strong increase in the reactivity is observed. Some examples of good dienophiles are provided in Figure 2.6.

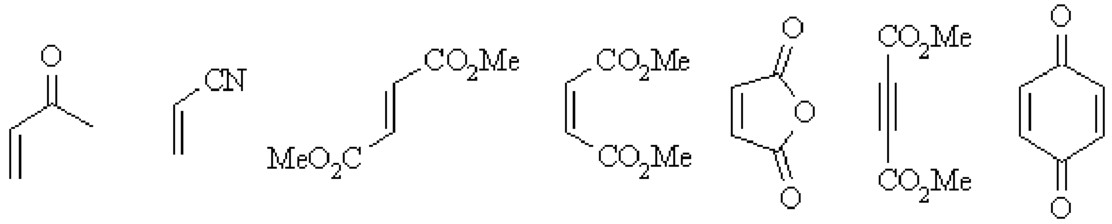


Figure 2. 6. Examples of good dienophiles that can undergo Diels-Alder reaction.

Mechanism. The reaction is usually thermodynamically favorable because it involves the conversion of two π-bonds into two stronger σ-bonds. A representation of the mechanism is given in Figure 2.7; the double bond of the dienophile (ethylene) and one of the diene (C1-C2 bond in 1,3-butadiene) are broken at the same time that the two new σ-bonds are formed (concerted reaction) to give cyclohexene. Most of the thermal cycloadditions can be described by the one-step mechanism, but some investigations report the cycloaddition should be explained with more than one step mechanism. One of the simplest Diels-Alder reaction is shown in Figure 2.7; it requires strong reaction conditions and gives poor yield of cyclohexene because the poor dienophile character of ethylene.

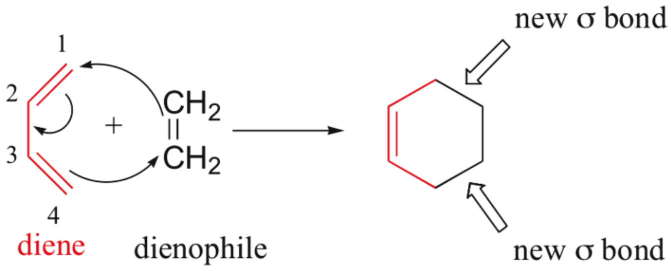


Figure 2. 7. Diels-Alder reaction mechanism of 1,3-butadiene with ethylene.

Regioselectivity. The cycloaddition involving asymmetric diene and dienophile will give two possible regioisomer adducts caused by two different chemical orientations of the reactants. The position of the substituents in the product is indicated with the words *ortho*, *meta* and *para,* when possible; the application of those words is inadequate when the reagents are disubstituted. Examples of the regioselectivity of the reaction are given in Figure 2.8.

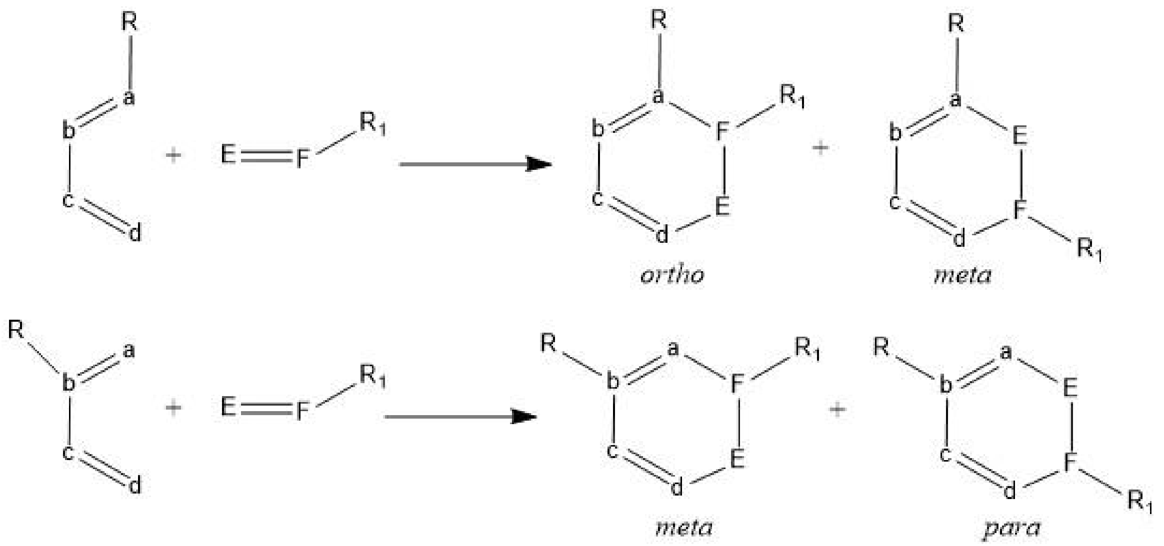
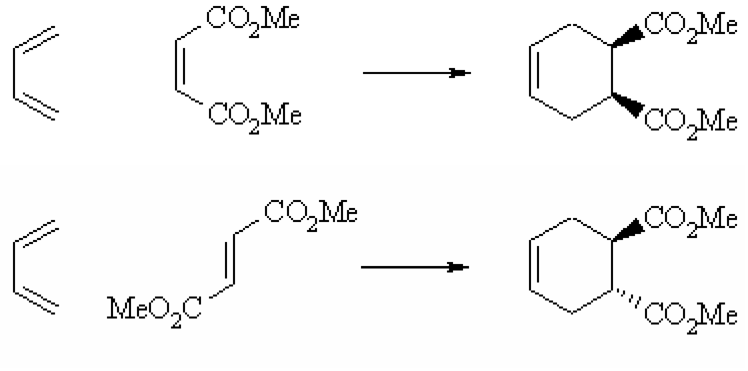


Figure 2. 8. Regioselectivity in Diels-Alder reaction.

Stereoselectivity. One of the characteristics of the reaction is its stereospecific behavior. The initial groups' configuration of both the diene and the dienophile is maintained in the products. Thus, a *cis*-dienophile gives *cis*-substituents in the product, a *trans*-dienophile gives *trans*-substituents. In the case of the diene if the substituents have the same stereochemistry, then both diene substituents end up on the same face. Examples of the stereospecific character of the cycloaddition are shown in Figure 2.9.



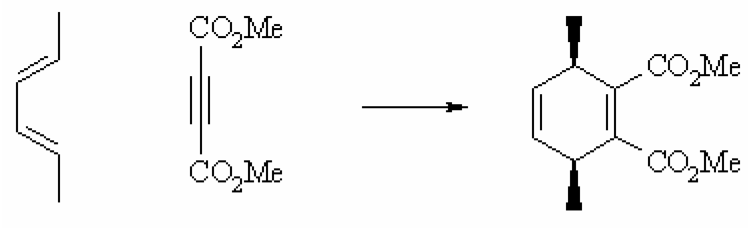


Figure 2. 9. Stereoselectivity in Diels-Alder reaction.

The reaction can be accelerated by heating or using some catalysts. Since 1960 the use of Lewis acids as catalyst in Diels-Alder reaction has become important, because it allows to use lower temperatures and helps to increase the reactivity of poor dienophiles. The cycloaddition of isoprene with 2-methyl-2-cyclohexenone can be achieved in 17 hours at 25°C with high yield if Aluminum trichloride is used, whereas the thermal treatment gives poor yield even at 150°C and 142 hours of reaction. The way the catalyst acts is by forming a complex with the EWG of the dienophile, polarizing the dienophile center and making the dienophile even more electrophilic. Besides shorter reaction times and higher yields, the inclusion of a Lewis catalyst increases regioselectivity and stereoselectivity in the reaction.

References

(1) Speight, J. G. Refining Heavy Oil and Extra-heavy Oil. In *Heavy and Extra-heavy Oil Upgrading Technologies*; 2013; pp 1–13.

(2) Speight, J. G. *Heavy Oil Production Processes*; Gulf professional publishing: Oxford, 2013.

(3) Hsu, C. S.; Robinson, P. R. *Practical advances in Petroleum Processing*; Springer: New York, 2006; Vol. 1.

(4) Raseev, S. Theoretical Background of Thermal Processes. In *Thermal and Catalytic Processes in Petroleum Refining*; 2003.

(5) Hengstebeck, R. J. *Petroleum Processing, Principles and Applications*; McGraw-Hill: New York, 1959.

(6) Schwartz, F. G.; Whisman, M.; Allbright, C.; Ward, C. *Storage stability of gasoline-Fundamentals of Gum Formation Including a Discussion of Radiotracer Techniques.*; Washington, D.C, 1964.

(7) Pradelle, F.; Braga, S. L.; Martins, A. R. F. A.; Turkovics, F.; Pradelle, R. N. C. Gum Formation in Gasoline and Its Blends: A Review. *Energy Fuels* **2015**, *29* (12), 7753–7770.

(8) Pereira, R. C. C.; Pasa, V. M. D. Effect of mono-olefins and diolefins on the stability of automotive gasoline. *Fuel* **2006**, *85* (12-13), 1860–1865.

(9) De La Puente, G.; Sedran, U. Formation of gum precursors in FCC napthas. *Energy Fuels* **2004**, *18* (2), 460–464.

(10) Kawahara, F. K. Composition of gum in cracked naphtha. *Ind. Eng. Chem.* **1965**, *4* (1), 7–9.

(11) Gray, M. R.; McCaffrey, W. C. Role of chain reactions and olefin formation in cracking, hydroconversion, and coking of petroleum and bitumen fractions. *Energy Fuels* **2002**, *16* (3), 756–766.

(12) Anderson, J.; McAllister, S. H.; Derr, E. L.; Peterson, W. H. Diolefins in Alkylation Feedstocks. *Ind. Eng. Chem.* **1948**, *40* (12), 2295–2301.

(13) Badoni, R. P.; Bhagat, S. D.; Joshi, G. C. Analysis of olefinic hydrocarbons in cracked petroleum stocks: a review. *Fuel* **1992**, *71* (5), 483–491.

(14) Cagogan, J. I.; Cais, M. *The chemistry of alkenes*; Interscience Publishers: London, 1964.

(15) D1159-07. Standard Test Method for Bromine Numbers of Petroleum Distillates and

Commercial Aliphatic Olefins by Electrometric Titration 1. *Astm* **2010**, *20* (Reapproved 2012), 1–10.

(16) Oil, H.; Ortega, L. C.; Lopez-, F. Analysis of Olefins in Heavy Oil, Bitumen, and Their Upgraded Products. In *Analytical methods in petroleum upstream applications*; CRC press, 2015; pp 81–109.

(17) De Andrade, D. F.; Figueiredo, E. Proposal of a voltammetric method for the determination of conjugated dienes in Brazilian naphtha. *Fuel* **2006**, *85* (17-18), 2578–2585.

(18) Andrade, D. F.; Azevedo, D. a. Comparison of UOP-326, voltammetric and gas chromatographic/mass spectrometric methods for the determination of conjugated dienes in Brazilian Naphtha. *Fuel* **2006**, *85* (7-8), 1024–1031.

(19) Kamínski, M.; Kartanowicz, R.; Gilgenast, E.; Namieśnik, J. High-Performance Liquid Chromatography in Group-Type Separation and Technical or Process Analytics of Petroleum Products. *Crit. Rev. Anal. Chem.* **2005**, *35* (3), 193–216.

(20) Mckay, F. High Performance Liquid Chromatographic Separation of Olefin, Saturate, and Aromatic Hydrocarbons in High-Boiling Distillates and Residues. *Anal. Chem.* **1980**, *52* (11), 1618–1621.

(21) Schug, K. a.; Sawicki, I.; Carlton, D. D.; Fan, H.; McNair, H. M.; Nimmo, J. P.; Kroll, P.; Smuts, J.; Walsh, P.; Harrison, D. Vacuum ultraviolet detector for gas chromatography. *Anal. Chem.* **2014**, *86* (16), 8329–8335.

(22) Cortiñas, F. Determination of conjugated dienes in petroleum products by supercritical fluid chromatography and ultraviolet detection. *J. Sep. Sci.* **2003**, *26* (15-16), 1403–1406.

(23) Maxxam-CAPP. Test Method for Determination of Olefin Content of Crude Oils, Condensates and Diluents by H-NMR. Edmonton 2005, pp 1–11.

(24) Altbach, M. I.; Fitzpatrick, C. P. Identification of conjugated diolefins in fossil fuel liquids by H n.m.r. two-dimensional correlated spectroscopy. *Fuel* **1994**, *73* (2), 223–228.

(25) Altshuller, A. P.; R., C. I. Spectrophotometric methods for olefins- Colorimetric determination of conjugated diolefins. *Anal. Chem.* **1960**, *32* (13), 1843–1848.

(26) Vollhardt, P.; Schore, N. *Organic Chemistry: Structure and Function*; W.H. Freeman: New York, 2007.

(27) Reger, D.; Goode, S.; Ball, D. *Chemistry: Principles and practice*; Brooks/Cole: Belmont, 2010.

(28) Minachev, K.; Mortikov, Y. Hydration of Olefins on Zeolite Catalysts. *Pet. Chem. U.S.S.R.* **1976**, *16* (4), 216–223.

(29) Ehwald, H.; Fiebig, W.; Lischke, G.; Parlitz, B.; Reich, P. High pressure catalytic hydration of olefins over various proton-exchanged zeolites. *Appl. Catal.* **1987**, *34*, 275–287.

(30) Jense, J.; Uaprasert, V.; Fujii, C. Acid-Catalyzed hydration of dienes. 2. Changes in activity coefficient ratios, enthalpy and entropy as a function of sulfuric acid concentration. *J. Org. Chem.* **1976**, *41* (10), 1675–1680.

(31) Stunnenberg, F.; Niele, F. G. M.; Drent, E. Hydration of conjugated dienes to produce ketones catalyzed by ruthenium complexes. *Inorganica Chim. Acta* **1994**, *222* (1-2), 225–233.

(32) Roberts, J.; Caserio, M. *Basic principles of organic chemistry*, Second.; W. A. Benjamin, Inc: Menlo Park, 1977.

(33) Cheremisinoff, N. P. *Industrial Solvents Handbook, Revised And Expanded*; Marcel Dekker: New York, 2003.

(34) De Klerk, A. *Fischer-Tropsch refining*; Weinheim: Wiley-VCH: Weinheim, 2011.

(35) Clark, J. J. J. tert-Butyl Alcohol: Chemical Properties, Production and Use, Fate and Transport, Toxicology, and Detection in Groundwater and Regulatory Standards. *Oxyg. Gasol.* **2001**, *799*, 92–106.

(36) Speight, J. G. *Heavy and Extra-heavy Oil Upgrading Technologies*; Gulf professional publishing: Oxford, 2013.

(37) Bond, G. C. *Metal-Catalysed Reactions of Hydrocarbons*; Springer, 2005.

(38) Mitsui, S.; Kasahara, A. Hydrogenation of Alkenes. In *The chemistry of alkenes. Vol 2*; Interscience Publishers: London, 1970.

(39) Rylander, P. Hydrogenation of Olefins. In *Catalytic Hydrogenation in Organic Syntheses*; Academic Press: New York, 1979; pp 31–63.

(40) Augustine, R. L. *Catalytic hydrogenation*; Marcel Dekker: New York, 1965.

(41) Fringuelli, F.; Taticchi, A. *Dienes in the Diels-Alder reaction*; John Wiley & Sons, Inc.: New York, 1990.

(42) Wassermann, A. *Diels-Alder reactions organic background and physico-chemical aspects*; Elsevier publishing company, 1965.

CHAPTER 3. IDENTIFICATION OF DIOLEFINS IN THERMALLY CRACKED NAPHTHA

Abstract

Problems during pipelining and refining processes result as a consequence of gum and coke formation caused by high amounts of diolefins in mixtures like thermally cracked naphtha. To develop a mitigation strategy the first step is identifying the diolefin species present in the cracked naphtha; a challenging task due to the variety of compounds present in the naphtha along with the low concentration of the molecules of interest. The analytic approach followed employed gas chromatography coupled with mass spectrometry (GC-MS) in combination with two reactive preparation procedures. Hydrogenation at mild conditions served to identify potential olefins and diolefins by comparing chromatograms before and after reaction. Knowing that conjugated diolefins undergo electrophilic additions, the Diels-Alder reaction was likewise used to identify potential diolefins. Identification by mass spectrometry was confirmed when practical by model compounds. All of the diolefins were found to be in the C_5 to C_7 carbon number range, although the presence of heavier diolefins could not be ruled out with certainty due to the complexity of the matrix. After confirming the presence of certain molecules, gas chromatography with a flame ionization detector (GC-FID) was used to stablish the amount of those molecules present in the mixture.

Keywords: Diolefins, thermally cracked naphtha, hydrogenation, Diels-Alder, GC-MS, GC-FID

1. Introduction

As part of the field upgrading of bitumen, the deasphalted oil (DAO) goes through thermal cracking and fractionation processes to produce lighter compounds that are going to be sent through the pipeline for further refining. High concentrations of unsaturated and polyunsaturated (diolefins) compounds are generated as products of that process, in many cases exceeding the specification of < 1 wt% as 1-decene equivalent set by the Canadian Association for Petroleum

Producers. This is not unique to thermal cracking of bitumen, but a general outcome of thermal cracking processes.[1]

The reactive diolefins are present mainly in the light boiling material, [2] i.e. thermally cracked naphtha. Having those polyunsaturated molecules becomes an issue that needs to be addressed not only to contribute meeting pipelining specifications but also to avoid problems in subsequent processes. Their stability during storage is not high, they are known for reacting with oxygen to produce hydroperoxide and initiate free radical chain reactions; [3] as a result of their polymerization and deposits formation, the clogging of pipelines and process vessels is commonly experienced; and in the refining processes the coke formation at high temperatures is responsible for fouling catalysts.

The need to prove that diolefins are present in cracked naphtha, as well as to identify their structure and quantify them comes before providing a solution to deal with them. Methods for determining diolefins in petroleum products are mainly concerned with quantification of total diene concentration, rather than identification of the individual species. [4] Although chromatographic separation can be performed, the diolefins must still be identified among all the other compounds. Having said that, the objective of this chapter was to develop a strategy for the characterization of diolefins in thermally cracked naphtha, task that was not trivial, due to the complexity of the mixture.

Diolefin separation and identification was performed GC-MS in combination with reactions and derivatizations. It was of interest to identify conjugated and non-conjugated diolefins. The approach taken involved the following:

(a) Analysis of the thermally cracked naphtha sample in the GC-MS to identify compounds in the mixture that could correspond to diolefins. A list of names was generated after this step.
(b) Analysis of the sample after partial hydrogenation under mild conditions to preferentially hydrogenate diolefins. Compounds that decreased in concentration could potentially be diolefins.

(c) Derivitization of the diolefins with maleic analydride to confirm conjugated diolefin character. An alternative approach that could be used is to perform the Diels–Alder reaction with 4-methyl-1,2,4-triazoline-3,5-dione in conjunction with a nitrogen selective detector. [5],[6]

(d) Spiking with model compounds to confirm tentative diolefin identifications. That was necessary particularly when there was a risk of misidentifying a cyclic olefin as a diolefin. The mass spectra of cyclic olefins and diolefins are quite similar.

Once some compounds were identified, it was of interest to know the amount present in the mixture. For such purposes, GC-FID was used. For the quantitative analysis an internal standard calibration curve was developed for each compound detected. The results obtained during the characterization of diolefins were presented at an international conference.[7]

Due to the complexity of the mixture a high matrix interference was seen. It is common for techniques such as the GC-MS to have some difficulties distinguishing between acyclic and cyclic hydrocarbons of the same molecular formula, but being strong when identifying olefins from aromatic hydrocarbons. That, and the fact that techniques such as GC-VUV can distinguish between paraffinic and olefinic molecules led to support this characterization process with that technique, available in an external laboratory in Alberta Innovates-Technology Future (AITF). By joining both findings a broader knowledge of the nature of the compounds present in the thermally cracked naphtha sample was acquired.

2. Experimental

2.1 Materials

All the compounds used during the diolefins identification are cited in Table 3. 1, along with the gases required to the correct functioning of the analysis instruments.

Table 3. 1. Material used during, calibration, reaction and model comparison stages.

Compound	Formula	CASRN [a]	Mass fraction purity [b]	Supplier
Materials for reactions and model compounds identification				
Maleic anhydride	$C_4H_2O_3$	108-31-6	99.0%	Sigma Aldrich
Acetone	C_3H_6O	67-64-1	99.5%	Fisher Scientific
Tetrahydrofuran	C_4H_8O	109-99-9	99.9%	Fisher Scientific
Toluene	C_7H_8	108-88-3	99.8%	Fisher Scientific
Isoprene	C_5H_8	78-79	99.9%	Sigma Aldrich
2,3-Dimethyl-1,3-butadiene	C_6H_{10}	513-81-5	99.5%	Sigma Aldrich
1-Nonene	C_9H_{18}	121-11-8	96%	Sigma Aldrich
trans-1,3-Pentadiene	C_5H_8	2004-70-8	90.0%	Sigma Aldrich
1,4-Pentadiene	C_5H_8	591-93-5	99.0%	Sigma Aldrich
2,4-Hexadiene (mixture of isomers)	C_6H_{10}	592-46-1	90.0%	Sigma Aldrich
2,5-Dimethyl-2,4-hexadiene	C_8H_{14}	764-13-6	96.0%	Sigma Aldrich
1,3-Hexadiene (mixture of isomers)	C_6H_{10}	592-48-3	95.0%	Sigma Aldrich
1.4-Hexadiene (mixture of *cis* and *trans*)	C_6H_{10}	592-45-0	99.0%	Sigma Aldrich
1,5-Hexadiene	C_6H_{10}	592-42-7	97.0%	Sigma Aldrich
2-Methyl-1,5-hexadiene	C_7H_{12}	4049-81-4	97.0%	Sigma Aldrich
1-methyl-1-cyclohexene	C_7H_{12}	591-49-1	97.0%	Sigma Aldrich
Cyclohexene	C_6H_{10}	110-83-8	99.7%	Sigma Aldrich
1-Hexene	C_6H_{12}	592-41-6	97.0%	Sigma Aldrich
methylenecyclobutane	C_5H_8	1120-56-5	96.0%	Sigma Aldrich
3-methyl-1,3-pentadiene (mixture of *cis* and *trans*)	C_6H_{10}	4549-74-0	98.0%	Sigma Aldrich
Vinylcyclopentane	C_7H_{12}	3742-34-5	99.0%	Sigma Aldrich
1-Methylcyclopentene	C_6H_{10}	693-89-0	98.0%	Sigma Aldrich
Ethylidenecyclopentane	C_7H_{12}	2146-37-4	90+%	Alfa Aesar
3-Methyl-2,4-hexadiene (mixture of *cis* and *trans*)	C_7H_{12}	28823-42-9	97.0%	Alfa Aesar
1,3-Cycloheptadiene	C_7H_{10}	4054-38-0	95.0%	Sigma Aldrich
1,3-Cyclohexadiene	C_6H_8	592-57-4	97.%	Sigma Aldrich
Cylinder gases				
Compressed Air	Air	132259-10-0		Praxair
Helium	He	7440-59-7	0.99999 [c]	Praxair
Hydrogen	H_2	1333-74-0	0.99999 [c]	Praxair
Catalyst				
Platinum on activated charcoal,	Pt/C		5% Pt basis	Sigma Aldrich

[a] CASRN = Chemical Abstracts Services Registry Number

[b] This is the purity of the material guaranteed by the supplier; material was not further purified.

[c] Mole fraction purity.

The identification stage of the project was done by taking industrial samples of thermally cracked naphtha and making them react with hydrogen and maleic anhydride, to do a partial hydrogenation and a Diels-Alder reaction respectively. Details regarding the composition of the naphtha sample used are provided in Table 3.2. The naphtha characterization given was not done in this work, it was part of previous research done on the olefins treatment during the field upgrading process.[8]

Table 3. 2. Summary of thermally cracked naphtha characterization.

Property	**Units**	**Naphtha**
Density	kg/m^3 @ 20^oC	762.7
API Gravity	-	53.5
Sulfur	wt %	0.90
Nitrogen	wt %	0.09
Carbon	wt %	84.34
Hydrogen	wt %	13.76
Oxygen	wt %	0.25
Viscosity	cSt @ 25^oC	0.85
^1H NMR analysis		
aliphatic saturate	mol %	96.42
aliphatic olefin	mol %	1.26
aromatic	mol %	2.32
Olefin content	wt % as 1-decene eq	4.7
Diene Number	g I_2/100g	0.62
Bromine Number	g Br_2/100g	27.84
CCR	%wt	45.12 ± 2.55
Acid Number	mg KOH/g	0.123 ± 0.003

2.2 Equipment and procedure

To do the partial hydrogenation, a 15 ml micro-batch reactor manufactured by Swagelok in 316 stainless steel tubing and fittings was employed (length 8.6 cm, internal diameter 2.1cm and outside diameter 2.6cm). The reactor served as pressure container. In a 10ml vial, 2g of the industrial sample were added along with a magnetic stirrer and 2wt % Platinum on carbon catalyst that equals to 4mg of Platinum. The main objective was to hydrogenate the diolefins present. The use of Platinum was preferred over Palladium to avoid other reactions such as double bond isomerization which is promoted when the hydrogenation catalyst is Palladium. Although according to Table 3. 2 the naphtha sample has 0.9 wt % of sulfur compounds and it is known that sulfur is a poison for noble metal catalysts, excess catalyst was used to decrease the impact of the sulfur poisoning. The vial was introduced into the reactor and the system was closed, purged with nitrogen and loaded with hydrogen to a pressure of 1MPa. Because the reaction set up was a batch reactor, the pressure decreased as the reaction proceeded. The reactor was heated up to 130°C with an oil bath supported on a hot plate. A thermocouple was fitted inside the micro-batch reactor to accurately measure the reaction temperature. After 2 hours from the time the desired temperature was reached, the reactor was removed of the oil bath and let to cool down, then opened. A sample was filtered through a syringe filter of 0.2µm and analyzed with GC-MS.

The Diels Alder reaction was carried out in a 50 ml round bottom flask, connected to a condenser operating at total reflux. The flask was immerse in an oil bath supported on a hot plate and temperature in the bath was kept at 60°C. The naphtha sample (20ml) was refluxed for three hours with 2g of maleic anhydride; the solution was then cooled down, 5ml of water were added and the reflux was started again for 15min. The process of cooling, water addition and reflux was repeated twice afterwards. The solution was transferred to a separating funnel, the aqueous phase discarded and the organic phase filtered through a syringe filter of 0.22 µm. A sample of the reacted mixture was analyzed with the GC-MS.

2.3 Analyses

2.3.1 GC-MS for identification

The GC-MS has been used as the main analysis tool to identify the potential diolefins. The instrument to perform the qualitative analysis was an Agilent Model 7820A gas chromatography (GC) coupled with an Agilent Model 5977E MSD mass spectrometry (MS) system. The column used was a HP-5 capillary column (30m x 0.25mm i.d) coated with 0.25µm (5%-Phenyl)-methylpolysiloxane. The temperature program started at 30 °C, holding that temperature for 2 min; the oven was ramped up to 70 °C at a rate of 2.5 °C/min, held for 2 min and then raised up until 220°C at a rate of 10°C/min. The transfer line was kept at 325 °C, the injection volume was 1µl and the split ratio was 100:1. The carrier gas was Helium at a flow rate of 1 ml/min. The product identification was done using the National Institute of Standards and technology (NIST) data base

NIST MS Search 2.0 – Mass Spectra Library by comparison of the ion spectra obtained with the ion spectra of the library's suggested compounds. The compounds with the highest chance of being present in the mixture were purchased and processed under the same temperature program to check their retention time, although some of them were not available in the market.

2.3.2 GC-VUV for identification

The PerkinElmer Clarus 680 gas chromatograph coupled with VGA-100 VUV detector was used for this study. The UVU detector was supplied by VUV Analytics Austin, Texas USA. The instrumental set-up allowed auto-injection of samples via an attached autosampler. A 15 meter RTX1 capillary column of 280nm diameter and 3µm of film thickness was used for the study. The injection port was operated with initial split flow of 30mL/min. The compounds eluting from the gas chromatograph entered the detector via a heated transfer line. At the end of the transfer line a makeup flow of the helium carrier gas was introduced. The analyte stream from gas chromatograph upon entering the detector flow cell was exposed to the collimated VUV light beam generated by the deuterium lamp. A continuous full spectroscopic absorption data from 125nm to 240nm was recorded and integrated across the entire range. The olefins present in the analyte stream absorbed the light from the light beam resulting in reduced transmission and a detectable signal. The temperature program started at 12°C holding that temperature for 5minute. Four heating ramps were used: at a rate of 1.2°C/min up to 50°C, then with a rate of 2.4°C/min up to 130°C, the third with a rate of 4.8°C/min to 180°C, holding 1minute and finally at 10°C/min to 280°C holding for 4minutes.

2.3.3 GC-FID for quantification

The instrument to carry out the quantification analyses was an Agilent Model 7890A gas chromatography (GC) equipped with a flame ionization detector (FID). The column used was an Agilent J&W 122-5532 capillary column with 30m length, 0.25mm internal diameter and 0.25µm film thickness. The carrier gas was Helium at a flow of 1 ml/min. The injection volume was 1 µl, the injector and detector temperatures were set to 280 and 325°C respectively and the split ratio was 100:1. The temperature program used was the same as for GC-MS analysis.

2.4 Calibrations

For quantification purposes the GC-FID was used. The calibration technique selected was the internal standard method (ISTD). Four compounds were calibrated in this stage of the project. To use the technique a calibration curve was determined for each analyte. The details about the calibration samples can be seen in Apendix A1, Table A1.1.

3. Results

3.1 Identification using GC-MS

The first step was to analyze the thermally cracked naphtha with the GC-MS. Six temperature programs were developed, changing conditions such as the heating rate or the split ratio, looking for the higher peaks resolution in the less amount of time. The final method lasts 38 minutes and although a good resolution was obtained, some peaks were still overlapping, which was expected taking into account the variety of compounds present in the mixture. The final temperature program is specified in section 2.3.1. The resulting chromatogram of that temperature program is depicted in Figure 3. 1 and shows how complex is the sample.

All the peaks were studied to stablish what could be their nature e.g. paraffinic, olefinic, aromatic, this was done by doing a screening on the list of compounds suggested by the library. Doing that, the peaks that could be diolefins were highlighted; during that process 30 peaks were identified as possible polyunsaturated compounds. For a lot of them, along with a diolefin, there was also the suggestion of the presence of a cyclo-olefin, which can be interpreted as an interference from one type of molecule to another. A summary of their retention time as well as the number of carbons in each compound is provided in Table 3. 3. The structures of some of the suggested diolefins are shown in Figure 3. 2.

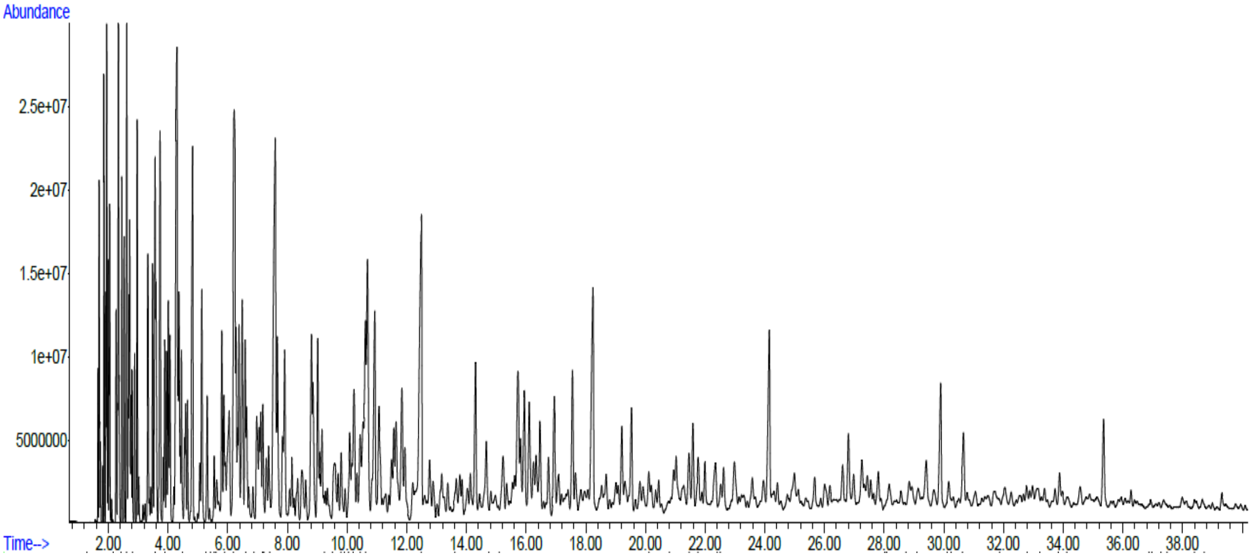


Figure 3. 1. Chromatogram of thermally cracked naphtha.

Table 3. 3. List of Retention Times (RT) and Carbon Numbers (CN) of Compounds Identified as Possible Diolefins[a]

Peak	RT [min]	CN	Peak	RT [min]	CN
1	*2.069*	5	16	5.771	7
2	*2.142*		17	6.305	
3	*3.071*		18	7.341	8
4	3.298	6	19	7.889	
5	3.806		20	8.056	
6	4.294	7	21	8.203	
7	4.334		22	8.277	
8	4.555		23	8.510	
9	*4.708*		24	9.139	
10	*4.855*		25	9.393	
11	4.962	8	26	9.540	9
12	*5.363*	7	27	9.780	
13	*5.423*		28	11.711	
14	5.604	8	29	12.667	
15	5.677		30	14.979	

[a] Peaks in italics were most likely to be diolefins based on hydrogenation.

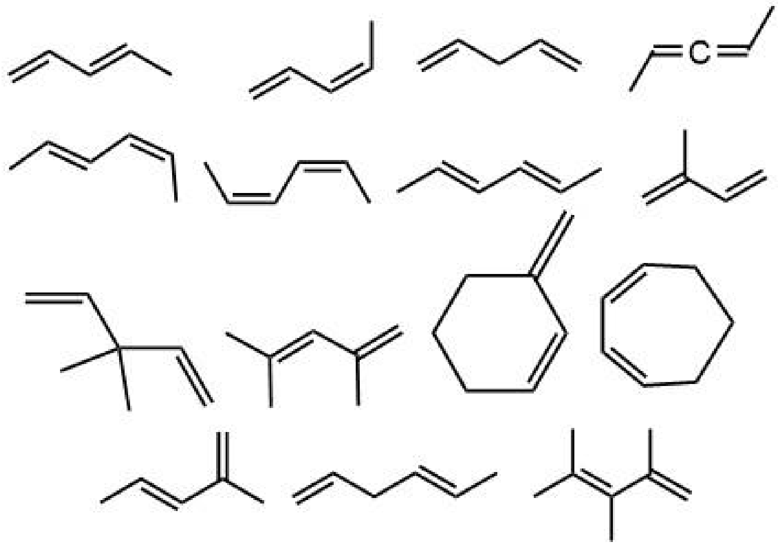


Figure 3. 2. Structures of some of the possible dienes present in the naphtha boiling range sample coming from thermally cracked Deasphalted Oil. (Not all the suggested structures were shown).

Partial hydrogenation is a useful tool to assist with the identification of diolefins. It is well-known that Syncrude has a diolefin hydrogenation stage prior to the Hydrotreater to remove those compounds when their concentrations are too high. [9] The diolefins hydrogenation takes advantage of their much more reactive nature and is done to remove them from the mixture in order to avoid fouling of equipment such as heat exchangers and in the inlet section of the hydrotreaters. They have shown that diolefins are hydrogenated to produce mono-olefins under mild hydrogenation conditions and despite the fact that hydrogenation of mono-olefins to paraffins could not be ruled out, the conversion of mono-olefins to paraffins at temperatures lower than 210°C over a typical sulfide based metal catalyst is not significant.

Following that thinking, a mild hydrogenation reaction using Pt on Carbon as catalyst was done, the decrease or elimination of peaks that were tentatively identified as diolefins (Table 3. 3) would likely indicate that it was olefinic in nature. The extent of hydrogenation would be suggestive of whether it was a diolefin or not. It was expected that after hydrogenation the peaks representing compounds that were possible dienes would disappear or be diminished significantly compared to that of mono-olefins.

By comparing the peaks in the chromatograms before and after reaction it was seen that peaks 1, 2, 3, 9, 10, 12 and 13 had changed, all of them within the first 6 minutes of the chromatographic method. From Table 3. 3 can be seen that all those compounds had carbon numbers between 5 and 7. Figure 3. 3 shows a zoomed in section of the chromatogram before hydrogenation in the first 14 minutes of the technique.

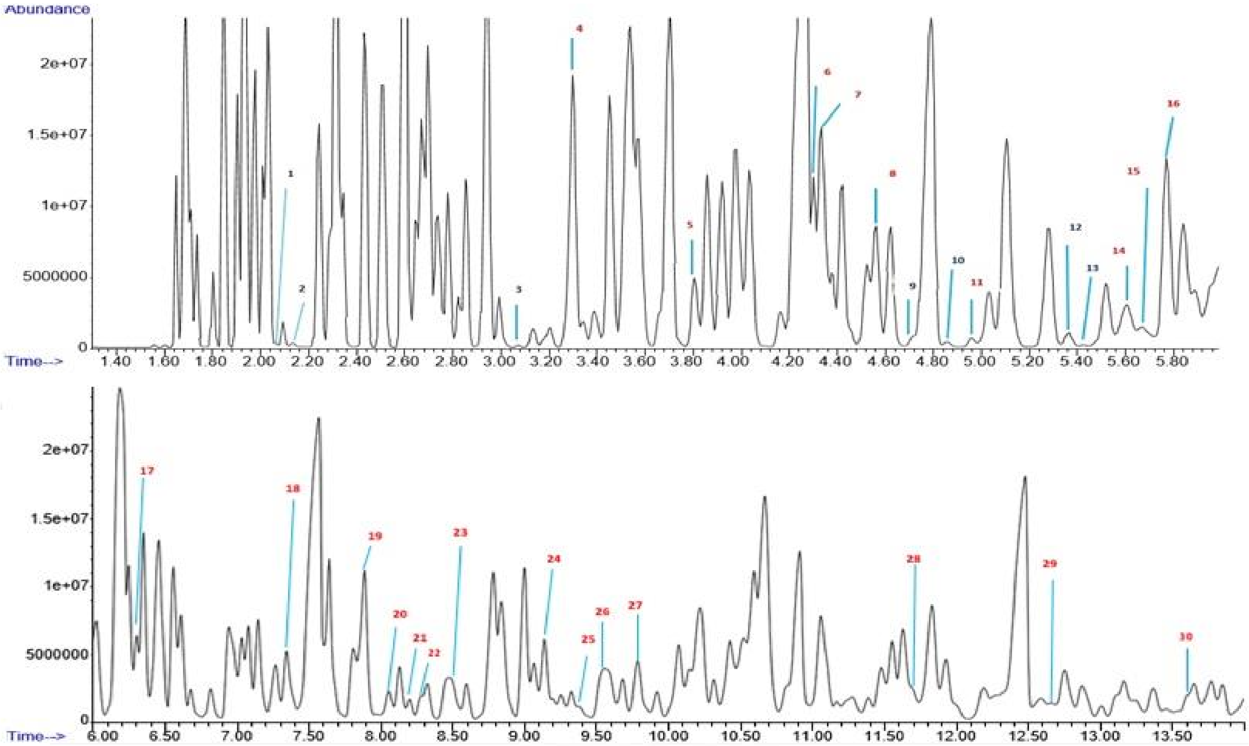
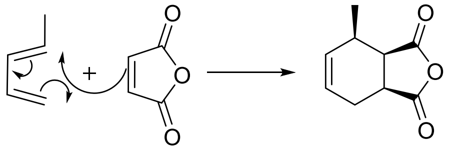


Figure 3. 3. Chromatogram of thermally cracked naphtha between 0 and 14 minutes, highlighting the 30 potential diolefins.

3.2 Derivatization of the diolefins with maleic anhydride

Besides proving that diolefins are present, it was of interest to define their nature, which could be isolated, cumulated or conjugated. The Diels–Alder reaction is the basis of the UOP-326 method[10] for the determination of conjugated diolefins in petroleum and it was used as model reaction to check which of the compounds could be conjugated diolefins. The reaction involves the addition of conjugated diolefins to some substituted alkene better known as dienophile to produce cyclohexene derivatives of one or more rings. Following the procedure of the UOP-326 method, maleic anhydride was used as dienophile to react with the possible conjugated diolefins present as indicated in reference Scheme 3. 1.



Scheme 3. 1. Diels-Alder reaction of *trans*-1,3-pentadiene with maleic anhydride

After reaction with maleic anhydride, peaks 1, 2, 3 and 13 had changed, fact taken as a confirmation of the conjugated nature of those diolefins. Figure 3. 4 zooms in those sections of Figure 3. 3 where chromatographic peaks changed due to the reaction.

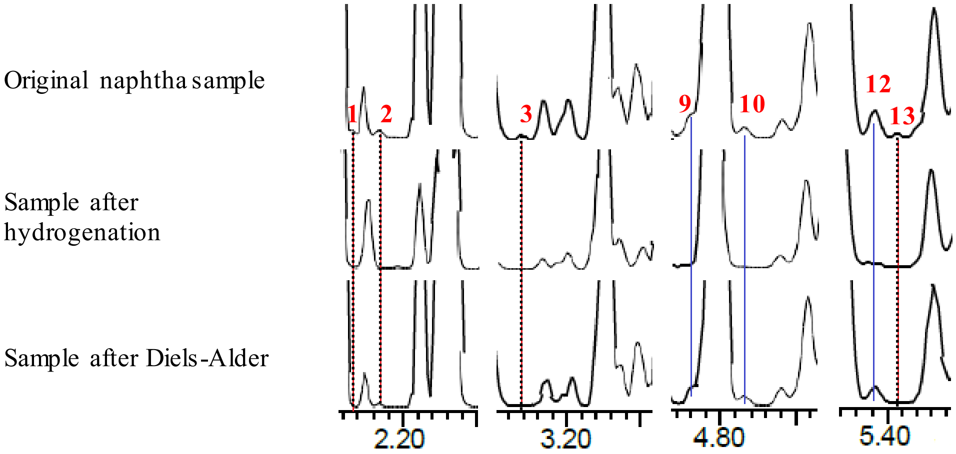
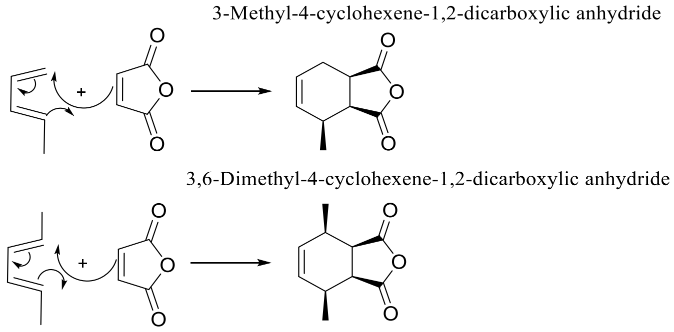


Figure 3. 4. Change in peaks after hydrogenation and Diels–Alder reactions. Dashed line represents the peaks that disappeared after both, hydrogenation and maleic anhydride addition.

It was of interest to be certain about the reactivity of conjugated dienes, especially of those which potentially could be present in the naphtha. To verify that, a mixture of diolefins was also treated with maleic anhydride. The compounds chosen for such mixture were common suggestions of the library, like 1,3-pentadiene, 1,4-hexadiene, 2,4-hexadiene stereoisomers, 1,4-pentadiene and 2-methyl-1,5-hexadiene. The results of that reaction are shown in Scheme 3. 2. It is seen that *trans*-1,3-pentadiene and *trans*-*trans*-2,4-hexadiene peaks are gone after reaction. The reaction products are heavy molecules with retention times higher than 28min. Some of the peaks seen in during that time, correspond to the following products, although the structure of the molecules represented by each peak was not confirmed:



Scheme 3. 2. Structure of some of the products from the maleic anhydride addition to the dienes mixture.

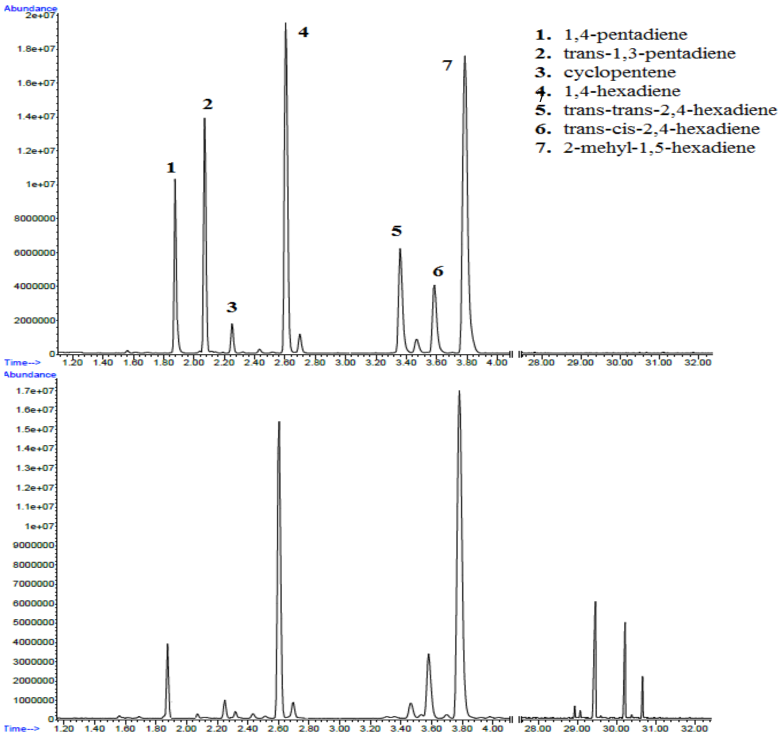


Figure 3.5. Chromatogram before and after Diels-Alder reaction between mixture of dienes and maleic anhydride. Note that despite being isolated dienes, peaks 1 and 4 did react. Cyclopentene appeared as an impurity in one of the compounds.

When the reaction was done with naphtha, the verification of the presence of those products could not be done due to coelution of compounds in that range of time (28-32min). Besides, the low concentration of diolefins is indicator of a low concentration of product, thus the peak is for sure hidden under that of another compound.

3.3 Model compound based identification

From a careful visual comparison of the mass spectra of each peak and that of the suggested conjugated dienes, standards of those compounds with the most resemblance in the spectra and that were available in the market were purchased to compare and check their retention times. Those peaks that changed only with hydrogenation belong to another type of compounds; such is the case of peaks 4 and 5 that were thought could be diolefins due to the GC-MS suggestion, but with the Diels-Alder reaction and further analysis, proved they could be cycloalkenes. The following is a brief summary of what is known so far about the possible conjugated diolefins listed in Table 3. 3:

- *Peak 1*: Has 5 carbons, is a conjugated diolefin and from comparison with standards it was concluded that this peak could correspond to *trans*-1,3-pentadiene. The unknown peak has a retention time of 2.069 min and the standard appears at 2.062 min.
- *Peak 2*: Has 5 carbons and was consumed in both reactions. Among the suggestions are *trans*- and *cis*-1,3-pentadiene. The boiling point of both isomers is really close (*trans*-42°C and *cis*-44°C), which explains the proximity of the peaks. Since the first option could be peak 1, it seems rational to state that peak 2 might be *cis*-1,3-pentadiene. This standard was not available and the retention time could not be confirmed.
- *Peak 3*: Has 6 carbons, it reacted in the Diels–Alder reaction and appears at 3.071min. Of all the possibilities, *trans*-2-methyl-1,3-pentadiene*,* *trans*-3-methyl-1,3-pentadiene and 1,3-hexadiene were the compounds with the highest resemblance based on their mass spectra. Only the first one was not found in the market. The retention time of *trans*-3-methyl-1,3-pentadiene and 1,3-hexadiene are 3.285 and 2.965 min respectively. It is therefore concluded that peak 3 could be *trans*-2-methyl-1,3-pentadiene.
- *Peak 4*: Has 6 carbons, it did not react in the Diels–Alder reaction. Among the suggested options were 1,4-hexadiene, *cis-cis*-2,4-hexadiene, *trans-trans*-2,4-hexadiene, 1-mehtylcyclopentene and 3-methylcyclopentene. All standards except 3-

methylcyclopentene were bought and analyzed by GC-MS. The unknown peak has a retention time of 3.298 min whereas the mentioned diolefins showed at 2.600, 3.359 and 3.579min respectively and 1-methylcyclopentene showed up at 3.312min. Based on the retention times and the lack of reactivity towards the maleic anhydride addition, peak 4 could be 1-methylcyclopentene. Although 3-methylcyclopentene cannot be rejected as an option, if the boiling point of both cyclopentene derivatives is taken into account (1-methylcyclopentene, 76°C and 3-methylcyclopentene, 66°C) it is speculated that 3-methylcyclopentene would have appeared at a time before 3.298min, the retention time of the peak of interest.

- *Peak 5*: Appears at 3.806 min, has 6 carbons and changed in small proportion after hydrogenation but remained the same after maleic anhydride addition. Some suggestions were 1,4-hexadiene, *cis*-*cis*-2,4-hexadiene, *trans*-*trans*-2,4-hexadiene, *cis*-*trans*-2,4-hexadiene, 4-methyl-1,3-pentadiene (RT=3.400 min), *trans*-3-methyl-1,3-pentadiene (RT=3.285 min) and cyclohexene. All conjugated dienes were discarded because if one of them were, they would have reacted with maleic anhydride; the isolated too because its retention time did not match. Cyclohexene was analyzed and appeared at 3.840 min.
- *Peak 10*: Has 7 carbons, it was consumed during hydrogenation but did not present any significant change with maleic anhydride addition. Vinylcyclopentane and ethylidene-cyclopentane were the two strongest suggestions. The standard of ethylidene-cyclopentane has a retention time of 6.847min whereas the Vinylcyclopentane appeared at 4.943min that compared with the time of the unknown peak (4.855min) is a better match. Taking into account the retention time and the fact that thermal cracking gives α-olefins, Vinylcyclopentane is considered to be the compound represented by peak 10.
- *Peak 13*: Has 7 carbons. In contrast to the other 3 peaks, for this compound, all the strongest suggestions were cyclic dienes such as 1,3-cycloheptadiene, 1-methylcyclohexa-2,4-diene, and 5,5-dimethyl-1,3-cyclopentadiene. 1,3-cycloheptadiene was rejected as option because the model compound showed a retention time of 8.724 min and peak 13 appeared at 5.423 min. Since the other two options are not commercially available, the presence of either compound.

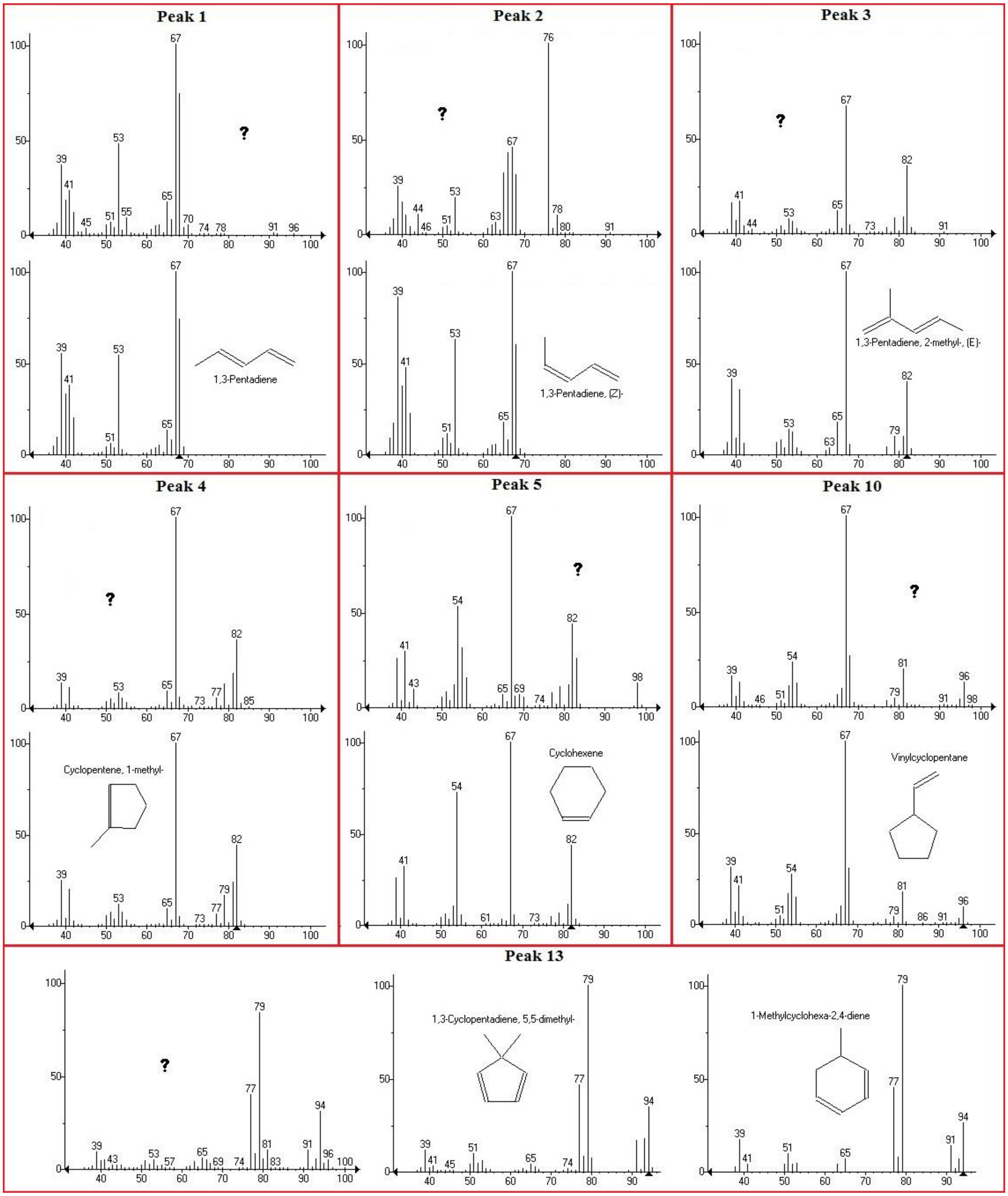


Figure 3. 6. Electron impact mass spectra of the possible conjugated dienes and molecules detected from the cracked naphtha sample and their tentative identification.

The mass spectra of the unknown peaks that showed a change after reaction and those of the most possible compounds are shown in Figure 3. 6. Note that the mass range scanned was truncated from m/z=30.

As discussed earlier, there is a higher certainty about the presence of *trans*-1,3-pentadiene, 1-methylcyclopentene, cyclohexene and vinylcyclopentane in the cracked naphtha sample. Taking that into account a naphtha sample spiked with the mentioned compounds was run in the GC-MS,for which the chromatogram is shown in Figure 3. 7.

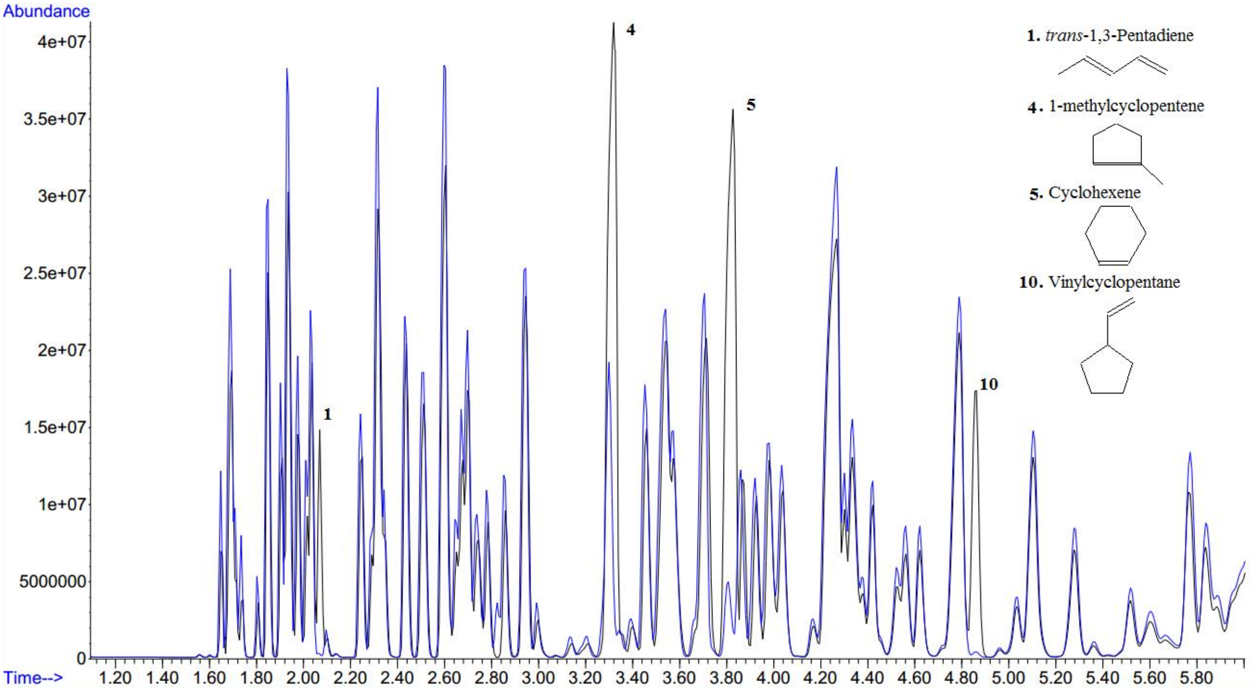


Figure 3. 7. Spiked naphtha sample. The four identified compounds were added to check if they match the retention time when they are being part of the mixture.

Regarding the other peaks mentioned in Table 3. 3, their structure has not been defined, but according to the GC-MS suggestions, those peaks correspond mainly to derivatives of cyclopentene, cyclohexene and some cyclic α-olefins. This is just a speculation that has not been experimentally confirmed; is a statement based on the repeated observation of structures like those presented in Figure 3. 8 as likely candidates for the mass spectra found during analysis.

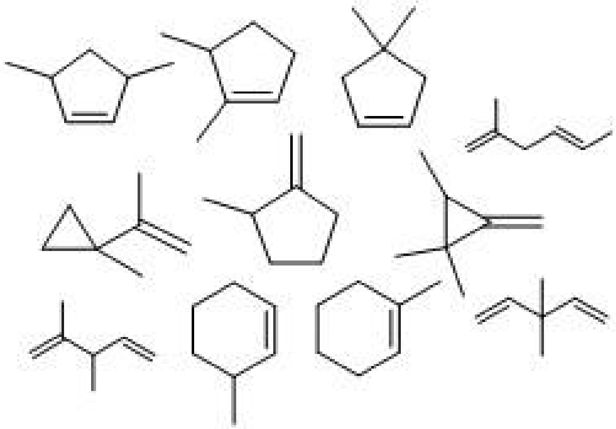


Figure 3. 8. Example of the possible structure of the peaks with lack of reactivity towards hydrogenation and Diels-Alder reactions.

3.4 Quantification with GC-FID

Four calibration curves were prepared to develop the GC-FID method for quantifying *trans*-1,3-pentadiene, 1-methylcyclopentene, cyclohexene and vinylcyclopentane. The calibration curves showed satisfactory results according to the value for the correlation coefficient that were higher than 0.996. The curves, their corresponding response and correlation factors can be seen in the Apendix 1, Figure A1.1, Figure A1.2 and Table A1.1.

After adding naphtha to the ISTD, the samples were processed in the GC-FID by triplicate as was done for the standards. The idea was to have an approximate value for the amount of the four molecules identified in the mixture. The quantification results are shown in Table 3. 4.

Table 3. 4. Concentration calculated for the four identified compounds.

Peak	Compound	Concentration [ppm]
1	*trans*-1,3-pentadiene	140
4	1-methylcyclopentene	6700
5	Cyclohexene	1400
10	Vinylcyclopentane	110

3.5 Identification using GC-VUV

From the work developed by AITF a list of 54 olefins was given; among which 13 correspond to diolefins. Not all of them could be confirmed, some are present as traces and some have not been quantified. Calls the attention the fact that GC-VUV was able to identify diolefins of all nature; there are 2 conjugated, 2 isolated and 1 cumulated according to their results. It is worth also to highlight that the conjugated diolefin *trans*-1,3-pentadiene, identified with GC-MS is not confirmed by AITF, but its presence cannot be ruled out either. Table 3. 5 shows a list with the names of the olefins detected.

Table 3. 5. List of olefins identified present in the sample (blank concentration result means NOT quantified yet) detected by AITF using GC-VUV.

	Name of Olefin	**Time (min)**	**Conc. (ppmw)**	**Comments**
1	Isobutylene	1.7726		
2	1-Butene	1.7816		
3	*trans*-2-Butene	2.0628		
4	*cis*-2-Butene	2.3039		
5	1,4-Pentadiene	3.6477		Noise or below detection limit
6	1-Pentene	4.0451	4037.45	Out of the method calibration range
7	2-Methyl-1-butene	4.3174	2014.60	Out of the method calibration range
8	2-Methyl-1,3-butadiene	4.6791		Noise or below detection limit
9	*trans*-2-Pentene	4.8532		
10	*cis*-2-Pentene	5.2059		
11	2-Methyl-2-butene	5.4603		
12	*trans* 1,3-Pentadiene	5.6121		Noise or below detection limit
13	Methylenecyclobutane	6.9292		Noise or below detection limit
14	Cyclopentene	7.2997	741.21	Out of the method calibration range
15	3-Methyl-1-butene	7.6346		
16	*trans*-3-Hexene	8.3489		
17	Unknown olefin 1	8.4516		
18	*trans*-2-Hexene	8.7730		
19	1,5-Hexadiene	9.0096		Noise or below detection limit
20	1-Hexene	10.2999		
21	***trans*-1,4-Hexadiene**	10.8222	62.59	With absolute error of 1% (at mid-level calibration)

22	*cis*-3-Hexene	11.8401		
23	*trans*-3-Hexene + unknown olefin 2	11.8580		
24	2-Methylpentene-2	12.1080		
25	*cis*-2-Hexene	12.7018		
26	**2,3-Dimethyl-1,3-butadiene**	13.3715	860.83	Out of the Method Calibration Range
27	3,3-Dimethylpentene-1	13.3715		
28	unknown olefin 3	13.3715		
29	1,3-Hexadiene	13.4518		Noise or below detection limit
30	unknown olefin 4	14.4162		
31	2,4-Hexadiene	16.2600		Noise or below detection limit
32	1-Methylcyclopentene	16.3806	3873.83	Out of the Method Calibration Range
33	**3-Methyl-1,3-pentadiene**	16.9610	426.44	Absolute error of -30% at mid-level calibration
34	Cyclohexene	18.7111		
35	2-Methyl-1,5-hexadiene	19.3807		Noise or below detection limit
36	**Tetramethylallene**	21.3942		
37	1-Heptene	21.7514		
38	*cis*-3-Methyl-3-hexene	23.1175		
39	*cis*-2-Heptene	23.7247		
40	Methylcyclohexane	23.9256		
41	*trans*-2-Heptene	24.0953		
42	*trans*-3-Heptene	24.5149		
43	*cis*-3-Heptene	25.1400		
44	Vinylcyclopentane	25.4614	326.63	With poor Precision, 21.7 % (at 95% confidence interval)
45	**3-Methyl-2,4-hexadiene**	28.1267		Noise or below detection limit
46	1-Methylcyclohexene	32.2698	3958.19	Out of the Method Calibration range
47	Ethylidenecyclopentane	33.7922	96.77	Absolute error of 9% (at mid-level calibration)
48	**1,7-Octadiene**	33.8949	93.26	Absolute error of -35%
49	*trans*-2-Nonene	33.9217		
50	2-Ethyl-1-hexene	35.8236	1945.88	Out of the method calibration range
51	1-Octene	36.4308	2399.88	Out of the method calibration range
52	1-Nonene	48.7395	1249.93	Out of the method calibration range
53	Dicyclopentadiene	60.3294		Noise or below detection limit
54	1-Undecene	65.7091	1080.21	Out of the method calibration range

4. Discussion

4.1 Identification using GC-MS

Figure 3. 1 shows what was expected since the beginning, the thermally cracked naphtha sample was analytically complex and interfered with the identification of diolefins, due to the wide range of organic functions present in the mixture. This affects the qualitative analysis because the compounds of interest i.e. diolefins, could have been present as trace compounds that were masked under others with a stronger signal, in other words they could not be identified in the sample, because their signal was hidden by the matrix.

According to Table 3. 3 and Figure 3. 4 the compounds detected in the present study have a number of carbons that ranged between 5 and 7 (which helps to narrow the carbon distribution where diolefins could be expected). Despite that, the carbon number cannot be assumed as non-variable because changes in the operation conditions, the bitumen composition and the severity of the thermal cracking, influence the carbon distribution. [6] Besides, as can be seen from Figure 3. 3 and Figure 3. 4 the peaks of interest are always the smallest and the fact that they appeared in the first 6 min of the method does not mean that dienes with a longer carbon chain are not present, it rather means they could have been overlapping with other compounds (matrix interference) and thus, changes after the model reactions could not be detected.

Methodologies for the analysis of olefins and diolefins in cracked petroleum stocks have been known to couple physical and chemical methods. [4] The present work is not an exception; chemical methods such as the maleic anhydride and hydrogen addition along with physical methods like GC-MS were used to identify the diolefins present. However, when each peak is compared with its possible matching compound as shown by Figure 3. 6, one can infer that GC-MS results do not allow to be certain regarding which isomer of a molecule is present, especially for those cases where all the required standards were not available. For instance, peak 13 and its possible compounds have fragment ions 39, 51, 65, 71 and 94 in the highest proportion and without the standards is a very difficult task to stablish which one is present in the mixture, even though the molecular formula (C_xH_y) can be determined reliably.

From Figure 3. 8, one can state that the other peaks that did not react during hydrogenation nor Diels-Alder reactions have an olefinic nature. All the structures shown belong to some of the following categories: acyclic isolated diolefins, branched cyclopentene derivative, branched cyclohexene derivative or cyclic α-olefin, however taking into account that cyclic compounds with five or six carbons in their ring are the most common due to their stability it could be expected that

It is worth to highlight that out of the 30 possible dienes initially detected, only 4 have been identified as such with certainty. This helps to illustrate the impact of the high matrix interference present in this work. Thermal cracking products go from alkanes, cycloalkanes, alkenes and cycloalkenes to aromatics along with all the isomers in those categories and most of the times those peaks that could be thought as diolefins ended being cycloalkenes (peaks 4 and 5). The GC-MS is capable of clearly distinguishing between alkenes and aromatics, but has problems differentiating between linear and cyclic molecules whereas techniques such as gas chromatography with vacuum ultraviolet detector (GC-VUV) is more suitable for distinguishing between diolefins and aromatics.

The found amount of *trans*-1,3-pentadiene expressed in ppm is relatively low (~140) as was expected from a qualitatively comparison of the peaks from Figure 3. 3. Based on the size of the other peaks identified as conjugated diolefins but that could not been quantified due to the lack of standards, one would expect to have values for their concentration around the same order of magnitude. The fact that such values are that low, brings the question of how are those diolefins interacting in the mixture to be able to generate coke deposits and gums.

4.2 Identification using GC-VUV

In Table 3. 5 there are 13 diolefins highlighted in bold letter. It must be clarified that the comment *noise or below detection limit*, according to AITF, cannot be interpreted as the absence of the compound; its presence cannot be ruled out. One of the advantages of the VGA-100 VUV detector is the ability to deconvolve co-eluting analytes which could explain why diolefins like *trans*-1,4-hexadiene, 2,3-dimethyl-1,3-butadiene, 3-methyl-1,3-pentadiene, tetramethylallene, and 1,7-

octadiene, listed in Table 3. 5 that were not identified with the GC-MS (even though standards of the first three were bought to compare retention times and mass spectra) were confirmed using GC-VUV.

Another benefit of that kind of detector is the facility to differentiate between isomers. It can be seen in the list provided that stereoisomers of acyclic mono-olefins having carbon numbers between 5 and 11, proper of naphtha samples were identified. This is still a work in progress and according to the feedback given by AITF, the method requires more validation and the results here shown are indicatives only.

The mono-olefins found correspond to lineal hydrocarbons (C_5 to C_{11}) with their isomers, including branched species, cyclic alkenes with 5 and 6 carbon atoms and alpha olefins attached to a cycloparaffin e.g. Methylenecyclobutane and Vinylcyclopentane.

5. Conclusions

The main purpose of this chapter was to analyse a thermally cracked naphtha sample in order to identify and quantify the diolefins present. Three elements were vital to assist with the identification; partial hydrogenation, Diels-Alder reaction with maleic anhydride and GC-MS analysis. The key findings of the study are the following:

1. Using their mass spectra four potential conjugated diolefins were identified in the thermally cracked naphtha sample.
2. Around 140ppm of *trans*-1,3-pentadiene are present in the sample according to the GC-FID quantification.
3. The carbon number of diolefins identified by GC-MS ranges between 5 and 7, but the presence of compounds with a higher carbon number cannot be ruled out.
4. Using GC-VUV five diolefins were identified in the thermally cracked naphtha sample, two conjugated, two isolated and one cumulated.
5. The abundance in the mixture of diolefins quantified by GC-VUV, *trans*-1,4-hexadiene, 2,3-dimethyl-1,3-butadiene, 3-methyl-1,3-pentadiene and 1,7-octadiene is 62, 860, 420 and 93 ppm respectively.
6. The carbon number of diolefins identified by GC-VUV ranges between 6 and 8, but the presence of compounds with lower or higher carbon number cannot be ruled out.
7. According to the results of both methodologies, conjugated diolefins are in greater proportion compared to isolated diolefins, their concentration in the sample is one order of magnitude higher.
8. Most of the diolefins identified are acyclic compounds with and without branching. Cyclic diolefins could not be confirmed.
9. The presence of molecules like 1-methylcyclopentene, cyclohexene and vinylcyclopentane, interfered in the identification of diolefins; chemical methods such as hydrogenation or Diels-Alder were used to distinguish between diolefins and cyclic mono-olefins isomers.
10. More work needs to be done, in order to identify all the peaks initially thought as diolefins, knowing that a compound is not a diolefin is equally useful as knowing if it is.

References

(1) Raseev, S. *Thermal and catalytic processess in petroleum Refining*; Marcel Dekker: New York, 2003.

(2) Carbognani, L.; Lopez-Linares, F.; Trujillo, M.; Wu, Q.; Carbognani, J.; Pereira-Almao, P. Olefin content estimation in heavy oil, bitumen and their upgraded products. *Prepr. Pap.-Am. Chem. Soc., Div. Energy Fuels* **2013**, *58* (2), 507–508.

(3) Von Zanier, a.; Jäckle, H. W. Thermal-oxidative stability of motor gasolines. *Erdoel Erdgas Kohle* **2000**, *116* (3), 109–115.

(4) De Andrade, D. F.; Fernandes, D. R.; Miranda, J. L. Methods for the determination of conjugated dienes in petroleum products: A review. *Fuel* **2010**, *89* (8), 1796–1805.

(5) Edwards, K. E.; Qian, K.; Wang, F. C.; Siskin, M. Quantitative analysis of conjugated dienes in hydrocarbon feeds and products. *Energy Fuels* **2005**, *19* (5), 2034–2040.

(6) Badoni, R. P.; Bhagat, S. D.; Joshi, G. C. Analysis of olefinic hydrocarbons in cracked petroleum stocks: a review. *Fuel* **1992**, *71* (5), 483–491.

(7) Paez, N. Y.; De Klerk, A. *Diolefin characterization in thermally cracked naphtha*; Edmonton, 2016.

(8) Garcia, J.; do Prado, I. *Olefin conversion for field upgrading*; Edmonton, 2014.

(9) Gray, M. R. Hydrotreating Processes. In *Upgrading Oilsands Bitumen and Heavy Oil*; The University of Alberta Press: Edmonton, 2015.

(10) Andrade, D. F.; Azevedo, D. A. Comparison of UOP-326, voltammetric and gas chromatographic/mass spectrometric methods for the determination of conjugated dienes in Brazilian Naphtha. *Fuel* **2006**, *85* (7-8), 1024–1031.

CHAPTER 4 – HYDRATION AS POTENTIAL TREATMENT FOR DIOLEFINS

Abstract

In this study a hydrogen free and low temperature strategy is proposed as solution to the high amount of diolefins present in a thermally cracked naphtha sample coming from a field upgrading facility. The reaction chosen as possible treatment of the stream was of the electrophilic addition type, the hydration of alkenes. It is special because of its simplicity by using a reagent as common and abundant as water. The methodology involved the hydration of a model compound, the branched conjugated diene, 2,5-dimethyl-2,4-hexadiene; the reaction was carried out in a micro-batch reactor at 110°C, 3MPa with a Nitrogen atmosphere, using water in excess with a molar ratio of water to diene of 6:1 and using different type of catalysts. Sulfuric acid in aqueous solution, solid phosphoric acid, Siral-5 and H-ZSM-5 catalysts were employed. All catalysts showed to be active under the reaction conditions, but the sulfuric acid showed the highest selectivity towards the formation of oxygenated products. Besides the selectivity, the conversion of diene when the mineral acid was used was also the highest. After the positive results of hydration of 2,5-dimethyl-2,4-hexadiene, a diluted mixture of different types of dienes was prepared to be hydrated under the same conditions with sulfuric acid as catalyst. The solution formed by *trans*-1,3-pentadiene, 1,5-hexadiene, 1,3-hexadiene, 1,3-cycloheptadiene and 2,5-dimethyl-2,4-hexadiene in decane. The presence of oxygenated species coming from alcohols and alkenes was detected. Reactions such as double bond-isomerization, skeletal isomerization, and cyclization were proposed to explain the varied range of products obtained.

Keywords: Hydration, acid catalysis, oxidation, diolefins.

1. Introduction

As was highlighted in the previous chapter, high-temperature processes involve the formation of a substantial amount of olefins and diolefins in light boiling materials that, if not removed before pipelining or refining operations, could be detrimental to equipment and processing. For instance, during full upgrading of bitumen in facilities where delayed coking is employed, one of the products is coker naphtha; coker naphtha has a considerable amount of heteroatoms as well as olefins and diolefins. To improve the quality of the product before sending it through the pipeline, heteroatoms must be removed and a hydrotreatment step is required. However, the conditions of the process (high temperatures) favor the polymerization of diolefins. Thus, the process is done in two stages, the first one to saturate diolefins at low temperatures and the second to reduce sulfur and nitrogen compounds.

When upgrading of bitumen is done by means of partial upgrading, the economic viability of using hydrogen related processes to deal with diolefins decreases because those are expensive and large scale methods as opposed to a typical field upgrader facility that is of small size. But the problem remains, compounds that can polymerize and cause fouling are still present and the challenge is that a hydrogen-based treatment is not an option.

There is not extensive research in hydrogen-free and low temperature treatment of diolefins in naphtha boiling range fractions. Most of the methodologies are related with hydrogenation and the investigations done, focus mainly on the selective hydrogenation of diolefins rather than their elimination through a different route. The hydroprocessing of pyrolysis gasoline for instance, requires a special set-up. Due to the large amount of diolefins, HDS unit can be fouled on account of their rapid polymerization at temperatures above 200°C. Therefore diolefins are first hydrogenated to mono-olefins over a Ni or Pd sulfide catalyst.[1] Taking that into account, the work presented in this chapter had the intent to find an alternative treatment with the ultimate goal of decreasing the amount of poly-unsaturated compounds present in thermally cracked naphtha, coming from a field upgrader facility.

Is has been proven that when strong mineral acids are used as catalyst to treat alcohols under high temperatures, water is lost and an alkene is formed; that is the known dehydration of alcohols to produce alkenes done at relatively high temperatures (120-170°C).[2] That is an equilibrium process, meaning the reaction can be shifted to the opposite direction to achieve the alkene hydration. Conditions favoring the hydration reaction are using low acid concentrations, water in excess and working under low temperatures. The manufacture of ethanol, isopropanol and butanol in the industry is done by reacting ethylene, propylene and isobutylene with water in the form of steam, using solid phosphoric acid as catalyst at low temperatures.[3] The reaction is governed by the equilibrium; in the manufacturing of ethanol, for instance it is possible to achieve an overall 95% conversion, after removing the ethanol and recycling the ethene not converted into the reactor.[2] Besides the use of mineral acids as catalysts, Y type zeolite was used as catalyst to hydrate short chain olefins (C_2-C_4), and was promoted using calcium, rare-earth elements and chromium as cations.[4] Ferrierite and pentasil-type zeolites showed high activity towards olefin hydration when working at high pressure;[5] the results were comparable to those obtained using solid phosphoric acid.

Extrapolating the application of that reaction to diolefins, it was intended to try the hydration of diolefins as a way of treatment. This is not new, several investigations have been conducted aiming the hydration of diolefins using sulfuric acid[6] and ruthenium complexes with an acid component.[7] In the case of conjugated dienes, they undergo electrophilic additions just like alkenes, although with unique characteristics; for instance, addition takes place at either carbons 1 and 2 or 1 and 4 of the four-atom system.[2] If this reaction were to be used as treatment, water is a cheap and abundant reagent, which makes of this, a relatively simple solution to the problem.

The approach taken involved proving the feasibility of hydration using a model compound and then apply it to a model mixture sample. The next lines describe the methodology followed:

1. Hydration reaction of 2,5-dimethyl-2,4-hexadiene at low temperature (110°C) using four different catalysts. Solid phosphoric acid (SPA), sulfuric acid, Siral-5 and Zeolite ZSM-5.
2. Once the hydration of 2,5-dimethyl-2,4-hexadiene proved to be achievable under the indicated conditions, the same reaction was repeated using a mixture of diolefins and the catalyst that showed the highest conversion, i.e. closest to the equilibrium conversion.

2. Experimental

2.1 Materials

Solid phosphoric acid catalyst was PolyMax 843, a silica-based support impregnated with phosphoric acid obtained from Clariant Sasol, South Africa. The zeolite H-ZSM-5 with reference CBV 28014 was supplied by Zeolyst International, USA (SiO_2/Al_2O_3 = 280, surface area of 400 m^2/g and 0.05wt% Na_2O). The amorphous silica-alumina catalyst used in this study was Siral-5, purchased from Sasol, Germany (contains 5wt% SiO_2, surface area of 370 m^2/g and 0.005wt% Na_2O). The amorphous silica-alumina and the zeolite were activated at 550°C for 6h as indicated by the supplier and done in previous works.[8] The catalysts were not characterized, grinded, sieved or further purified before working with them; the composition and surface areas above shown were provided by the supplier. Distilled water was used. The other reagents are described in Table 4.1 along with the gases required for the proper functioning of the analysis instruments.

Table 4. 1. Materials description

Compound	Formula	CASRN [a]	Mass fraction purity [b]	Supplier
Materials for reactions and model compounds identification				
Sulfuric acid	H_2SO_4	7664-93	98.5%	Fisher Scientific
Decane	$C_{10}H_{22}$	124-18-5	≥99%	Sigma Aldrich
trans-1,3-Pentadiene	C_5H_8	2004-70-8	90%	Sigma Aldrich
1,5-Hexadiene	C_6H_{10}	592-42-7	97%	Sigma Aldrich
1,3-Hexadiene (mixture of isomers)	C_6H_{10}	592-48-3	95%	Sigma Aldrich
2,5-Dimethyl-2,4-hexadiene	C_8H_{14}	764-13-6	96%	Sigma Aldrich
1,3-Cycloheptadiene	C_7H_{10}	4054-38-0	95%	Sigma Aldrich
Cylinder gases				
Nitrogen	N_2	7727-37-9	0.999995 [c]	Praxair
Helium	He	7440-59-7	0.999995 [c]	Praxair

[a] CASRN = Chemical Abstracts Services Registry Number

[b] This is the purity of the material guaranteed by the supplier; material was not further purified.

[c] Mole fraction purity.

2.2 Equipment and procedure

Hydration reactions were done using a micro-batch reactor as pressure container (the same set up of the partial hydrogenation described in Chapter 3 of this work). Inside the reactor a 7 ml glass vial loaded with the reacting mixture and a magnetic stirrer was inserted. The reaction mixture was formed by 2 ml of 2,5-dimethyl-2,4-hexadiene and distillated water; water was present in excess on a molar base of 6:1 which corresponds to a mass ratio of water to diene of 0.96:1. The catalyst loading varied. For the reaction with sulfuric acid, an aqueous solution of 3M was prepared. In the case of the Solid Phosphoric Acid, Siral-5 and the Zeolite H-ZSM-5 an amount corresponding to 10% of the mass of diene was loaded. The reactor was closed, the system was purged three times with Nitrogen and then pressurized to 3MPa with the same gas; that pressure was set to keep the reagents in the liquid phase. The heating system was an oil bath supported on a heating plate; the temperature in the oil bath was controlled and set to 110°C and when it was reached the reactor was immersed; after the internal temperature of the reactor reached the mentioned value, time was started. Stirring was turned on to 1000 rpm. When 3 hours of reaction were concluded, the reactor was taken out of the oil bath, allowed to cool down, depressurized and then opened. The reaction mixture formed two phases, so a sample of the organic phase was taken with a micropipette, transferred to a chromatography vial and analyzed with GC-MS. Regarding to the water phase, it was not further analyzed to check for dissolved organic molecules.

For the reactions done with the model mixture a solvent was used; decane. The mixture was formed by several diolefins: *trans*-1,3-pentadiene, 1,5-hexadiene, 1,3-hexadiene, 1,3 cycloheptadiene and 2,4-dimethyl-2,4-hexadiene were included. The solution was prepared by mixing 2 ml of solvent with 50μl of each diene. The moles of diene to hydrate were calculated, to find the amount of water necessary keeping the mass ratio of water to diene of 0.96:1. The reaction was carried out using sulfuric acid as catalyst; that catalyst was chosen over the other three used before, because it showed a higher conversion. The reaction lasted 3 hours, but a longer reaction time was later used (6 days) to confirm approach to equilibrium and/or potential non-equilibrium side-reactions. The model mixture was highly diluted; when the time was the same of 2,4-dimethyl-2,4-hexadiene hydration, significant changes were not seen. The details of the volumes and corresponding amounts of compounds added to hydrate the model mixture, are in Table 4.2.

Table 4. 2. Compounds forming the model mixture for hydration with sulfuric acid

Diene	Volume (ml)	Density (g/ml)	Mass (g)	MW (g/mol)	Moles
Solvent (decane)	2.00	0.73	1.46	142.29	1.03E-02
trans-1,3-pentadiene	0.05	0.68	0.07	68.12	1.00E-03
1,5-hexadiene	0.05	0.69	0.07	82.14	8.42E-04
1,3-hexadiene	0.05	0.71	0.07	82.14	8.69E-04
1,3 cycloheptadiene	0.05	0.87	0.09	94.16	9.22E-04
2,4-dimethyl-2,4-hexadiene	0.05	0.77	0.08	112.21	6.86E-04
Water added[a]	0.23	1.00	0.23	18.00	2.59E-02

[a] The volume of water added came from a sulfuric acid solution of 3M concentration

2.3 Analyses

The identification of the product of hydration was done by means of the GC-MS. The working conditions were the same described in Chapter 3 section 2.3.

3. Results

3.1 Experiments with 2,5-dimethyl-2,4-hexadiene

The first thing done was the hydration reaction of 2,5-dimethyl-2,4-hexadiene at low temperature (110°C) using four different catalysts, SPA, Siral-5, Zeolite ZSM-5 and sulfuric acid. The possible products from the water addition to 2,5-dimethyl-2,4-hexadiene are shown in Figure 4. 1.

3.1.1 Material balance

The outlet gas stream was not weighed, the amount reported as gas phase corresponds to the initial nitrogen loaded plus the difference in the total weight of the vial before and after reaction. The mass balance for all catalysts is shown in Table 4.3. As can be seen, the mass balance closure is closed to 100%. Some things to have in mind are: the targeted mass ratio water to diene was 0.96:1, but the real average mass ratio was around 1:1. The aqueous phase in the products is higher than the water initially loaded in the vial; that might be because of dissolution of some organic compounds, but also during the separation of the phases. When the organic phase was removed a thin film of it still remained in the aqueous phase.

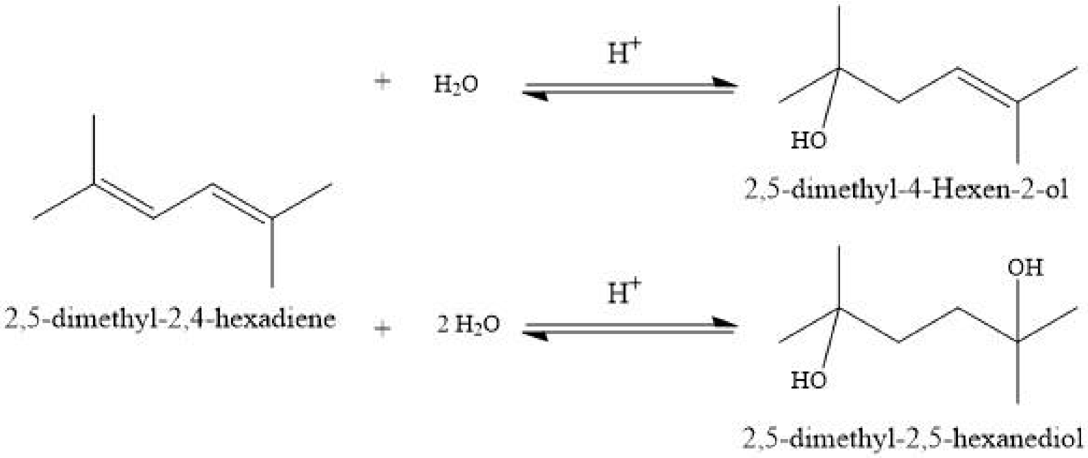


Figure 4. 1. Expected product for the hydration of 2,5-dimethyl-2,4-hexadiene.

Table 4. 3. Mass balance for hydration reactions of 2,5-dimethyl-2,4-hexadiene with four catalysts.

	Reagents Before reaction (g)				Products After reaction (g)			
Catalyst	**Water**	**Diene**	**N_2**	**Catalyst**	**Aqueous phase**	**Organic phase**	**Gas phase**	**Mass balance closure (%)**
SPA	1.5413	1.5536	1.300	0.1612	1.8243[a]	1.2203	1.512	100.0
Sulfuric acid	1.5402	1.5431	1.280	0.4346	1.9911	1.2796	1.527	100.0
Siral-5	1.5306	1.5340	1.300	0.1580	1.7670[a]	1.3773	1.378	100.0
H-ZSM-5	1.5444	1.5227	1.290	0.1548	1.7872[a]	1.3927	1.332	100.0

[a] The aqueous phase had an emulsified appearance, formed by the water and the solid catalysts.

3.1.2 Conversion and selectivity

As was noted earlier, the main analytical tool was the GC-MS. This is the reason why the conversion and selectivity of the reactions are semi-quantitative analyses based on the areas of the GC-MS peaks. As general observation is the fact that reaction products for all four catalyst were distributed in three distinctive areas respect to the feed diolefin; there are products eluting before, around the same time or after the feed. Since the column employed for separation is a non-polar column, elution times can roughly be related to boiling point differences. Having that in mind the selectivity calculations were done dividing the products into groups as: (1) degradation products with a smaller carbon chain or lower boiling point, not necessarily a lower carbon number, (2) products with nearly the same carbon number as the feed, possibly showing the addition of the hydroxyl group and (3) heavy products maybe due to acid catalyzed addition reactions.

Table 4. 4. Conversion and selectivity for hydration reactions of 2,5-dimethyl-2,4-hexadiene with four catalysts.

	Group selectivity (%)			
Catalyst	**1**	**2**	**3**	**Conversion (%)**
SPA	50	10	40	7
Sulfuric acid	87	4	9	10
Siral-5	44	28	28	2
H-ZSM-5	66	20	12	4

3.1.3 Product identification and quantification

3.1.3.1 Solid phosphoric acid

The complete chromatogram obtained for SPA catalysed hydration after the analysis with GC-MS is in Figure 4.2. The products obtained are separated into the three groups mentioned earlier.

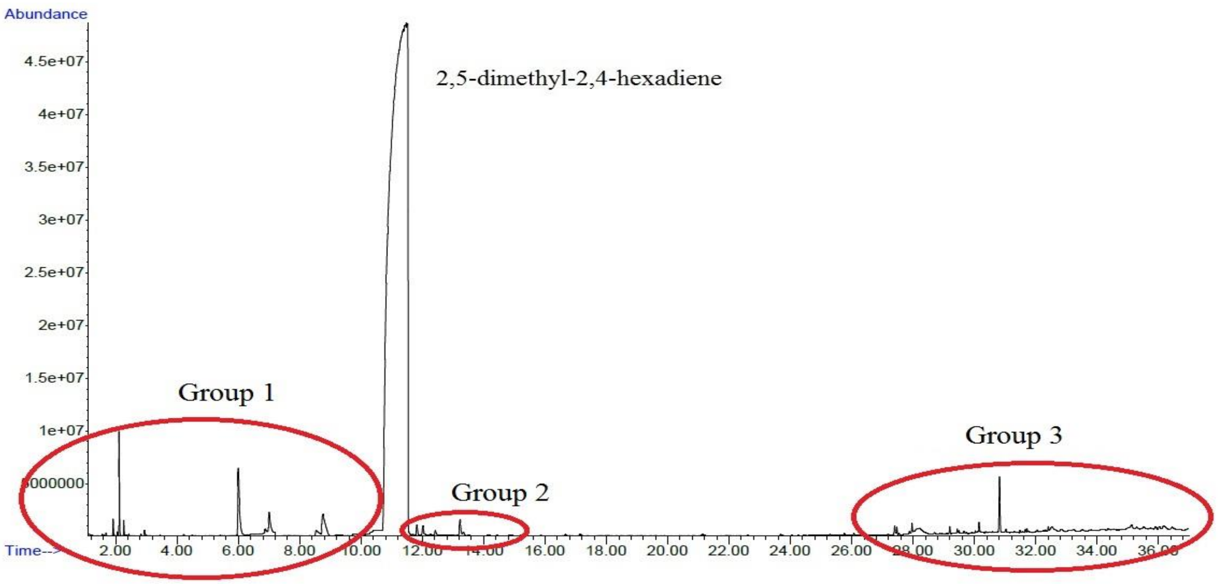


Figure 4.2. Chromatogram for 2,5-dimethyl-2,4-hexadiene hydration using SPA as catalyst.

As can be noticed from Figure 4.2, based on the peaks that appeared after reaction with SPA, a wide range of compounds were formed. Figure 4.3 is a composite of different sections from the previous chromatogram shown in Figure 4.2 using SPA as catalyst. A number was assigned to some of the peaks with the purpose of comparing the reaction products between the catalysts used. The idea was to extract information such as the organic function formed and the molecular formula of the compound represented by a peak. The identification instrument was the GC-MS and although it helps to identify the molecular formula, the molecular ion was not always apparent and it is difficult to distinguish between isomers; for some peaks the carbon number and the organic function varied from one suggestion to another, so not all the peaks were numbered. Those peaks being present mostly in retention times higher than 27 minutes. Although there is no certainty about the structures suggested by the MS library, the chemical function of the peaks is shown later in Table 4.5 and corresponds to products with functionalities resulting from the reaction of alcohols such as ketones, aldehydes, carboxylic acids and esters. The expected alcohols were not found.

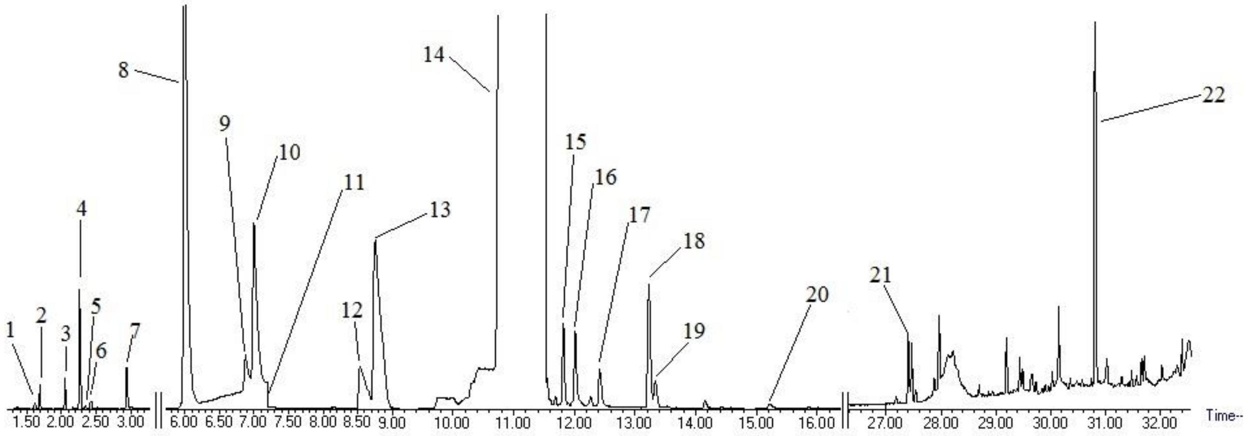


Figure 4. 3. Zoom in of chromatogram shown in Figure 4.2 for 2,5-dimethyl-2,4-hexadiene hydration using SPA as catalyst.

3.1.3.2 Sulfuric acid

Regarding to the results obtained when mineral sulfuric acid in solution was used, some things stand out. As can be seen in Figure 4.4 the production of light and high boiling products both decreased considerably respect to SPA. Specifically those compounds identified with peak numbers 1 to 7 and 21 to 22, decreased their intensity and were a smaller fraction of the reaction products. With no doubt, the major product with sulfuric acid corresponded to peak 8 in Figure 4.3, that peak has a retention time of 6.004min. The conversion of the reaction increased (10.42%) compared to SPA (6.52%) and the selectivity towards lighter products in the region of compounds labeled 8 to 14, was higher (group 1 products).

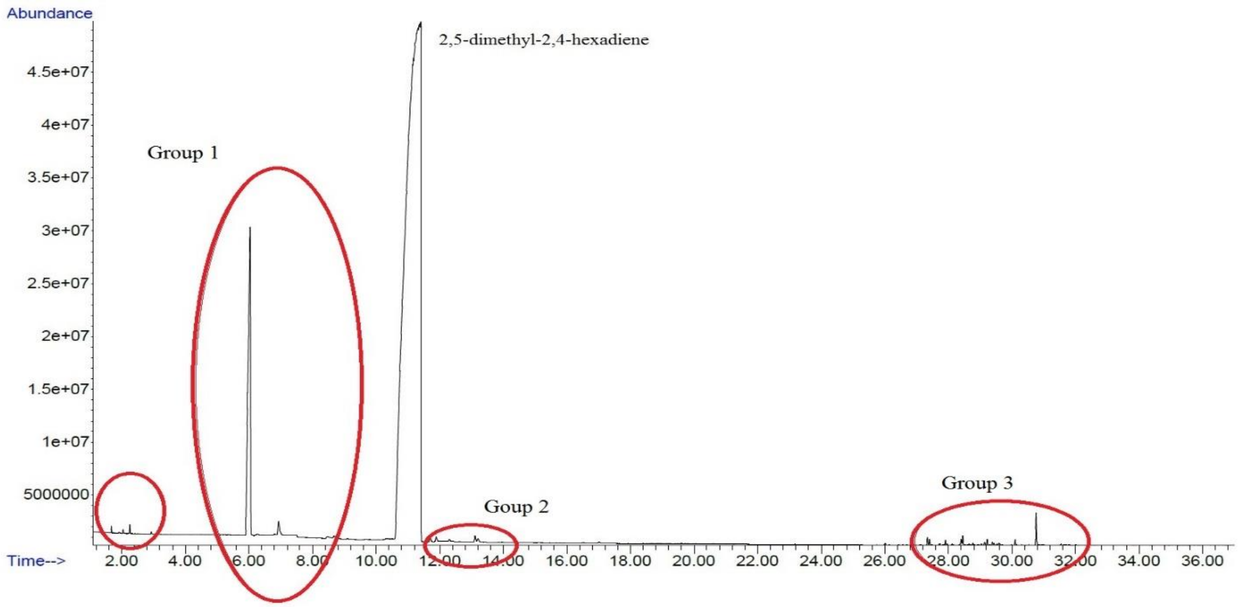


Figure 4.4. Chromatogram for 2,5-dimethyl-2,4-hexadiene hydration using H_2SO_4 as catalyst.

3.1.3.3 Siral-5

Figure 4.5 illustrates the reaction products for Siral-5. The two main products corresponded to peaks 13 and 22 in Figure 4.3. Compared to the hydration with sulfuric acid and SPA, the presence of peak 8 (the major reaction product with the other two catalysts) is so small that can be considered as negligible.

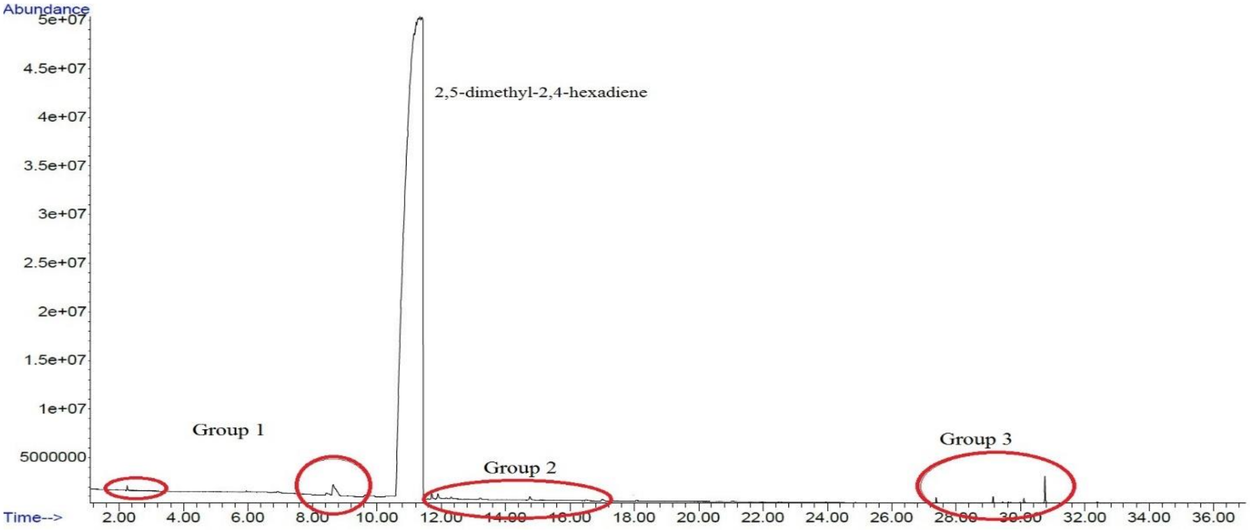


Figure 4. 5. Chromatogram for 2,5-dimethyl-2,4-hexadiene hydration using SIRAL-5 as catalyst.

3.1.3.4 Zeolite H-ZSM-5

In the case of the reaction over the zeolite catalyst (Figure 4.6) the most abundant reaction product is peak 10, followed by peak 22 and 18. A small peak corresponding to peak 8 can be seen as well.

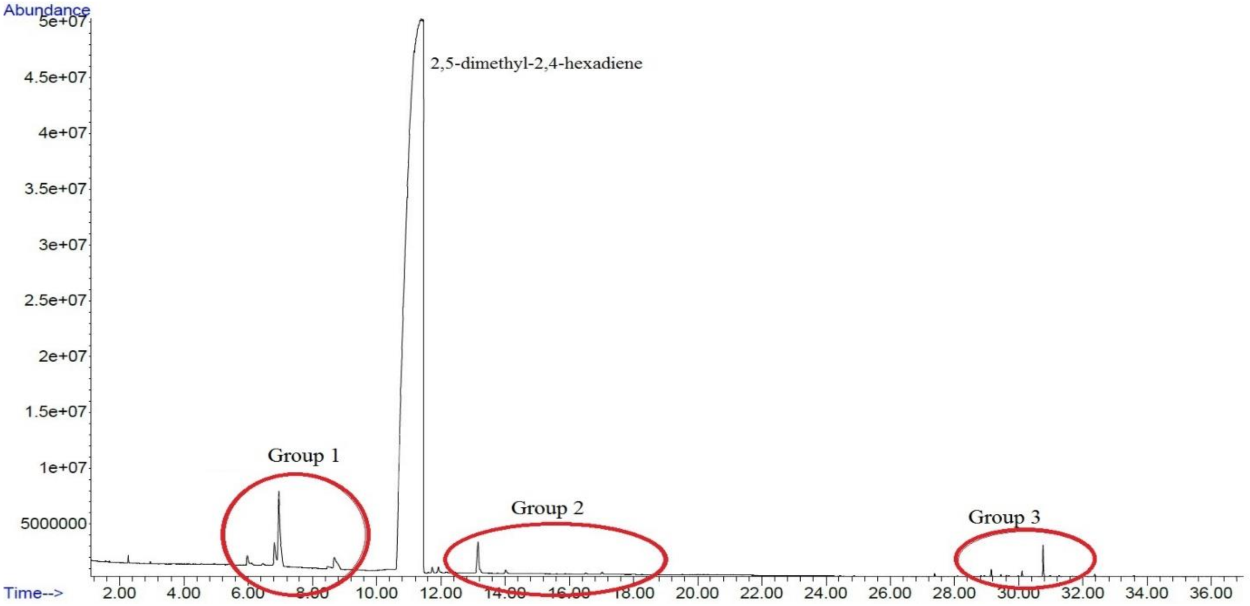


Figure 4. 6. Chromatogram for 2,5-dimethyl-2,4-hexadiene hydration using H-ZSM-5.

The fully hydrated product, the diol, was not seen for any of the catalysts. The results obtained with each catalyst varied regarding the selectivity of the products but in general terms, all showed a tendency to form the same compounds. The one with a more varied product distribution was the SPA; that, taking into account the amount of peaks seen in Figure 4.2. In three out of the four catalysts the same product (peak 8, retention time of 6.004min) was seen; all the catalyst showed the formation of peak 22.

Table 4. 5. Information collected for all the numbered peaks for all catalysts used: organic function, molecular formula and peak area. Peaks with nor value of area, where not seen with that catalyst.

Peak	**RT (min)**	**Organic Function**	**Molecular Formula**	**SPA**	**H_2SO_4**	**SIRAL-5**	**H-ZSM-5**
1	1.568	Alkene	C_2H_4	1.5E+06	3.8E+05	-	-
2	1.688	Alkene	C_4H_8	2.5E+06	5.4E+06	-	-
3	2.049	Alcohol	$C_4H_{10}O$	3.8E+06	3.8E+06	-	-
4	2.269	Aldehyde	C_4H_8O	1.6E+07	9.5E+06	6.4E+06	7.5E+06
5	2.356	Aldehyde	$C_4H_6O_2$	5.0E+05	-	-	-
6	2.423	Diene	C_6H_{10}	2.2E+06	-	-	-
7	2.944	Alcohol	$C_4H_{10}O$	8.2E+06	3.7E+06	-	-
8	6.005	Cyclic ether	$C_8H_{18}O_2$	2.2E+08	1.5E+09	-	2.3E+07
9	6.873	Diene	C_8H_{14}	1.0E+07	3.2E+06	-	8.8E+07
10	7.014	Diene	C_8H_{14}	6.6E+07	4.8E+07	-	3.1E+08
11	7.187	Carboxylic acid	$C_4H_8O_2$	6.2E+06	1.9E+07	-	-
12	8.551	Alcohol	$C_7H_{14}O_2$	3.6E+07	1.2E+07	2.0E+07	3.1E+07
13	8.771	Ester	$C_8H_{16}O_2$	1.5E+08	1.4E+07	8.8E+07	7.5E+07
14	***11.233***	***2,5-dimethyl-2,4-hexadiene***	***C_8H_{14}***	**1.7E+10**	**1.7E+10**	**1.8E+10**	**1.8E+10**
15	11.818	Ketone	$C_8H_{16}O$	2.6E+07	1.2E+07	1.4E+07	1.3E+07
16	12.012	Aldehyde	$C_8H_{16}O$	2.9E+07	1.4E+07	1.6E+07	1.4E+07
17	12.42	Ketone	$C_7H_{12}O$	1.4E+07	6.0E+06	7.8E+06	-
18	13.235	Alcohol	$C_8H_{16}O$	4.1E+07	1.6E+07	6.7E+06	1.1E+08
19	13.335	Ester	$C_8H_{16}O_2$	3.0E+06	7.2E+06	-	-
20	15.226	Alcohol	$C_{10}H_{18}O$	2.5E+06	2.9E+06	-	-
21	27.401	Ketone	$C_{15}H_{24}O$	1.6E+07	1.2E+07	1.1E+07	5.1E+06
22	30.815	Alcohol	$C_{15}H_{24}O$	1.0E+08	5.3E+07	4.5E+07	4.7E+07
Not identified peaks			-	5.6E+08	2.1E+08	1.3E+08	1.3E+08

Taking as reference Figure 4.3 and by comparison with the results of the other catalysts, a summary of the compounds formed during the hydration is given in Table 4.5. The specific identity of the peaks was not confirmed with standards, which is the reason why their name is not given, but important information such as the number of carbons present in the molecule and the organic function is provided.

Comparison of the mass spectra does not allow to have certainty about which product was present. But in the case of peak 8, the two molecules with the highest possibility of being formed were 2,5-dimethyl-2,5-hexanediol and 2,2,5,5-tetramethyl-tetrafurane. In Figure 4.7, the mass spectra obtained for the product of hydration (left part of the figure) is shown next to the two mentioned compounds. Iinitially peak 8 was thought to correspond to the diol, because it was the expected product. Using the information of the boiling point for the alcohol and the cyclic ether, the last one was chosen. The feed diolefin, 2,2,5,5-tetramethyl-tetrafurane and 2,5-dimethyl-2,5-hexanediol have a boiling point of 112°C, 134°C and 214°C respectively. Peak 8 appears before 11.233 minutes, the retention time of the feed diolefin (see Table 4.1), therefore the reaction product must have a lower boiling point; the compound that meets that requirement is the cyclic ether.

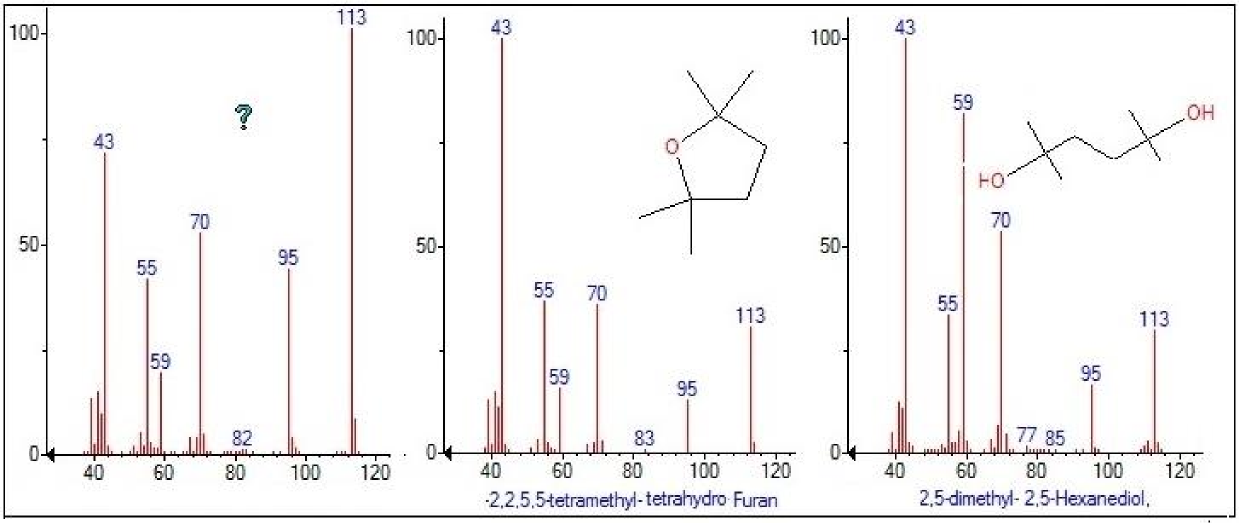


Figure 4. 7. Mass spectra comparison of peak 8 and the two compounds with the highest chance of representing the structure of the product: 2,5-dimethyl-2,5-hexanediol and 2,2,5,5-tetramethyl-tetrafurane.

The other peak that appears with all the catalysts, is peak 22, it has a retention time of 30.816 minutes and the suggestion more common given by the library of the GC-MS was an aromatic compound with the hydroxyl group in its structure as can be seen in Figure 4.8.

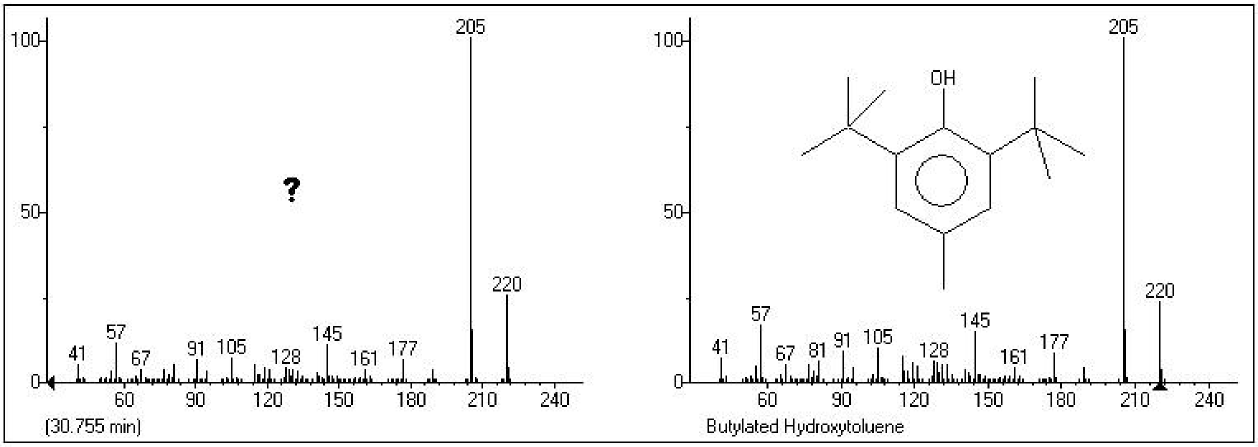


Figure 4. 8. Mass spectra comparison of peak 22 and the compound suggested by GC-MS, Butylated Hydroxytoluene

3.2 Experiments with mixture of dienes

Sulfuric acid was selected as catalyst for the reaction of the model mixture based on the results obtained for 2,5-dimethyl-2,4-hexadiene. The mineral acid showed higher conversion relative to the other catalysts, as can be corroborated in Table 4.4. The mixture was formed by diolefins of conjugaded, isolated, lineal and cyclic nature. The compounds added were *trans*-1,3-pentadiene, 1,5-hexadiene, 1,3-hexadiene, 1,3 cycloheptadiene and the same used before 2,4-dimethyl-2,4-hexadiene. Two other molecules were present as impurities from the reagents, those were cyclopentene and benzene. The hydration for the reaction mixture was done under the same conditions, but as was mentioned in the experimental section, a solvent was included and a 6 days reaction was also carried out. Hence, two reactions were done for the model mixture of dienes. Figure 4.9 shows the chromatograms for the initial mixture and the mixture after 3 hours and 6 days of reaction for retention times between 1.5 and 12 minutes. Figure 4.10 shows the same comparison but for higher retention times, the objective of the figure was to illustrate the heavy products formed in both reactions. The peak of the solvent, corresponding to decane (retention time of 17.398 minutes) was omitted.

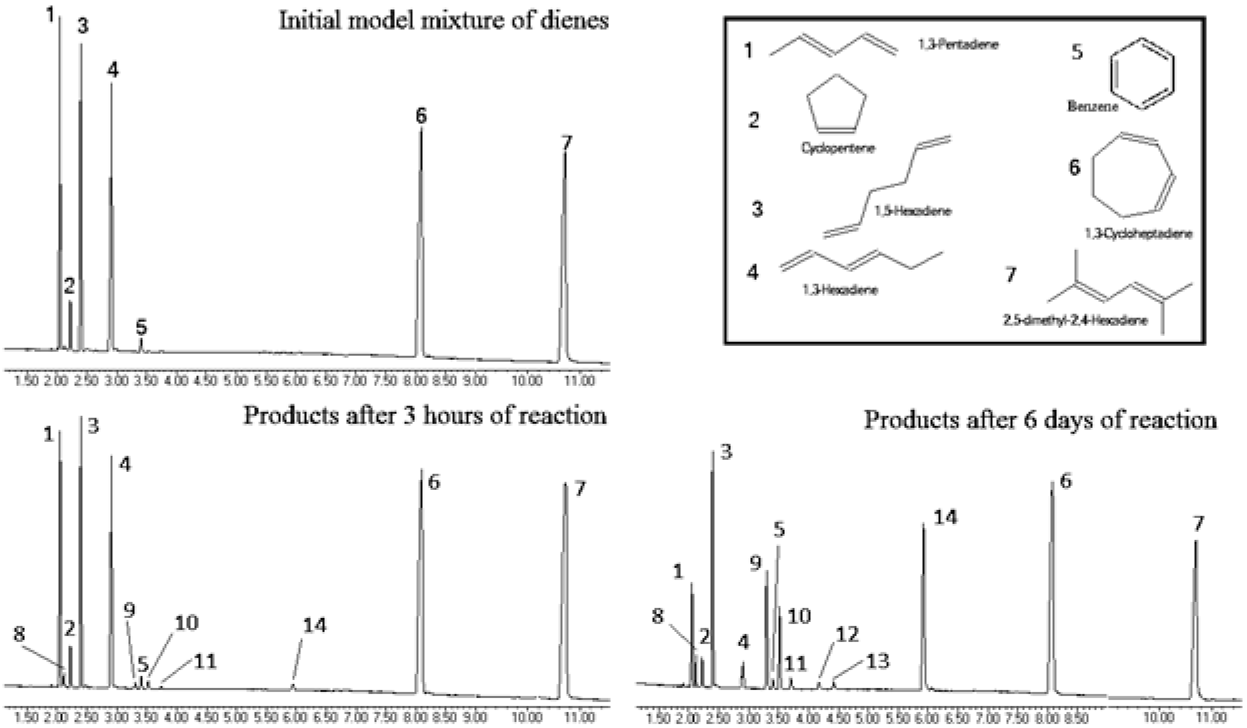


Figure 4.9. Comparison of dienes model mixture hydration for times 0, 3h and 6 d of reaction.

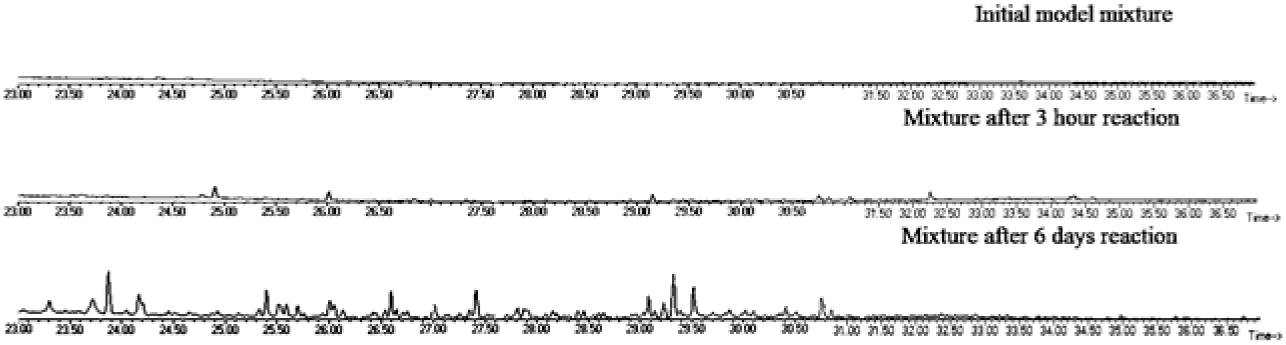


Figure 4. 10. Comparison of heavy products formed during the dienes model mixture hydration for times 0, 3h and 6 d of reaction.

3.2.1 Material balance

The dienes forming the solution were added on a volume basis, and the mass value of individual compounds was not recorded; the mass shown in Table 4.7 is the total mass of all the dienes added. The feed for the 6 hours reaction was the outlet liquid stream of the previous reaction. The mass balance for both reactions is shown in Table 4.6. As can be seen, the mass balance closure is 100%

for both reaction times, because the gas phase after reaction was calculated as the sum of the initial nitrogen loading and the amount of organic liquid compounds lost in the gas phase. That difference helps to close the balance completely; the outlet gas was not weighed.

Table 4. 6. Material balance for hydration of model mixture during 3 h and 6 d.

	Stream	**3 hours**	**6 days**
Reagents	Water	0.2398	0.2428
	Diene	0.1828	1.6288
	Decane	1.4632	
	N_2	1.2600	1.2700
Products	Aqueous phase	0.2428	0.2763
	Organic phase	1.6288	1.5823
	Gas phase	1.2742	1.2830
% mass balance closure		100.00	100.00
Organic compounds to gas phase		0.0142	0.0130
Organic compounds remaining		1.6318	1.6158

3.2.2 Conversion and selectivity

The conversion of each compound in both reactions, was first calculated as the difference in the area of the initial peak (time=0) and that after reaction (time=3 hours or 6 days) divided by the initial area of the peak as shown in equation 4.1. It is important to clarify that before doing the calculation, the areas of the peaks were scaled relative to benzene. The approach taken tried to emulate as if benzene was the internal standard in the quantification (the area of benzene should not have changed between experiments). The limitations of the methodology are evident, negative values of conversion were obtained in Table 4.7. Although, benzene is a relatively stable compound, there is no certainty respect to the amount of compound lost in the vapor phase, which might be the reason of such results.

$$\boldsymbol{X = \frac{(A_i - A_t)}{A_i}}$$ **Equation 4. 1**

After having those results, the approach taken to find the conversion of reagents was to find the amount of organic compounds present for each reaction time. To do that, the percentage of organic compounds lost in the gas phase was calculated (for each reaction time); then, the amount of organic matter remaining (dienes plus solvent) after reaction was obtained. By relating the area of each peak representing a reagent, with the total area of all peaks and the total mass of organic compounds present, as shown in Equation 4.2, the amount of each diene for each reaction time was found. The conversion was determined as shown in Equation 4.3.

$$\boldsymbol{Mass\ of\ diene\ [g] = \frac{Peak\ Area\ of\ diene * (mass\ of\ organic\ compounds\ [g])}{Total\ Area\ of\ peaks}}$$ **Equation 4. 2**

$$\boldsymbol{Conversion = \frac{Mass\ diene\ (t=0h) - Mass\ diene\ (t=3h,6d)}{Mass\ diene\ (t=0h)}}$$ **Equation 4. 3**

Table 4. 7. Conversion of dienes present in model mixture expressed as percentage. The results of both methods for the calculation are shown.

Peak	RT	Compound	Benzene as reference		Using mass of dienes	
#	(min)	Name	3 h	6 d	3 h	6 d
1	2.056	*trans*-1,3-pentadiene	14	59	23	72
2	2.23	cyclopentene	10	23	19	47
3	2.403	1,5-hexadiene	3	-1	13	30
4	2.911	1,3-hexadiene	3	85	13	90
5	3.412	benzene	0	0	10	31
6	8.096	1,3-cycloheptadiene	-4	-7	6	26
7	10.716	2,5-dimethyl-2,4-hexadiene	-7	-5	4	28

As can be seen in Figure 4.9, several products were seen after reactions. A peak number was assigned to the products, continuing the numeration previously used to identify the reagents. The selectivity shown is the ratio between the areas of the peaks representing a product and the total area of all the products, reagents and solvent were not included. The results for selectivity calculations are shown in Table 4.8.

Table 4. 8. Product selectivity in reactions with model mixture. Expressed as percentage.

Peak	RT (min)	Possible compound	3 hours	6 days
Peak 8	2.122	cis-1,3-pentadiene	7.4	2.5
Peak 9	3.305	2,4-hexadiene	3.2	14.4
Peak 10	3.532	2,4-hexadiene	4.3	10.2
Peak 11	3.746	2,4-hexadiene	1.5	1.7
Peak 12	4.214	Oxygenated	0.0	0.8
Peak 13	4.421	Oxygenated	0.0	1.3
Peak 14	5.938	Oxygenated	8.7	32.6
Heavy products	-	Not defined	74.9	36.3

3.2.3 Product identification

In Figure 4.9, after 3 hours of reaction a few new peaks appeared; one between *trans*-1,3-pentadiene and cyclopentene (peak 8), some others around 3.5 minutes (peaks 9, 10, 11) and one in 6 minutes (peak 14). Some heavy products were formed as can be seen in the Figure 4.10, a number was not assigned for those peaks and their structure could not be resolved using mass spectrometry. It is important to take into account that this was a dilute solution (low concentration of reagents) and the reaction was carried out at a relative low temperature which led to think that under those conditions the reaction rate was very slow and the system required more time to reach the maximum equilibrium conversion; as was mentioned in the introduction section, hydration is an equilibrium limited reaction. Therefore the same reaction product was pressurized and allowed to react during 6 days. In Figure 4.9 the chromatogram for that reaction time is also presented.

Table 4.7 shows that the conversion after 6 days increased considerably being *trans*-1,3-pentadiene and 1,3-hexadiene the reagents consumed in higher proportion. The same peaks that appeared in the 3 hours reaction are present after 6 days, with the addition of peaks 12 and 13. A zoom in of different sections in the chromatograms of the initial model mixture and after 6 days of reaction was done to obtain Figure 4.11; that, to have more clarity in the visualization of the peaks. Figure 4.10 shows that heavy products were also formed after 6 days reaction, but they increased significantly respect to the 3 hours reaction, although the selectivity to the formation of heavy molecules decreased (see Table 4.8).

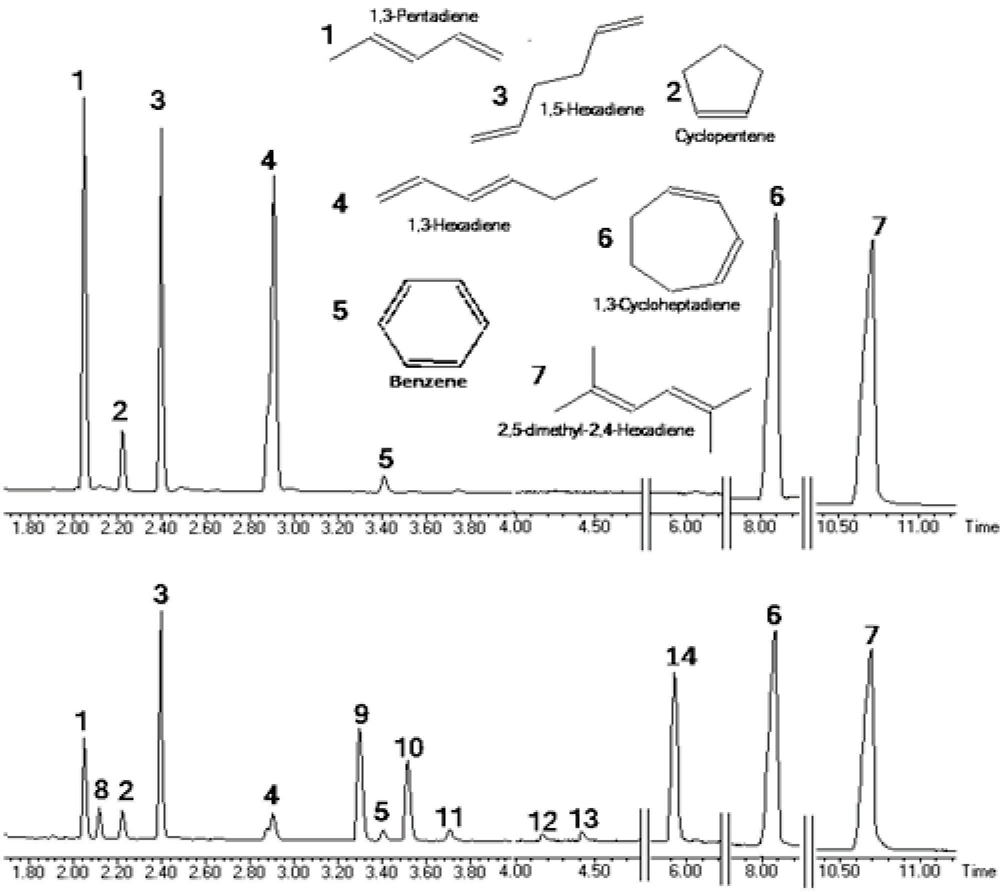


Figure 4.11. Comparison of dienes model mixture hydration for time zero and 6 days of reaction.

Using the electron mass spectra provided by the GC-MS, the new peaks identified after the hydration during 6 days could correspond to: (8) *cis*-1,3-pentadiene (9) *trans-trans*-2,4-hexadiene (10) *trans-cis*-2,4-hexadiene, (11) *cis-cis*-2,4-hexadiene, (12), (13) have not been identified, but the suggestions of the equipment showed oxygenated products, (14) 2,2,5,5-tetramethyl-tetrahydrofuran. Peak 8 is potentially the *cis* isomer of *trans*-1,3-pentadiene, because when that molecule was identified in the cracked naphtha sample a peak to the right corresponding to *cis*-1,3-pentadiene was also detected.

The compounds assigned to peaks 8, 9, 10 and 11, are based on the standards used in Chapter 3; 2,4-hexadiene was one of them and its stereoisomers had similar mass spectra and retention time to the reaction products represented by the peaks 9, 10 and 11. The mass spectra of peaks 9 and 10 and their corresponding compounds assigned are in Figure 4.12.

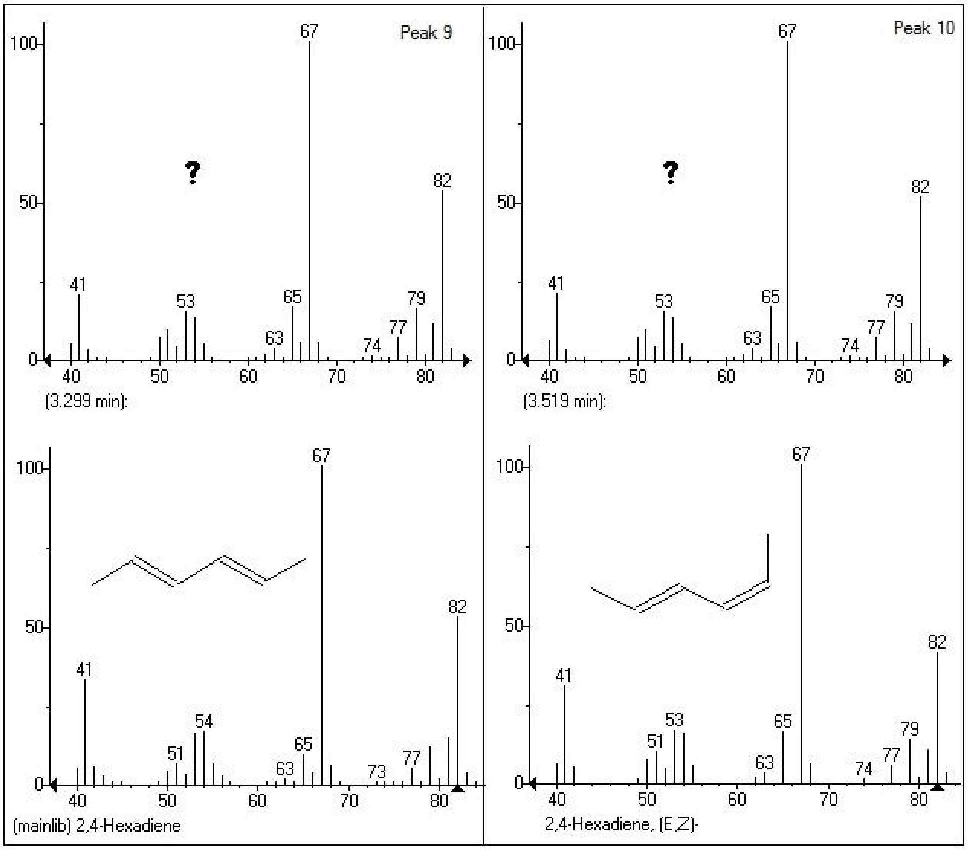


Figure 4. 12. Mass spectra comparison of peaks 9 and 10 and the compounds suggested by the library of GC-MS, *trans-trans*-2,4-hexadiene and *trans-cis*-2,4-hexadiene.

Regarding to peak 14, the retention time of the peak was 5.938 minutes and a peak seen in the reaction with 2,5-dimethyl-2,4-hexadiene alone (peak 8) had similar mass spectra and a retention time (6.008 minutes); the analysis for that peak showed that it was most likely 2,2,5,5-tetramethyl-tetrahydrofuran; the discussion about its formations will be provided later.

Heavy products cannot be identified with certainty, the diversity in the structures suggested by the library software of the GC-MS makes the process a difficult task. The molecular formula changed between suggestions as well as the organic function. As a general statement can be said that heavy products formed correspond to products modified by hydration (they could have oxygen in their structure) and addition products (the suspected structures have more carbons than the feed) or both. Some of the structures suggested for peaks of high retention times are shown in Figure 4.13.

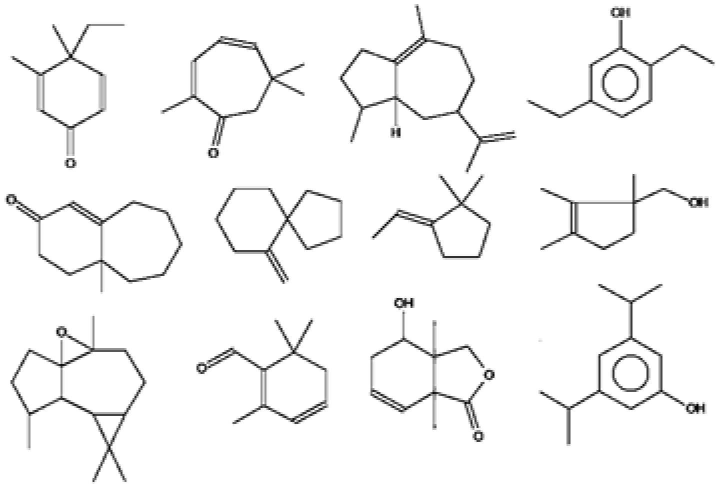


Figure 4. 13. Structures of some of the possible heavy products present after hydration of dienes model mixture (not all the suggested structures were shown).

4. Discussion

4.1 Experiments with 2,5-dimethyl-2,4-hexadiene

Regarding to the mass balance for hydration reactions of 2,5-dimethyl-2,4-hexadiene, Table 4.3 indicates that the amount of aqueous phase is always higher than the water weighed initially. During the separation of the phases, the aqueous-organic interphase remained in the aqueous phase, hence it is a fact that a portion of organic molecules formed are present in that phase. Besides that it is known that alcohols and organic acids with fewer than about five carbons dissolve in water, so if molecules with those organic functions and number of carbons were formed, they could be present in the aqueous phase. However, an experimental technique was not developed to analyze the organic compounds dissolved in water to corroborate that statement.

The mass of outlet gas is greater than the nitrogen fed to pressurize, which is an indication of other gases formed during the reaction. That could be explained by cracking of the diene, which is very likely given the presence of smaller molecules than 2,5-dimethyl-2,4-hexadiene (group 1). Some of the compounds forming part of the group 1 were ethylene and butene (peaks 1 and 2 in Figure

4.3 respectively). The presence of those small molecules in the liquid product allows to say that at least those two molecules were present in the outlet gas, due to vapor-liquid equilibrium. Besides, it is likely that a vapor-liquid-liquid-equilibrium was also present during the reaction. The final products were in three different phases, organic, aqueous and vapor phases; having the feed diolefin, the olefins and oxygenates produced and the remaining water. It would have been worth it to analyze the aqueous and gas product to verify the presence of acid cracking products or oxygenates with small carbon number than the feed diolefin.

SPA and sulfuric acids generate more gases than siral-5 and H-ZSM-5 on accordance with the higher selectivity of those catalyst towards the formation of group 1 products. Although in general all catalyst showed a tendency to form lighter compounds; the product selectivity of group 1 is the highest for all catalyst compared to the other two groups. Selectivity for products in group 2 was high in the case of the alumino-silicate followed by the zeolite, the SPA and the sulfuric acid. Without any doubt SPA was the catalyst that promoted the addition reactions the most (selectivity of ~40% towards group 3 products), followed by siral-5, H-ZSM-5 and sulfuric acid.

Based on the reaction products obtained with the four catalysts used for the hydration of 2,5-dimethyl-2,4-hexadiene, at first seems like the diol reaction product expected was not formed. The reaction showed a complex chemistry; several side reactions were taking place and products different to alcohols were formed. That is not a bad outcome, it is a normal result of a chemical process and provided interesting information for the treatment of diolefins.

The discussion regarding the products formed will be done by the group division done previously. The main products formed during reaction with SPA correspond to peaks 4, 8, 10, 13, 18 and 22 in Figure 4.3; those are common peaks to the other catalyst. To support the discussion, the individual selectivity towards those products is provided in Table 4.9 for each catalyst.

Table 4. 9. Individual selectivity of peaks 4, 8, 10, 13, 18 and 22. Expressed as percentage.

Peak	SPA	Sulfuric acid	Siral-5	H-ZSM-5
4	9	1	2	1
8	17	80	0	3
10	5	3	0	40
13	11	1	27	10
18	3	1	2	15
22	8	3	14	6

Goup 1. According to Table 4.5 most of the peaks in group 1 have a carbon number lower than the feed diolefin; it is said most because peaks 9 and 10 have the same molecular formula of the feed. Peaks 1 and 2 are alkenes of short chain (2 and 4 carbons respectively) that could only be present after cracking of the initial molecule; they were formed only when SPA and sulfuric acid were the catalyst. That leads to the thinking that acid catalytic cracking at mild conditions took place. Literature reports the catalytic cracking of olefins under mild conditions in presence of a solid acidic catalyst.[9] Research and applications of this type of process is extensive, fluid catalytic cracking is one example of the use of acid catalysts to break down molecules into small alkenes.[10]

Peak 3 is an alcohol, possibly of 4 carbon atoms; maybe after the short alkene was formed, the hydration did take place. That was a product seen only with the SPA. Peak 4 and 5 are aldehydes, which means that a primary alcohol underwent further oxidation; the individual selectivity to peak 4 was of 9, 1, 2 and 1% for SPA, sulfuric acid, siral-5 and H-ZSM-5 respectively, meaning that the production of that aldehyde prevailed in SPA. It is known that when a primary alcohol is oxidized, an aldehyde is obtained and if the alcohol is secondary the oxidation product is a ketone.[2] Therefore the formation of primary alcohols of short chain is verified based on the existence of a more oxidized species such as the aldehydes and the presence of peak 3 in SPA reaction.

According to the library of the GC-MS, peak 6 is a diene with two carbons less than the initial molecule. The product was only seen for SPA and could be the product of two groups methyl separated from the 2,5-dimethyl-2,4-hexadiene. That diene could have different characteristics (*cis* or *trans* conformation, conjugated or isolated) that cannot be defined just by using GC-MS. Regarding to peak 7, it is an isomer of peak 3, is an alcohol as well. Using the molecular formula suggested, those alcohols could be n-butanol, sec-butanol, isobutanol and tert-butanol. Thinking about the formation of the alcohol as the hydration of an alkene, the fact that isomers of the same alcohol are present can be interpreted as the presence of different isomers of the alkene as a consequence of some skeletal isomerization that could have been taking place.

Peak 8 is a very important reaction product because it was the major product in the case of SPA and sulfuric acid and it was found as well in the hydration of the model mixture. The individual selectivity towards that peak was 17 and 80% for SPA and sulfuric acid respectively.

Group 2. Peaks 9 and 10 have the same molecular formula of the diene fed in the reaction, but the structures suggested by the GC-MS have the unsaturation and branches in different carbons (some suggestions were 2,3-dimethyl-1,4-hexadiene and 5,5-dimethyl-1,3-hexadiene). That was taken as an indication of a double bond isomerization and skeletal rearrangement taking place. All the catalyst except for SIRAL-5 showed the formation of the isomers, more in the case of peak 10 for which the selectivity with SPA, sulfuric acid and H-SZM-5 was 5, 2.6 and 40%. That is showing that double bond isomerization and skeletal rearrangement were mainly favored when H-SZM-5 was used.

Peak 11 is a carboxylic acid that could have been formed by the oxidation of an aldehyde of 4 carbon atoms (peaks 4 and 5); the catalyst with more tendency to form peak 11 was SPA followed by sulfuric acid. Peak 12 corresponds to an alcohol of shorter chain than the feed diolefin (has 7 carbons), maybe after the removal of a methyl group from the 2,5-dimethyl-2,4-hexadiene the addition of the water molecule was effected. All catalyst gave the formation of that product, being SPA the one that formed it in higher proportion. Peak 13 is an ester with individual selectivity among the group selectivity of 11, 0.8, 27 and 9.6% using SPA, sulfuric acid, siral-5 and H-ZSM-5 respectively. The possible chemical route for its formation is the addition of an alcohol to a carboxylic acid, as seen from previous discussion, both functionalities were found in the media and the conditions for such addition were favored (acid catalysis), that is the so called Fischer esterification.[2]

Peak 14 is the branched diolefin used, that is still the main component after reaction which shows that the conversion of the process was low; it is worth to highlight that when the catalyst was sulfuric acid that condition improved. According to Table 4.4 the highest conversion obtained for the hydration was achieved using sulfuric with ~10%; in a decreasing order the conversion the other catalyst got was 6.5, 4.2 and 1.8% for SPA, H-ZSM-5 and siral-5 respectively. Probably a change in the reaction conditions needs to be evaluated, but is also important to have in mind that hydration is an equilibrium limited reaction. Possibly the equilibrium conversion was reached and removing the product is necessary to shift the equilibrium towards the product.

Peak 15 is a ketone with the same number of carbons of the diene, which is understood as the further reaction of a secondary alcohol which is another indication of an alcohol formation. For compounds with retention times longer than peak 15, all the functionalities are the same as those already described (alcohols, aldehydes, ketones, esters) and some possible chemical paths that could have originated them have already been mentioned.

Group 3. Most of the peaks in this group have not been identified. Even though the peaks seen are numerous, defining a molecular formula or organic function was not possible, the library software of the GC-MS gave different suggestions where those two factors varied from one to another. From the analysis of the mass spectra can be said that the carbon number is more than C_{12} which is suggesting some addition reactions. Only 2 peaks have been characterized, peak 21 and 22 that are a ketone and an alcohol respectively. Peak 22 is one of the most abundant for all catalysts with a selectivity of 8, 3, 14 and 6% for SPA, sulfuric acid, siral-5 and H-ZSM-5 respectively. Using Table 4.4 can be seen that SPA was the catalyst with the highest tendency to form heavy products, but siral-5 showed the highest individual selectivity towards that alcohol of higher carbon number than the feed.

A great number of chemical reactions took place and as a general observation, the incorporation of oxygenate functionality was the major reaction; the extent of the reaction could give one or another product and the interaction of those products in the acid media a new one. The fact that those products were formed to a different extent with each catalyst is showing the importance of the acidity of the catalyst. There were three solid catalysts and with them not only the total acidity but the type of acid sites has to be taken into account; different reactions can be promoted in different sites (i.e. isomerization over hydration or cracking over hydration). Although that is a really important part of the reaction it is out of the scope of this work to get into that discussion because the goal here was to define if a change in the organic function of diolefins could be done. Research on catalyst development needs to be done if this route should be taken. Besides experiments to determine the acidity of the solid catalysts were not carried out.

The following is an explanation for the formation of peak 8. If primary alcohols are in a strong inorganic acid medium (H_2SO_4) the hydroxyl group of the alcohol is protonated forming water as a leaving group.[2] Other alcohol molecule present that has not been protonated yet is a strong nucleophile. Once the protonation of the first molecule of alcohol occurs a nucleophilic attack begins ending with the condensation products, ether and water. That is a common route for the synthesis of ethers from alcohols using mineral acids.[2] When the two hydroxyl groups are within the structure of two separate molecules the corresponding ether is forming an open chain, but if those hydroxyl groups are in the same alcohol (diol) the ether will be the product of a dehydration and subsequent intramolecular cyclization. Such is the case of the tetrahydrofuran formation from the direct catalyzed dehydration of 1,4-butanediol where the cyclic ether is achieved in the presence of an acid catalyst at temperatures above 100 °C and near atmospheric pressure. [11]

But the synthesis of cyclic ethers is not restricted to alcohols, a reaction known as the Paal–Knorr furan synthesis is one of the oldest and most widely used methods for the construction of 2,5-disubstituted furans and uses ketones as departing molecules.[12] Having said that and taking into account that the cyclic ether 2,2,5,5-tetramethyl-tetrafurane, was a major product in the reactions carried with SPA and sulfuric acid, a reaction mechanism is proposed for the formation of the ether. The network reaction parts from the assumption that the diol expected was indeed formed but could not be seen in the chromatograms because it reacted further by cyclization. The mechanism is illustrated in Figure 4.13.

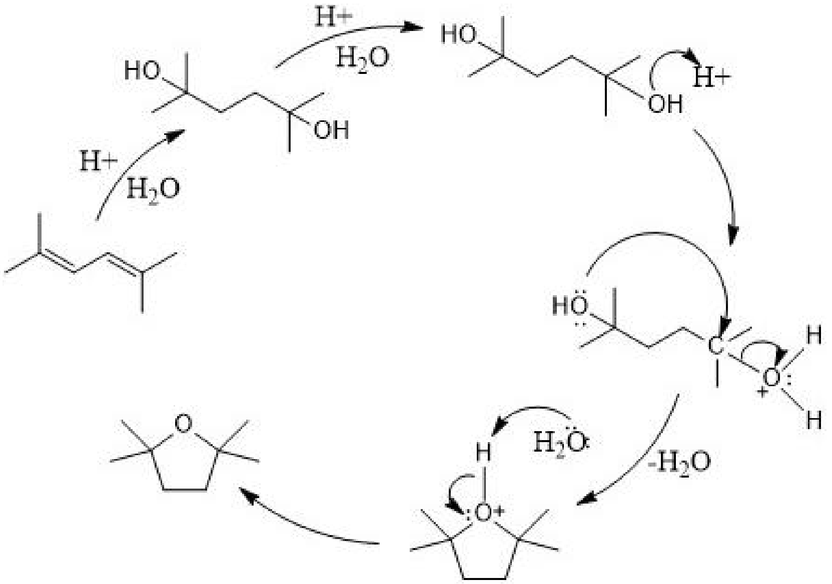


Figure 4.14. Reaction mechanism proposed for the formation of 2,2,5,5-tetramethyl-tetrafurane from 2,5-dimethyl-2,5-hexanediol.

4.2 Experiments with mixture of dienes

In the mass balance for the hydration of the model mixture during 3 hours can be seen that the amount of aqueous phase is higher than the water initially added by 0.0003g; some of the organic molecules could have migrated into the aqueous phase. The amount of organic phase is also lower respect to the organic compounds (dienes plus decane) with 1.6288 compared to 1.6460g. Based on the mass balance, around 0.0142g of the reagents loaded left the system as gas with the nitrogen. The results of the mass balance after 6 days of reaction gave an aqueous phase heavier than the initial by 0.0335g; compared to the 3 hours reaction can be seen much more organic compounds migrated to the aqueous phase. Something curious is the fact that a similar amount of liquid reagents (0.0130g) left the system as gases in that second reaction (6 days). For both mass balances is important to have in mind that as in the hydration of 2,5-dimethyl-2,4-hexadiene, in the separation of the phases, the aqueous-organic interphase remained in the aqueous phase.

The conversion for each compound varied significantly between the 3 hours and 6 days reaction (see Table 4.7). For *trans*-1,3-pentadiene (peak 1), had a conversion of 23 and 72% for 3 hours and 6 days respectively; rotational isomerization to give the *cis* conformation of the linear conjugated diolefin was verified by the formation of peak 8. Products with five carbons, different to *cis*-1,3-pentadiene (peak 8) were not detected. If the pentadiene was hydrated, alcohols with 5 carbons would have been formed; taking into account that alcohols of that number of carbons are soluble in water, they could have migrated to the aqueous phase. Also, it is likely that production of gases because of cracking was present, as speculated for 2,5-dimethyl-2,4-hexadiene, but the compounds were not dissolved in the liquid phase. Those could be the reasons why more products coming from the reaction of *trans*-1,3-pentadiene were not seen in the chromatogram.

After reacting for 3 hours and 6 days, the observed conversion for the 1,5-hexadiene (peak 3) was 13 and 30%, respectively; whereas, 1,3-hexadiene (peak 4) was converted 13 and 90%. This two compounds could have taken part in the formation of 2,4-hexadiene stereoisomers (peaks 9,10 and 11) although based on the conversion of 1,3-hexadiene it could be said that that compound was the main contributor in the production of 2,4-hexadiene. The presence of 2,4-hexadiene (isomer of bot, peak 3 and 4) indicates the double bond isomerization of the isolated and conjugated dienes. As was mentioned earlier in the discussion, acid catalysts promote the double bond isomerization of alkenes. In the acid catalyzed isomerization of linear unsaturated hydrocarbons, the product goes from the thermodynamically less stable alkene to a more stable one, through the formation of carbocations.[13] 1,5 hexadiene is less stable than 1,3-hexadiene or 2,4-hexadiene due to the resonance structure of the conjugated diolefins. So the hypothesis is that some of the 1,5-hexadiene was isomerized to 2,4-hexadiene, by changing the terminal double bonds to an internal position (1,5 to 2,4). However, even though 1,3-hexadiene is less stable than 2,4-hexadiene, because one of its carbons with double bond is a terminal carbon, it is easier to do the double bond shift with that molecule than with 1,5-hexadiene, because more stable carbocations will be formed. That could explain the higher conversion of 1,3-hexadiene respect to its 1,5 counterpart.

In the case of the cyclic diolefin, 1,3-cycloheptadiene (peak 6), the conversion reached was 6 and 26% during 3 hours and 6 days of reaction respectively. Products containing molecules with 7 carbons in their structure were not identified by GC-MS. Based on the conversion calculated in Table 4.7, it is evident that the impurities, cyclopentene and benzene had some interaction as well; they could have reacted or migrated to the vapor phase, reason why they showed a conversion. That is important because some of the structures suggested to represent the heavy products formed

(Figure 4.13) contain rings of 5, 6 and 7 carbon atoms; so one hypothesis to explain the change of the diolefin is the addition to molecules like cyclopentene and benzene to form bigger compounds.

2,5-dimethyl-2,4-hexadiene (peak 7) has a conversion similar to 1,3-cycloheptadiene for both reactions; those two molecules showed the lowest reactivity during reaction. The conversion value for 3 hours and 6 days was 4 and 28% respectively. One of the products of reaction (peak 14) could be 2,2,5,5-tetramethyltetrahydrofuran; making use of the discussion for the hydration of 2,5-dimethyl-2,4-hexadiene alone, it is speculated that 2,5-dimethyl-2,4-hexadiene reacted to form the cyclic ether. That is the only oxygenated compound that could be identified using the GC-MS. Peaks 12 and 13 correspond to oxygenated species with carbon number between 5 and 7, some suggestions are alcohols and others are cyclic ethers, nevertheless their structure, organic function and carbon number is not entirely known.

There is evidence about a change in the organic function of compounds treated (diolefins), however all those changes did not correspond entirely to modifications due to hydration of the molecules. The formation of oxygenates was seen, but addition, double bond shift, *cis-trans*-isomerization reactions were also present; the cracking of the molecules cannot be disregarded, it was seen during the hydration of 2,5-dimethyl-2,4-hexadiene and it could have been present with the model mixture as well. Using the information of Table 4.8 one can say that despite the reaction time, the selectivity was oriented towards the formation of heavy products. In the 6 days reaction the formation of oxygenates (peaks 12, 13 and 14), the double bond isomerization and the rotational isomerization were preferred in the order of more to less favor reactions. For the reaction time of 3 hours, the isomerization was preferred over formation of oxygenated compounds and *cis-trans* isomerization. The formation of alcohols as final product was not evident by chromatography, but based on the presence of peak 14 it could have been inferred, however dienes different to 2,5-dimethyl-2,4-hexadiene did not show any change, product of hydration unless some of the products suffered addition reactions and ended being part of the heavy products fraction.

5. Conclusions

An alternative route to hydrogenation of diolefins was proposed to change the nature of those molecules in a thermally cracked naphtha sample. The real sample was not used, but the feasibility of the reaction was facilitated by model compounds and model mixtures. The use of hydration with an acid catalyst as a possible way of treatment was proposed. After experimental work in the laboratory, the following are the main findings of this job:

1. The chemistry of the process proved to be complex. A great number of chemical reactions different to hydration took place, most of the products formed are oxygenated species, but acid cracking, double bond shift and *cis-trans* isomerization reactions were also present.
2. The reaction conditions favored the production of oxygenated molecules with a different degree of oxidation i.e. alcohols, aldehydes, ketones, esters, cyclic ethers.
3. The oxygenated products could have a lower, same or higher amount of carbons in their structure, compared to the initial feed diolefin when the reaction was done using only 2,5-dimethyl-2,4-hexadiene.
4. In the case of 2,5-dimethyl-2,4-hexadiene experiments, primary and secondary alcohols of a shorter chain or with the same amount of carbons respect to the feed diolefin were formed, this is concluded based on the presence of aldehydes and ketones respectively.
5. According to the formation of the reaction product 2,2,5,5-tetramethyl-tetrahydrofuran, the previous hydration of the branched diene, 2,5-dimethyl-2,4-hexadiene to obtain a diol, must have taking place.
6. SPA and sulfuric acid catalyst promoted the formation of cracking products in the 2,5-dimethyl-2,4-hexadiene hydration.
7. Double bond shift and skeletal rearrangement were mainly favored when H-SZM-5 was used in the 2,5-dimethyl-2,4-hexadiene hydration.
8. The model mixture reaction showed that lineal conjugated diolefins have a tendency to double bond shift and *cis-trans* isomerization.
9. The conjugated cyclic diolefin did not show reactivity towards the formation of alcohols, but is speculated that it underwent addition reactions.

10. Their products have not been identified with certainty but the diolefins with higher reactivity according to the conversion were the lineal conjugated diolefins (*trans*-1,3-pentadiene and 1,3-hexadiene).
11. Based on the conversion results of the model mixture, the dienes with the lowest reactivity during the hydration were 1,3-cycloheptadiene and 2,5-dimethyl-2,4-hexadiene.
12. Branched diolefins undergo hydration and further cyclization to give ethers under acid reaction conditions.
13. The reaction can be considered to show a positive result, because a change in the feed's nature was seen, forming products that were not olefinic, however the most pone to that transformation are the branched diolefins.

References

(1) Froment, G. F.; Bernard, D.; Grange, P. *Hydrotreatment and hydrocracking of oil fractions*; Elsevier, Ed.; Amsterdam, 1997.

(2) Vollhardt, P.; Schore, N. *Organic Chemistry: Structure and Function*; W.H. Freeman: New York, 2007.

(3) Richard, K. Process improvements in the direct hydration of olefins to alcohols. *Digital refining, processing, operations and maintenance*. May 2014.

(4) Minachev, K.; Mortikov, Y. Hydration of Olefins on Zeolite Catalysts. *Pet. Chem. U.S.S.R.* **1976**, *16* (4), 216–223.

(5) Ehwald, H.; Fiebig, W.; Lischke, G.; Parlitz, B.; Reich, P. High pressure catalytic hydration of olefins over various proton-exchanged zeolites. *Appl. Catal.* **1987**, *34*, 275–287.

(6) Jense, J.; Uaprasert, V.; Fujii, C. Acid-Catalyzed hydration of dienes. 2. Changes in activity coefficient ratios, enthalpy and entropy as a function of sulfuric acid concentration. *J. Org. Chem.* **1976**, *41* (10), 1675–1680.

(7) Stunnenberg, F.; Niele, F. G. M.; Drent, E. Hydration of conjugated dienes to produce ketones catalyzed by ruthenium complexes. *Inorganica Chim. Acta* **1994**, *222* (1-2), 225–233.

(8) Yuhan, X. Acid Catalyzed Aromatic Alkylation in the Presence of Nitrogen Bases MSc thesis, University of Alberta, Edmonton, AB, Canada, 2012.

(9) Kissin, Y. V. Chemical Mechanism of Hydrocarbon Cracking over Solid Acidic Catalysts. *J. Catal.* **1996**, *163* (1), 50–62.

(10) Hengstebeck, R. J. *Petroleum Processing, Principles and Applications*; McGraw-Hill: New York, 1959.

(11) Hunter, Shawn E. ; Ehrenberger, Carolyn E. ; Savage, P. E. Kinetics and Mechanism of Tetrahydrofuran Synthesis via 1,4-butanediol dehydration in high temperature water. *J.*

Org. Chem. **2006**, *71* (3), 6229–6239.

(12) Undeela, S.; Ramchandra, J. P.; Menon, R. S. A sequential synthesis of substituted furans from aryl alkynes and ketones involving a cerium (IV) ammonium nitrate (CAN) -mediated oxidative cyclization. *Tetrahedron Lett.* **2014**, *55* (41), 5667–5670.

(13) Hubert, A. J.; Reimlinger, H. The Isomerization of Olefins Part II. Thermal and Catalytic lsomerization of Olefins using Acids, Metals, Metal Complexes, or Boron Compounds as Catalysts. *Synthesis*. 1970, pp 405–430.

CHAPTER 5 –DIELS-ALDER CYCLOADDITION AS POTENTIAL TREATMENT OF DIOLEFINS

Abstract

A mitigation strategy for conjugated diolefins based on the Diels-Alder cycloaddition was studied. The reaction of 2,3-dimethyl-1,3-butadiene, *trans*-1,3-pentadiene, 1,3-hexadiene, 3-methyl-1,3-pentadiene, 1,3-cycloheptadiene, 2,4-hexadiene and 2,5-dimethyl-2,4-hexadiene with compounds having different electron withdrawing groups (dienophile) has been investigated in the liquid phase at 60°C without catalyst and using a Lewis acid as catalyst, i.e. $AlCl_3$. Two compounds were selected as dienophiles 3-buten-2-ol and methyl vinyl ketone (MVK). The inclusion of the catalyst proved to have a positive effect in the cycloaddition, making it possible to obtain a cyclohexene derivative at the working temperature. Acyclic dienes such as 2,4-hexadiene, 2,3-dimethyl-1,3-butadiene, 1,3-hexadiene, 3-methyl-1,3-pentadiene and 2,5-dimethyl-2,4-hexadiene reacted all to a different extent under the working conditions. The conjugated cyclodiene exhibited a poor reactivity even though is a diene permanently in the *s-cis* conformation required to undergo the Diels-Alder reaction. As expected the strategy proposed proved to change the nature of the diolefins at low temperatures to form a substituted cyclohexene ring.

Keywords: Diels-Alder cycloaddition, low temperature, conjugated diolefins

1. Introduction

As was mentioned in the previous chapters, the treatment of diolefins present in a stream coming from a thermal cracking process is imperative to avoid gum formation in pipelines and refining equipment. The common treatment to decrease the content of polyunsaturated compounds is hydrogenation at low temperatures using a hydrodesulfurization catalyst.[1] Looking for an alternative treatment, a typical reaction of alkenes, such as electrophilic addition, i.e. Hydration, was studied in Chapter 4. It showed that decreasing the content of dienes is possible by treating them with water.

The identification of diolefins in thermally cracked naphtha done in Chapter 3 gave as result that conjugated diolefins are present in greater proportion respect to isolated or cumulated diolefins. That kind of compounds are known to be the most reactive of all the diolefins,[2] so treating only the most reactive species could be another option. Having that in mind, another route explored is shown in this chapter with the particularity that is a reaction undergone specifically by conjugated diolefins. It is a special case of cycloaddition reactions that give cycloadducts when pi systems react.[3] This strategy is based in the well-known Diels-Alder cycloaddition, were a conjugated diolefin reacts with a dienophile or electron withdrawing group to give a cyclohexene derivative as product.

The only application that this reaction has related to petroleum stocks is the determination of the diene value by maleic anhydride addition, better known as UOP-326 method. That method helps to identify the amount of conjugated species in mixtures of hydrocarbons while making them react with a known amount of maleic anhydride. By titrating the anhydride remaining after reaction the amount of diolefins present can be calculated.[4] That reaction was used in Chapter 3 to define if potential diolefins, previously identified could have a conjugated nature. The industrial applications of the Diels-Alder reaction are more related with the synthesis of organic compounds used in areas such as pharmaceutical, agrochemical, flavors and fragances.[5]

In this section several acyclic and cyclic conjugated diolefins reacted with different dienophiles at low temperature. The experimental procedure used is similar to that presented in Chapter 3 for the identification of conjugated species, but instead of using maleic anhydride, smaller molecules were selected. The steps followed during the experiments were:

a) Reaction of *trans*-1,3-pentadiene in decane with 3-buten-2-ol and methyl vinyl ketone.
b) Reaction of a mixture of isomers of 2,4-hexadiene in toluene with 3-buten-2-ol and MVK with $AlCl_3$.
c) Reaction of *tran*s-1,3-pentadiene in decane with MVK with $AlCl_3$.
d) Reaction of a mixture of diolefins in decane with MVK and $AlCl_3$.

2. Experimental

2.1 Materials

Table 5. 1. **Materials description.**

Compound	**Formula**	**CASRN** [a]	**Mass fraction purity** [b]	**Supplier**
Materials for reactions and model compounds identification				
Toluene	C_7H_8	108-88-3	99%	Fisher Scientific
Decane	$C_{10}H_{22}$	124-18-5	≥99%	Sigma Aldrich
2,3-dimethyl-1,3-butadiene	C_6H_{10}	513-81-5	≥99.5	Sigma Aldrich
trans-1,3-Pentadiene	C_5H_8	2004-70-8	90%	Sigma Aldrich
1,3-Hexadiene (mixture of isomers)	C_6H_{10}	592-48-3	95%	Sigma Aldrich
3-methyl-1,3-pentadiene (mixture of *cis* and *trans*)	C_6H_{10}	4549-74-0	98%	Sigma Aldrich
1,3-Cycloheptadiene	C_7H_{10}	4054-38-0	95%	Sigma Aldrich
2,4-hexadiene (mixture of isomers)	C_6H_{10}	592-46-1	90% [d]	Sigma Aldrich
2,5-Dimethyl-2,4-hexadiene	C_8H_{14}	764-13-6	96%	Sigma Aldrich
3-buten-2-ol	C_4H_8O	598-32-3	≥97%	Sigma Aldrich
Methyl vinyl ketone	C_4H_6O	78-94-4	99%	Sigma Aldrich
Catalyst				
Aluminium trichloride anhydrous, powder	$AlCl_3$	7446-70-0	99.99%	Sigma Aldrich
Cylinder gases				
Helium	He	7440-59-7	0.999995 [c]	Praxair

[a] CASRN = Chemical Abstracts Services Registry Number

[b] This is the purity of the material guaranteed by the supplier; material was not further purified.

[c] Mole fraction purity.

2.2 Equipment and procedure

The Diels Alder reaction was carried out in a 25 ml Erlenmeyer, connected to a condenser operating at total reflux. To 10 ml of solvent (decane or Toluene) 100µl of diene were added to form the reacting solution. The additions were done on a volume basis, because the procedure was easier; most of the compounds are toxic and working all the time inside the fume hood was safer. In the cases the catalyst was used, an amount corresponding to 15% of the mass of diene present was added. The molar ratio diene to dienophile was 1:1. The solution was under constant stirring (1000rpm) and the flask was immersed in an oil bath supported on a hot plate; temperature in the bath was kept at 60°C. The content of the Erlenmeyer was refluxed for three hours and then allowed to cool down. After finishing the procedure, a sample of the reacted mixture was taken, filtered through a syringe filter of 0.22 µm and analyzed with the GC-MS.

Several diolefins where identified in the characterization of the naphtha sample, as shown in the results section of chapter 3. Conjugated diolefins with different structures are present in the cracked naphtha, for this reason an experiment was also performed using a mixture of diolefins. The diolefins were dissolved in decane to do the cycloaddition in presence of MVK that showed better results compared to the alcohol and $AlCl_3$. The dienes present in the solution were 5 in total, the idea was to include conjugated diolefins with and without branching with an open chain or in a cyclic configuration; the following were the compounds used; 2,3-dimethyl-1,3-butadiene, 1,3-hexadiene, 3-methyl-1,3-pentadiene (mixture of *cis* and *trans*), 1,3-cycloheptadiene and 2,5-dimethyl-2,4-hexadiene. The same volume (100µl) of diolefin added in the individual experiments was used in the mixture. The catalyst was 10 or 15% of the total mass of diene in the mixture and the amount of dienophile added was equal to the sum of all the moles of diene present in the mixture, that having in mind that the molar ratio diene to dienophile was 1:1. The details of the volumes and corresponding amounts of diolefins used in the cycloaddition of the mixture are in Table 5.2.

Table 5. 2. Compounds forming the dienes mixture for cycloaddition with MVK.

Diene	Volume (ml)	Density (g/ml)	Mass (g)	MW (g/mol)	Moles
Decane (Solvent)	10.00	0.73	7.30	142.29	5.13E-02
2,3-dimethyl-1,3-butadiene	0.10	0.73	0.07	82.14	8.84E-04
1,3-hexadiene	0.10	0.71	0.07	82.14	8.69E-04
3-methyl-1,3-pentadiene	0.10	0.73	0.07	82.14	8.89E-04
1,3 cycloheptadiene	0.10	0.87	0.09	94.16	9.24E-04
2,4-dimethyl-2,4-hexadiene	0.10	0.77	0.08	112.21	6.86E-04
MVK	0.35	0.84	0.30	70.00	4.25E-03

2.3 Analyses

The GC-MS has been used as the main analysis tool to identify the reaction products. The same conditions presented in section 2.3 of Chapter 3 were used in the present work, if further detail about the chromatographic technique is needed please go the mentioned section.

3. Results

3.1 Reaction of *trans*-1,3-pentadiene in decane with 3-buten-2-ol and MVK.

In the methodology developed for the characterization of diolefins (chapter 3), it was found that *trans*-1,3-pentadiene is present in the thermally cracked naphtha sample. That molecule was used as starting material to check the feasibility of the use of Diels-Alder cycloaddition as treatment of conjugated diolefins. The UOP-326 method for determination of diolefins usually uses maleic anhydride, but the use of smaller molecules acting as dienophiles was preferred to avoid the formation of big molecules that could be harder to identify by the GC-MS. Hence, MVK and 3-buten-2-ol were chosen as dienophiles.

Analyses of the feed and products after 3 hours of reaction are shown in Figure 5.1. The decane is not shown in the figure for practical reasons (peaks corresponding to reaction product were not seen in that area either). Except for an impurity from the solvent (tridecane) seen around 28 minutes, other peaks corresponding to cyclohexene derivatives (expected products) are not seen at longer retention times. Although an obvious change in the diene was not detected, that is not enough to assure that the diene did not react.

The concentration of compounds *trans*-1,3-pentadiene y cyclopentene in Figure 5.1 relative to each other is shown as the area of the peaks in Table 5.3. Comparing the values of the ratio of 1 to 2 before and after reaction for both dienophiles, it is evident that the amount of *trans*-1,3-pentadiene decreased. Maybe the product from the reactions might not be soluble in the reaction medium and is therefore not seen. It could have been precipitated, but the amount of product formed was small and it was not detected in the final solution. During the identification of trans-

1,3-pentadiene in cracked naphtha (Chapter 3) using maleic anhydride as dienophile, a product was not identified, the reactivity of the conjugated diolefin was verified by the decrease of the diolefin.

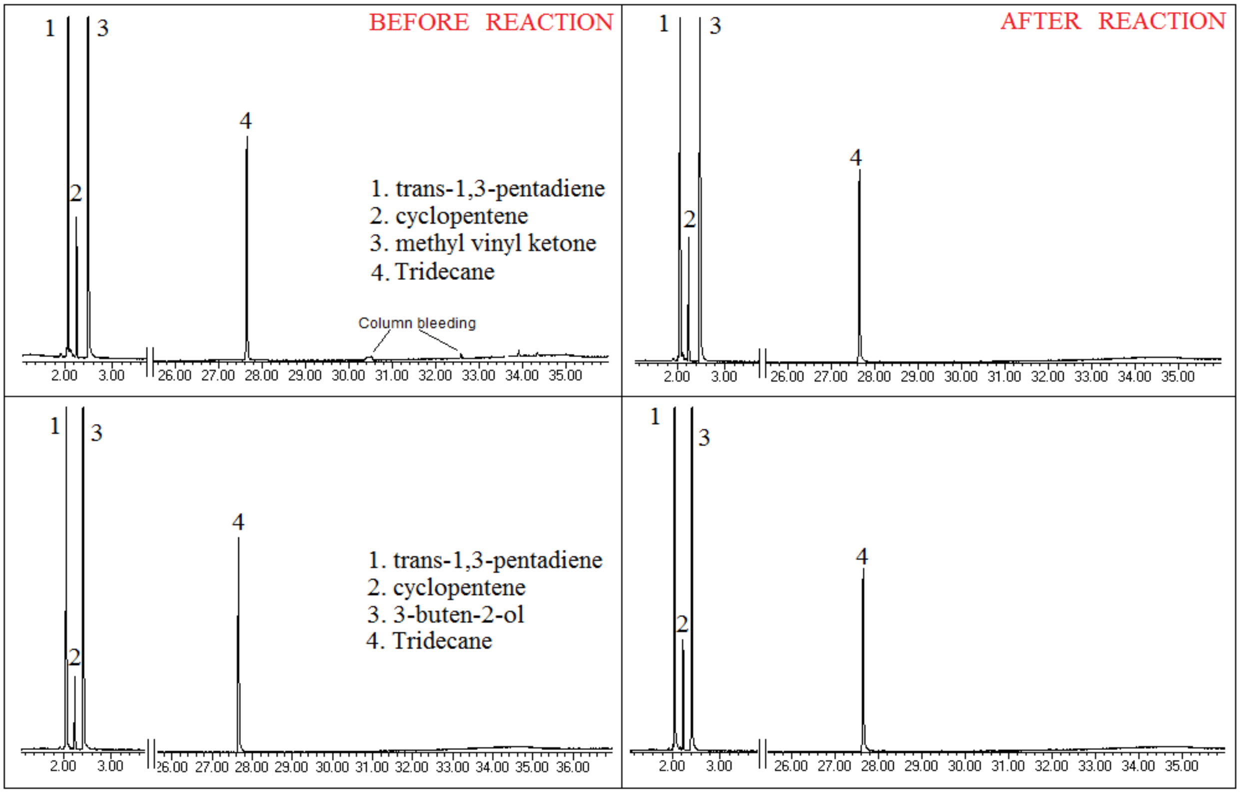


Figure 5. 1. Reaction of *trans*-1,3-pentadiene in decane with MVK and 3-buten-2-ol. No catalyst used.

Table 5. 3. Area of the peaks before and after reaction of *trans*-1,3-pentadiene in decane with MVK and 3-buten-2-ol. No catalyst used.

	Peak	RT (min)	Compound	Before	After
Methyl vinyl ketone	1	2.076	*trans*-1,3-Pentadiene	8.1E+07	7.2E+07
	2	2.256	Cyclopentene	1.2E+06	1.1E+06
	3	2.423	MVK	7.2E+07	5.9E+07
			Ratio 1 to 2	68.3	66.0
3-buten-2-ol	1	2.076	*trans*-1,3-pentadiene	7.1E+07	6.9E+07
	2	2.256	Cyclopentene	1.0E+06	1.0E+06
	3	2.343	3-Buten-2-ol	4.3E+07	4.2E+07
			Ratio 1 to 2	69.3	69.0

3.2 Reaction of 2,4-hexadiene in toluene with 3-buten-2-ol and MVK with AlCl$_3$.

Based on the results for *trans*-1,3-pentadiene, two things could have been done to improve the performance of the reaction. The first one was to increase the temperature and the second was to include a catalyst; the literature reports an accelerating effect of the Diels-Alder reaction when a Lewis acid is present in the media.[6] The addition of the catalyst was preferred, therefore Aluminum trichloride was incorporated to the reaction, to see if it could promote the cycloaddition. The experiment including catalyst were done with a different solvent and diene, that was simply because decane and *trans* -1,3-pentadiene were not available at the moment. A mixture of 2,4-hexadiene stereoisomers reacted in Toluene with MVK and 3-buten-2-ol.

3.2.1 Experiments using MVK as dienophile

Figure 5.2 shows the results of the experiment. A peak number was assigned to the peaks representing the reagents (peaks 1 to 4) and the numeration continued for the products (peaks 5 and 6). The right part of Figure 5.2 is showing the reaction products, it is evident that peaks 1 and 2, which correspond to MVK and *E*,*E*-2,4-hexadiene reacted.

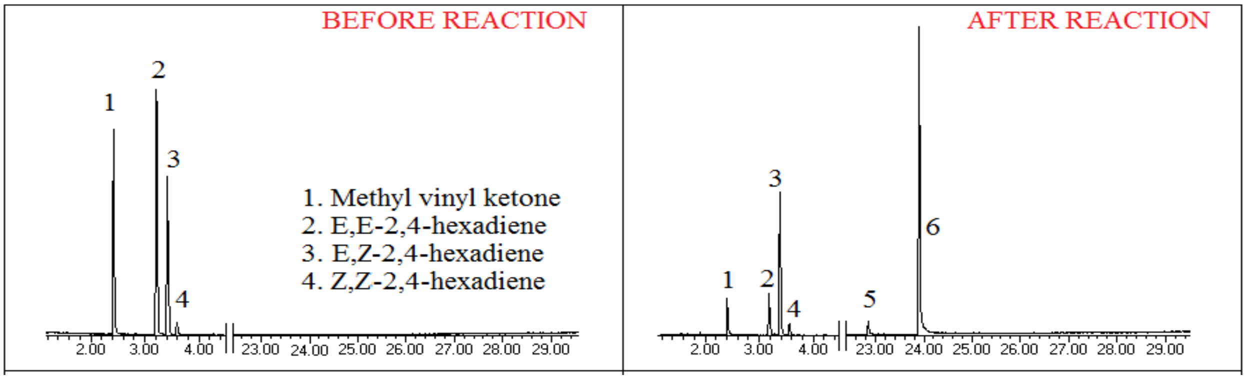


Figure 5. 2. Reaction of 2,4-hexadiene in Toluene with MVK and using AlCl$_3$ as catalyst.

The reaction products appeared approximately in 23 and 24 minutes, according to their mass spectrum, they are both substituted cyclohexenes, the expected product of the reaction. Figure 5.3 shows the mass spectrum of peak 6, the main reaction product and the compound suggested by the library of the GC-MS.

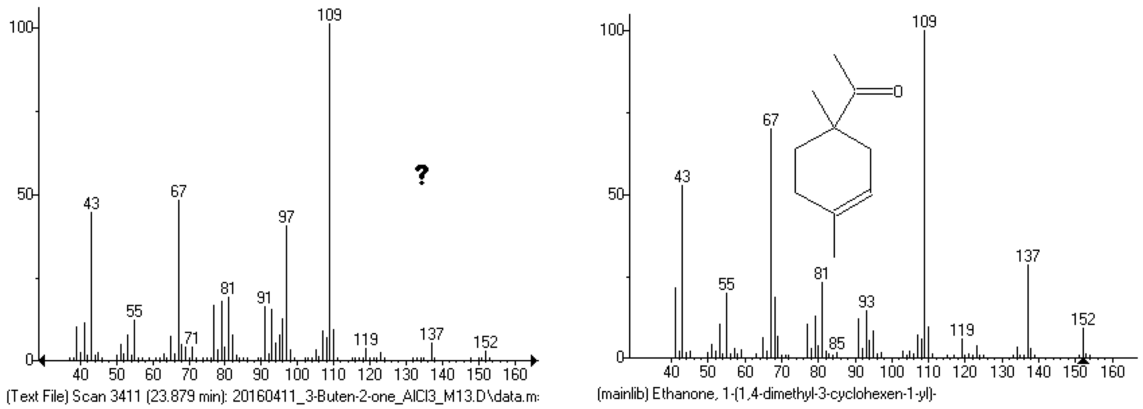


Figure 5. 3. Mass spectra of peak 5, the most abundant product in the reaction of 2,4-hexadiene in Toluene with MVK and using $AlCl_3$ as catalyst

Following the procedure of Chapter 4 the conversion and selectivity of the reactions were determined on a semi-quantitative basis using the areas of the GC-MS peaks. That information is shown in Table 5.4.

Table 5. 4. Conversion and selectivity for Diels-Alder reaction of 2,4-Hexadiene and MVK.

			Areas			
Peak	**RT (min)**	**Compound**	**Feed**	**Product**	**Conversion**	**Selectivity**
1	2.423	MVK	1.2E+07	3.9E+05	97	-
2	3.219	E,E-2,4-hexadiene	2.5E+07	6.3E+05	97	-
3	3.419	E,Z-2,4-hexadiene	1.2E+07	9.0E+06	23	-
4	3.593	Z,Z-2,4-hexadiene	9.1E+04	7.9E+04	13	-
5	22.837	Product	-	1.1E+05	-	4
6	23.879	Product	-	5.5E+07	-	96

3.2.2 Experiments using 3-buten-2-ol as dienophile

In contrast to the result obtained for the ketone, when the alcohol was acting as dienophile, there was not significant consumption of the reagents, only a small peak is seen around 24 minutes (peak 5 in the chromatogram after reaction). The calculation of conversion of reagents and product selectivity is provided in Table 5.5.

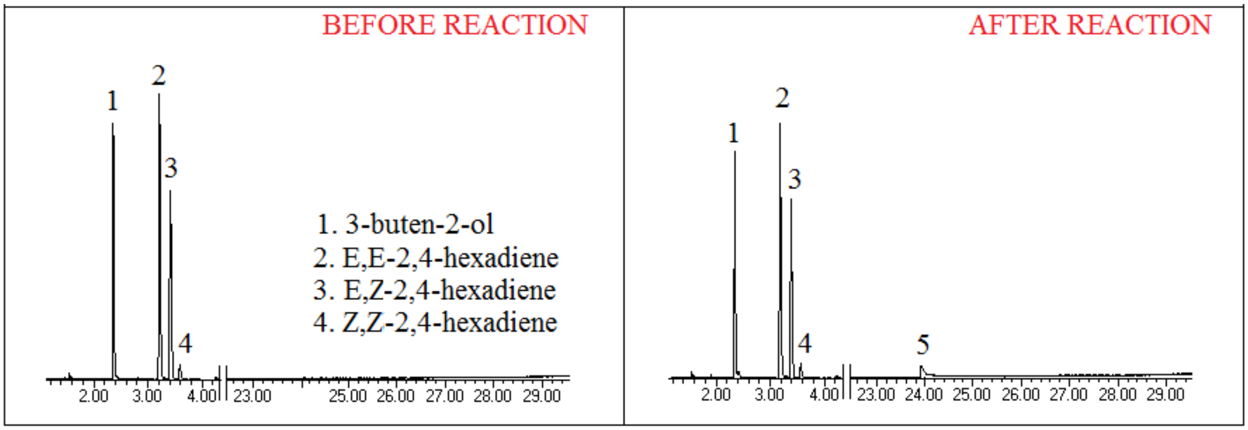


Figure 5. 4. Reaction of 2,4-hexadiene in Toluene with 3-buten-2-ol and using $AlCl_3$ as catalyst.

Table 5. 5. Conversion and selectivity for Diels-Alder reaction of 2,4-Hexadiene and 3-buten-2-ol.

			Areas			
Peak	**RT (min)**	**Compound**	**Feed**	**Product**	**Conversion**	**Selectivity**
1	2.343	3-buten-2-ol	1.2E+07	9.5E+06	19	-
2	3.219	E,E-2,4-hexadiene	2.6E+07	2.1E+07	19	-
3	3.419	E,Z-2,4-hexadiene	1.2E+07	1.2E+07	5	-
4	3.593	Z,Z-2,4-hexadiene	9.7E+04	8.6E+04	11	-
5	23.906	Product	-	3.1E+05	-	100

3.3 Reaction of *trans*-1,3-pentadiene in decane with MVK with $AlCl_3$.

The reaction of 2,4-hexadiene with MVK using catalyst can be considered as a reaction with a positive outcome; the diene reacted with the dienophile and most of it was converted. Those results motivated the decision of repeating the experiment using of *trans*-1,3-pentadiene in decane, but this time only with MVK and $AlCl_3$ as catalyst. The use of the alcohol was discarded due to its poor reactivity. The reaction of the pentadiene was carried out, but surprisingly the results were not the expected. Only three small peaks (peaks 4, 5 and 6) were seen after reaction as can be verified in Figure 5.4. The reaction gave a poor conversion according to the values presented in Table 5.6.

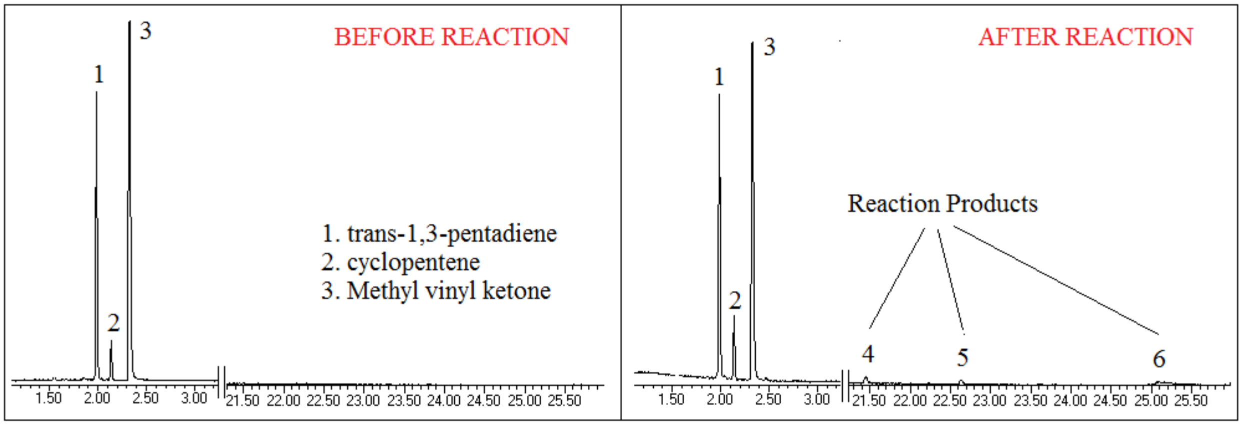


Figure 5. 5. Reaction of *trans*-1,3-pentadiene in decane with MVK using $AlCl_3$ as catalyst.

Table 5. 6. Conversion and selectivity for Diels-Alder reaction of *trans*-1,3-pentadiene and MVK

			Areas			
Peak	**RT (min)**	**Compound**	**Feed**	**Product**	**Conversion**	**Selectivity**
1	1.989	*trans*-1,3-Pentadiene	3.4E+07	3.1E+07	9	-
2	2.142	Cyclopentene	4.9E+05	4.7E+05	6	-
3	2.33	MVK	3.8E+07	3.4E+07	9	-
4	21.447	Product	-	2.9E+04	-	20
5	22.63	Product	-	1.1E+04	-	12
6	25.069	Product	-	3.4E+05	-	68

3.4 Reaction of a mixture of diolefins in decane with MVK and $AlCl_3$.

The results for the reaction of the mixture of dienes with MVK are shown in Figure 5. 6. It was corroborated that $AlCl_3$ has a positive effect on the conversion of the reagents; the information of the conversion for both catalyst loadings is provided in Table 5.7. The table shows that MVK was converted completely and peaks like 2,3-dimethyl-1,3-butadiene, 1,3-hexadiene, *cis*-3-methyl-1,3-pentadiene reached conversions higher than 60% going from a catalyst loading of 10 to 15%. Several observations can be made from the figure; when 10% of catalyst was added, eight peaks corresponding to reaction products were seen (peaks 8 to 15) with the particularity that one of them was in the same area where the dienes mixture were (peak 15). In the case where the catalyst loading was 15%, two of the previous products disappeared (peaks 13 and 14) and two new peaks appeared (peaks 16 and 17). Besides that, the ketone used as dienophile is practically gone and two of the most significant products increased their concentration.

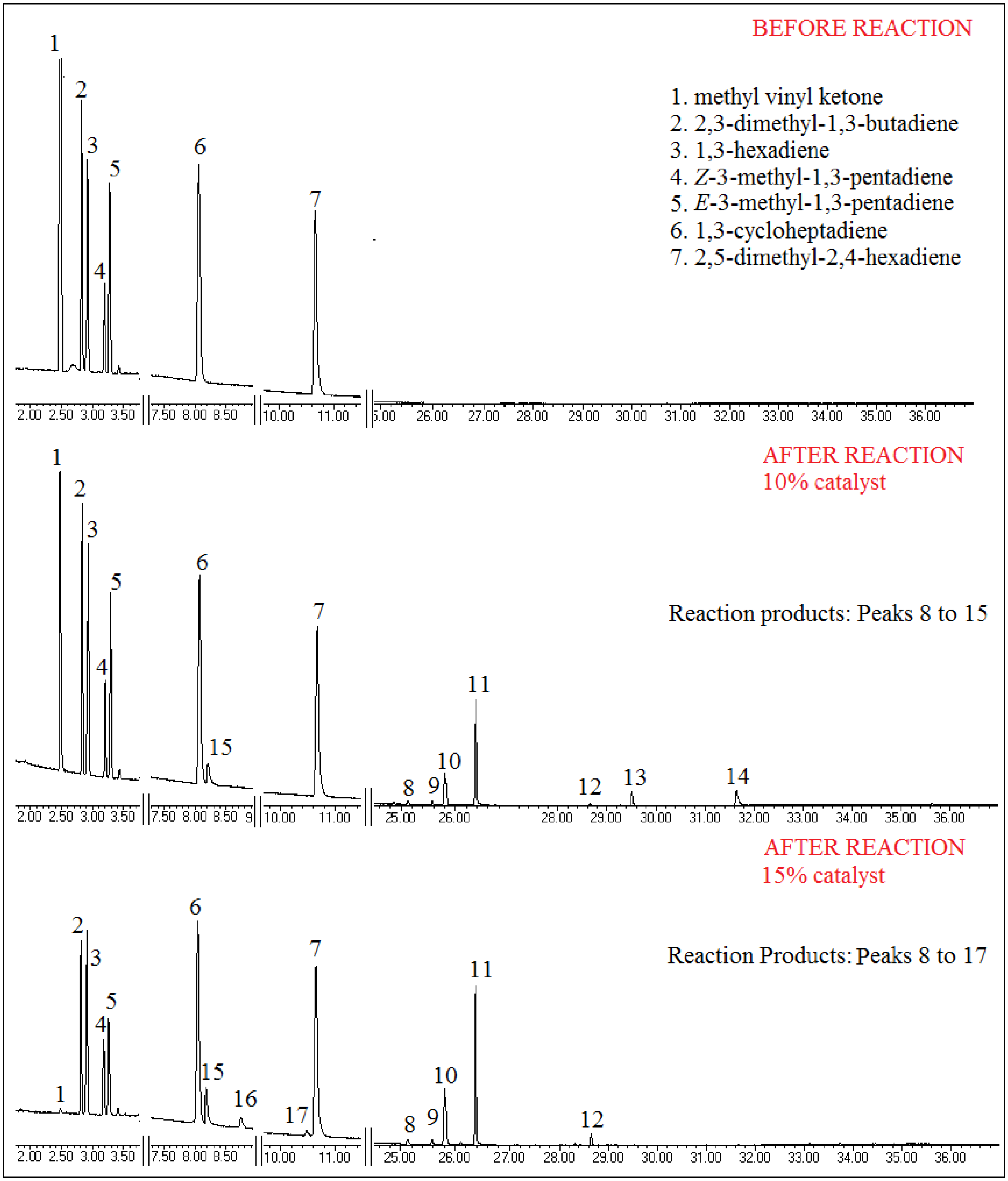


Figure 5. 6. Reaction of mixture of diolefins in decane with MVK using 10% and 15% of $AlCl_3$.

In Figure 5.6 peaks 8 to 15, were the reaction products. Peaks 8, 9, 10 and 11 were cyclohexene derivatives with a molecular formula $C_{10}H_{16}O$; that indicates that diolefins with 6 carbons in their structure could have been the reagents from which those products were formed. The reagents present with 6 carbons were, 2,3-dimethyl-1,3-butadiene (peak 2), 1,3-hexadiene (peak 3), *cis*-3-methyl-1,3-pentadiene (peak 4) or *trans*-3-methyl-1,3-pentadiene (peak 5).

Table 5. 7. Conversion and selectivity for Diels-Alder reaction of dienes mixture and MVK using two different loadings of $AlCl_3$.

Peak	RT		Initial	After reaction with catalyst		Conversion	
#	(min)	Compound	Sln	10%	15%	10%	15%
1	2.477	MVK	3.4E+08	1.9E+07	0.0E+00	95	100
2	2.811	2,3-dimethyl-1,3-butadiene	1.1E+07	1.1E+07	3.3E+06	6	71
3	2.911	1,3-hexadiene	1.2E+07	9.7E+06	5.1E+06	16	55
4	3.178	*cis*-3-methyl-1,3-pentadiene	1.3E+06	1.2E+06	7.2E+05	1	42
5	3.265	*trans*-3-methyl-1,3-pentadiene	6.4E+06	5.9E+06	1.4E+06	7	79
6	8.049	1,3 cycloheptadiene	2.8E+07	3.3E+07	2.4E+07	6	12
7	10.649	2,4-dimethyl-2,4-hexadiene	3.1E+07	3.7E+07	2.8E+07	9	11
8	25.129	-		5.5E+03	6.5E+03	-	-
9	25.576	-		3.0E+03	6.0E+03	-	-
10	25.81	-	-	7.3E+05	1.8E+06	-	-
11	26.378	-	-	3.3E+06	5.2E+06	-	-
12	28.65	-	-	1.0E+03	-	-	-
13	29.512	-	-	9.3E+04	-	-	-
14	31.637	-	-	2.5E+05	3.0E+04	-	-
15	8.183	-	-	2.5E+05	6.5E+05	-	-
16	8.886	-	-	-	6.5E+03	-	-
17	10.454	-	-	-	6.5E+03	-	-

The presence of peaks 13, 14 and 15 led to the control experiment of the dienophile (MVK) plus the solvent and 10% of the catalyst. It was seen that those mentioned peaks were formed during the control experiment. Figure 5.7 is showing the chromatogram of that reaction; the products match in their retention time and structure suggested by the library of the GC-MS.

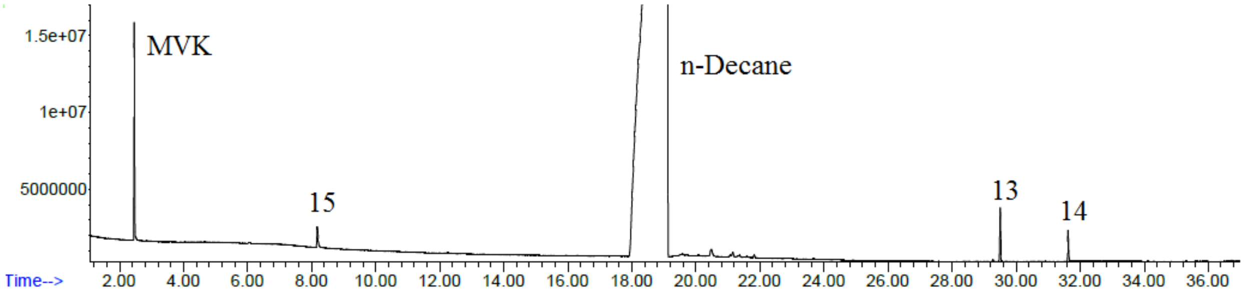


Figure 5. 7 Results of the control experiment done for MVK and decane with catalyst but no diene.

4. Discussion

4.1 Reaction of *trans*-1,3-pentadiene in decane with 3-buten-2-ol and MVK.

Figure 5.1 shows that *trans*-1,3-pentadiene and MVK or with 3-buten-ol did not give any product visible in chromatography. However, when the same reaction was done in Chapter 3, using maleic anhydride as dienophile the compound disappeared. As mentioned in the results section, maybe the product formed was not soluble and precipitated after formation, and due to the small amount produced, the solid was not detected. According to Table 5.3 the ratio of *trans*-1,3-pentadiene to cyclopentene decreased from 68.3 to 66.0 and 69.3 to 69.0 after reaction with MVK and 3-buten-2-ol respectively. That is taken as a proof of the *trans*-1,3-pentadiene reaction; as in the case of the Diels-Alder cycloaddition with maleic anhydride, the concentration of the diene decreased. It was not as evident (visually speaking) as in the case of the identification in chapter 3, because of the strength of the dienophile. All dienophiles have an electron withdrawing group (EWG) conjugated to the alkene.[7] If the dienophile has a stronger EWG it is going to be more reactive towards the diene. The two groups carbonyl (C=O) present in the anhydride make it a more reactive molecule, compared to the ketone that has only one carbonyl group. The anhydride is even more reactive if the comparison is done with the alcohol used.

4.2 Reaction of 2,4-hexadiene in toluene with 3-buten-2-ol and MVK with $AlCl_3$.

The diene fed in that solution was a mixture of stereoisomers as mentioned earlier; 2,4-hexadiene is a symmetrical molecule that forms the *trans-trans*, *cis-trans* and *cis-cis* (peaks 2, 3 and 4 respectively in Figure 5.2) stereoisomers. For the Diels-alder reaction to proceed the two double bonds must be on the same side of the single bond which is known as the *cisoid* conformation.[8] When a molecule is in its *transoid* conformer, a 180 degree rotation on the single bond can achieve such conformation. The following Figure shows the *cis* conformation for each stereoisomer of 2,4-hexadiene.

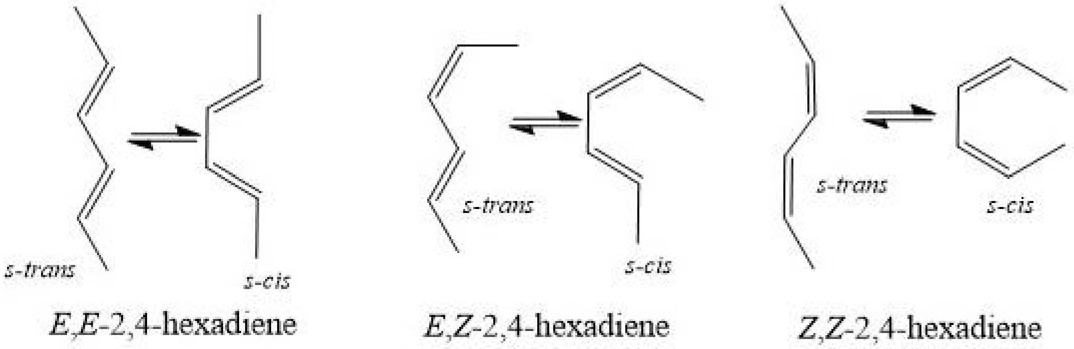


Figure 5. 8. *Cisoid* conformation of the stereoisomers of 2,4-hexadiene.

The importance of the precedent figure relies in the opportunity to see the reason why one stereoisomer is more prone to undergo the cycloaddition than another. In their *cis* conformation, *E,Z*-2,4-hexadiene and *Z,Z*-2,4-hexadiene have one and two methyl groups respectively pointing to the area of the diene moiety while *E,E*-2,4-hexadiene has both methyl groups out of that area. The methyl substituents of the *Z*-isomers destabilize the *cisoid* conformation and hence the transition state by steric hindrance, causing a lower reactivity.[6]

In the case where the reaction was attempted incorporating the Lewis acid as catalyst, a positive result was achieved while using MVK. Figure 5.2 shows a decrease in the intensity of peak 2; according to Table 5.4 such decrease corresponds to a conversion of 97% of *trans-trans*-2,4-hexadiene. The high reactivity of the mentioned stereoisomer is expected, based on the reasoning previously mentioned.

The compounds *trans-cis*-2,4-hexadiene (peak 3) and *cis-cis*-2,4-hexadiene (peak 4) had lower conversion, 15 and 9% respectively of the initial compound was converted. Probably the small peak number 5 in the products came from the E,Z and Z,Z isomers of hexadiene. The structures suggested by GC-MS for all the product peaks are substituted cyclohexenes which is in agreement with the expected reaction products as shown in Figure 5.9.

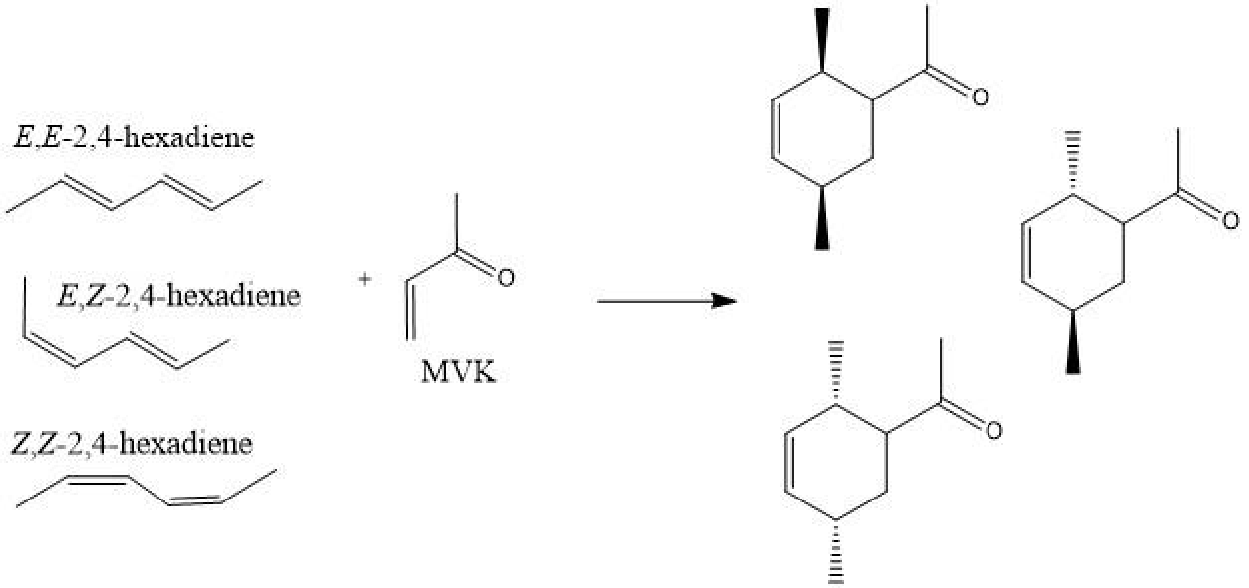


Figure 5. 9. Expected reaction products of the Lewis catalyzed Diels-Alder reaction of 2,4-hexadiene with MVK.

The attempts using 3-buten-2-ol resulted in low conversion of the diolefins with or without catalyst as can be interpreted from Figure 5.4. The dienophile is a molecule with a double or triple bond present; the reactivity of the molecule is increased by a EWG conjugated to the double or triple bond. Although in the cases where the hydroxyl group is attached to an alkyl chain, it has electron withdrawing character, in 3-buten-2-ol that group is next to an alkyl and an allylic chain. The p system of the double bond can stabilize an adjacent carbon, decreasing the strength of that dienophile compared to MVK. Such is the case of the 1,3-butadiene with ethylene, reaction that gives poor yield and requires high temperatures to afford the formation of the cyclohexene ring due to the poor dienophile that is ethylene.[6,7] It is speculated that Diels-Alder cycloaddition of 2,4-hexadiene with 3-buten-2-ol is a slow reaction as well, and maybe higher temperatures and longer reaction times could favor the formation of the adduct. The alcohol, 3-buten-2-ol did not give a significant amount of product, although a small peak can be seen after reaction (Figure 5.4, peak 5).

4.3 Reaction of *trans*-1,3-pentadiene in decane with MVK with $AlCl_3$.

The reaction with this compound did not improve significantly with the addition of catalyst. Despite the fact that, *trans*-1,3-pentadiene does not have a steric hindrance due to the substituents as in the case of 2,4-hexadiene and even though the Lewis acid was present, the compound did not show high reactivity. After using 10% of catalyst, only 9% was converted to products that according to the library of the GC-MS had a six membered ring in their structure. The reasons for such result are unknown; maybe for that specific compound the strength of the MVK as dienophile is not enough and stronger reaction conditions are required.

4.4 Reaction of a mixture of diolefins in decane with MVK and $AlCl_3$.

Based on Figure 5.6 it can be said that the Lewis acid present in the reacting media has an important effect on the conversion of the reaction. When 10% of the catalyst was used, the progress of the reaction was evident. The conversion of 2,3-dimethyl-1,3-butadiene (peak 2), 1,3-hexadiene (peak 3), *cis*-3-methyl-1,3-pentadiene (peak 4) or *trans*-3-methyl-1,3-pentadiene (peak 5) was 6, 16, 1 and 7% respectively. Taking into account those values, can be said that at those conditions, the conjugated diolefin with no branches in its structure was the most reactive. Figure 5.10 shows some of the chemical structures suggested by GC-MS for peaks 8 to 11. The structure of Peak 12 has not been stablished yet, the mass spectra suggests molecules with different number of carbons and with and without the alcoxy group in their structure. However, one thing that is recurrent is the molecular weight of the suggestions, which based on the GC-MS is around 164 g/mol. One might speculate that peak 12 is product of the reaction of 1,3-cycloheptadiene (peak 6) because it has a higher retention time, hence is a bigger molecule. Besides the reaction product of the MVK and the cyclic diene would have had a product with molecular weight of 164g/mol.

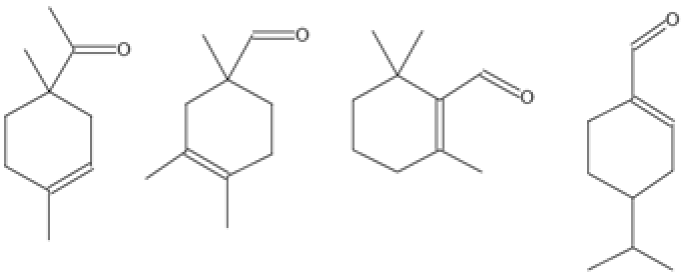


Figure 5. 10. Chemical structure suggested by GC-MS of the products in the Figure 5.4.

Peak 7, that represents 2,5-dimethyl-2,4-hexadiene showed a conversion of 9%, but a cycloaddition product that could have come from it, was not identified in the chromatogram. That peak showed a higher conversion than peaks 2, 4 and 5 for which products possibly coming from them were seen. It is guessed that as in the case of *trans*-1,3-pentadiene, the reaction product was insoluble and precipitated. The other reaction products (peaks 13, 14 and 15) were not six membered rings but aliphatic chains; as was explained in the results section, those peaks correspond to the interaction of the solvent with MVK in the presence of the catalyst.

Based on the conversion shown in Table 5.7 the *trans* isomer of 3-methyl-1,3-pentadiene is more reactive to the cycloaddition than the *cis* isomer; that can be explained by the same thinking exposed in section 4.2 to explain the reactivity of the 2,4-hexadiene stereoisomers. Figure 5.11 shows that in the *cisoid* configuration of the *cis* isomer the methyl branch is in the way, which reduces the reactivity of the molecule.

In the case where the catalyst loading was 15%, the conversion of 2,3-dimethyl-1,3-butadiene (peak 2), 1,3-hexadiene (peak 3) and *trans*-3-methyl-1,3-pentadiene (peak 5) was significantly higher than when 10% catalyst loading was used. On the other hand a small change was observed in the conversion of 1,3-cycloheptadiene and 2,5-dimethyl-2,4-hexadiene. The products formed were the same that when 10% of catalyst was used with the exception of two other small peaks (16 and 17) and the absence of some of the compounds generated from the interaction between the dienophile and the solvent (peaks 13 and 14). Maybe those two issues are related, because none of the molecules seemed to have a structure corresponding to the Diels-Alder cycloaddition. The reaction products expected for all the dienes used in the mixture are depicted in Figure 5.11. The number to the left corresponds to the number assigned to the peak of the diene in Figure 5.6. These compounds should be seen only as an indicative of the nature of the product. The true identities of the products have not been confirmed although Figure 5.10 already shows some of the molecules that according to the GC-MS were formed.

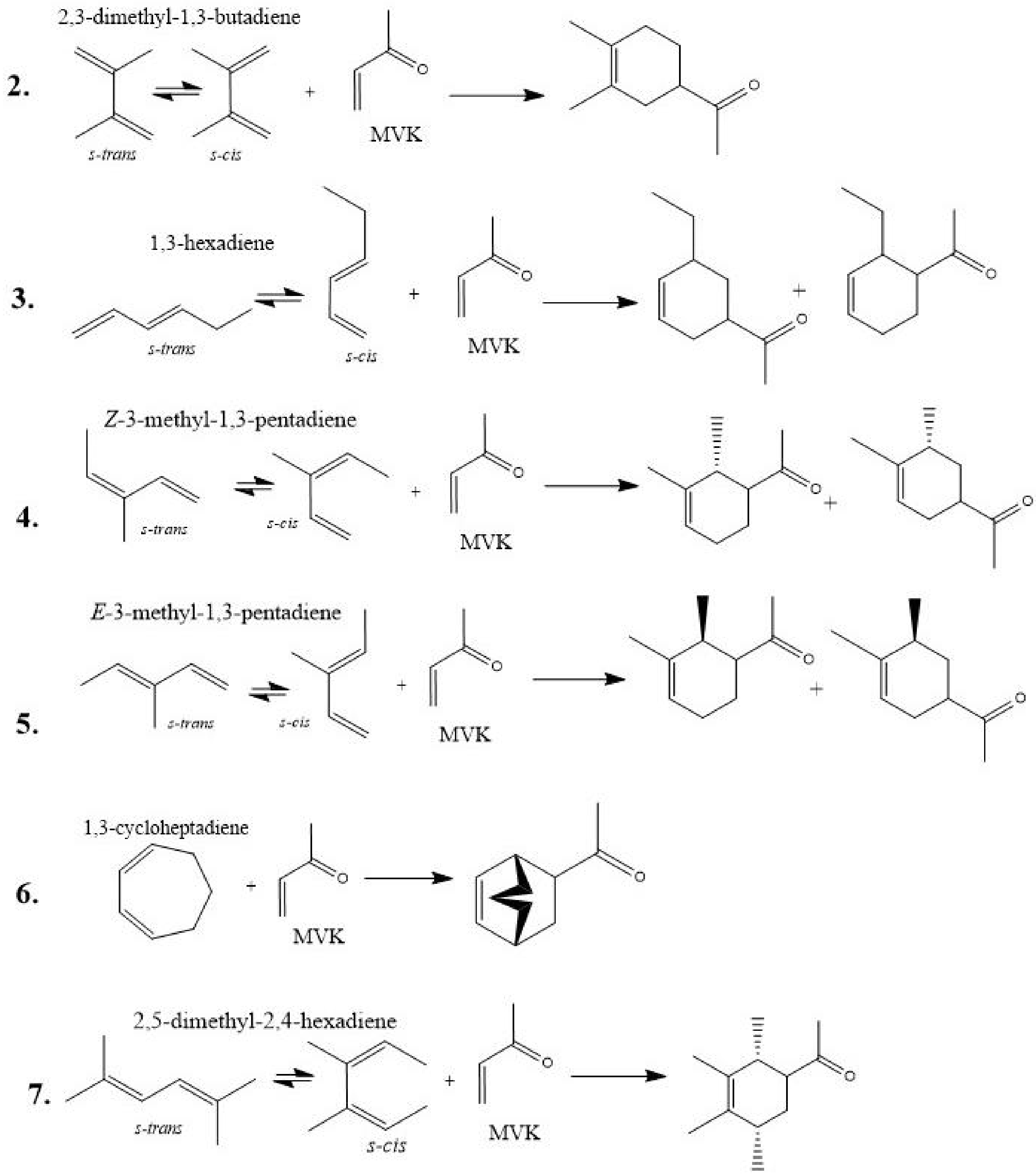


Figure 5. 11. Expected products from the Diels-Alder reaction of a model mixture of dienes with MVK using $AlCl_3$ as catalyst.

By increasing the amount of catalyst the conversion of the 1,3-hexadiene (peak3) was also increased (conversion went from 16 to 55%), but this time, that molecule was not the most reactive.

The highest reactivity based on the conversion calculated, was exhibited by *trans*-3-methyl-1,3-pentadiene, that again was more reactive respect to its *cis* configuration. A tendency respect to the effect of branching on the cycloaddition of acyclic conjugated diolefins is clear; mono-substituted compounds (*trans*-3-methyl-1,3-pentadiene) showed higher conversions than di-substituted molecules (2,3-dimethyl-1,3-butadiene). Based on the low conversion for 2,4-dimethyl-2,4-hexadiene another di-substituted compound, one can speculate that the number of carbons in the structure matters; maybe the cycloaddition is done first on small molecules.

Something particular to highlight is the reactivity of the cyclic diene. The conversion with 10 and 15% $AlCl_3$ was 6 and 12% respectively, a relative low value if one takes into account that the molecule is already in the *cisoid* conformation required to form the six carbon ring. Maybe the reaction is favored with the dienes of aliphatic chain, but if more time would have been given, a higher conversion could have been achieved. It would be a good approach to do more experiments without the presence of the other diolefins. Literature reports that cyclohexadiene and cycloheptadiene have a lower reactivity in the Diels-Alder reaction compared to cyclopentadiene. That, based on the concept of computational organic chemistry of distortion energies; apparently the energy required to go from the cyclic diene into the transition state geometry is less in the case of cyclopentadiene.[9] Going deeper into that discussion requires more study and touches a different field of knowledge.

The ketone was depleted (peak 1) when 15% of catalyst was used, but some of the compounds that showed reactivity were still present. Although the calculations were done to have a molar ratio 1:1 dienophile to diene, maybe when the MVK was added (remember it was added by volume) a lower amount of dienophile was present during the experiment.

The reaction was carried at really low temperature (60°C) and the use of such high amount of catalyst can be avoided maybe by increasing the reaction temperature, there is always a trade-off between those two variables. The analysis of which experimental conditions favor the most the reaction could be considered in future work.

From the previous findings it can be said that factors like the type of chain (open or closed) and the stereoisomerism present in the molecule, condition the Diels-Alder cycloaddition. Runs using thermally cracked naphtha were not done, but the Diels-Alder reaction was successful in a naphtha sample when maleic anhydride was used (chapter 3).

5. Conclusions

The purpose of the work here shown was to find a route to decrease the amount of diolefins, in light cracked fractions, targeting specifically conversion of conjugated diolefins. From the experimental work the following were the key findings:

1. The Diels-Alder cycloaddition was carried out with diolefins of different nature and it showed that the formation of a Diels-Alder product can be achieved.

2. The reactivity of a molecule towards the reaction depended strongly on their structure. Acyclic diolefins were the most prone to undergo the cycloaddition. The cyclic molecule used, 1,3-cycloheptadiene did not show high conversions.

3. Stereoisomerism plays an important role in the reaction, the place where the substituents of a molecule are located, limit the reactivity of the compound. Stereoisomers with a *cis* configuration are more reactive in the cycloaddition.

4. The selection of dienophile is an important factor to take into account when doing the reaction because it affects the reaction rate. In this specific case, methyl vinyl ketone was more reactive to the cycloaddition than 3-buten-2-ol.

5. It was verified that a Lewis acid catalyst can improve the Diels-Alder reaction under low temperatures (60°C).

6. The catalyst loading in the reaction is directly proportional to the conversion of diolefins. A catalyst loading of 10% favored the cycloaddition of the isolated diolefin, 1,3-hexadiene, whereas the 15% loading favored the cycloaddition of the branched diolefin, *trans*-3-methyl-1,3-pentadiene.

References

(1) Gray, M. R. Hydrotreating Processes. In *Upgrading Oilsands Bitumen and Heavy Oil*; The University of Alberta Press: Edmonton, 2015.

(2) Pereira, R. C. C.; Pasa, V. M. D. Effect of mono-olefins and diolefins on the stability of automotive gasoline. *Fuel* **2006**, *85* (12-13), 1860–1865.

(3) Vollhardt, P.; Schore, N. *Organic Chemistry: Structure and Function*; W.H. Freeman: New York, 2007.

(4) Andrade, D. F.; Azevedo, D. A. Comparison of UOP-326, voltammetric and gas chromatographic/mass spectrometric methods for the determination of conjugated dienes in Brazilian Naphtha. *Fuel* **2006**, *85* (7-8), 1024–1031.

(5) Funel, J.-A.; Abele, S. Industrial applications of the diels-alder reaction. *Angew Chem Int Ed* **2013**, *52* (14), 3822–3863.

(6) Fringuelli, F. Diels-Alder reaction. In *Dienes in the Diels-Alder reaction*; John Wiley & Sons, Inc., 1990; pp 1–44.

(7) Clayden, J.; Greeves, N.; Warren, S. Pericyclic reactions 1: cycloadditions. In *Organic chemistry*; Oxford University press: New York; pp 877–908.

(8) Wassermann, A. *Diels-Alder reactions organic background and physico-chemical aspects*; Elsevier publishing company, 1965.

(9) Levandowski, B. J.; Houk, K. N. Theoretical analysis of reactivity patterns in Diels-Alder reactions of cyclopentadiene, cyclohexadiene, and cycloheptadiene with symmetrical and unsymmetrical dienophiles. *J. Org. Chem.* **2015**, *80* (7), 3530–3537.

CHAPTER 6 – RELATIVE REACTIVITY OF ALKENES IN HYDROGENATION OVER PLATINUM CATALYST

Abstract

The relative reactivity of eight molecules containing unsaturations in their structure was studied using hydrogenation over Pt/C as reaction probe. It was of interest to analyze the reactivity of linear conjugated and isolated diolefins (*trans*-1,3-pentadiene and 1,4-pentadiene); a branched conjugated diolefin (3-methyl-1,3-pentadiene); a cyclic olefin (cyclohexene); a branched cyclic olefin (1-methyl-cyclohexene); a cyclic conjugated diolefin (1,3-cyclohexadiene); a cyclic paraffin with an allylic radical (vinylcyclopentane) and a linear mono-olefin as control molecule (1-hexene). Using the experimental data an observed initial reaction rate was calculated. By determining the initial reaction rate for the hydrogenation of each molecule, it was possible to stablish an order in their reactivity and to relate those results with the structural effects on stability and reactivity. Opposed to what was expected, the conjugated diolefin did not exhibited the highest reactivity, instead the isolated diolefin proved to react more rapidly. The rate of hydrogenation of the conjugated linear diolefin was slowed down by the presence of the cycloalkene.

Keywords: Hydrogenation, mono-olefin, diolefins, reactivity, initial reaction rate.

1. Introduction

Hydroprocessing of refining products involve hydrogen addition to petroleum fractions under different operation conditions. Technologies such as residue hydroconversion, residue hydrocracking or naphtha hydrotreating are clear examples of hydrogen addition processes. The goal is to obtain hydrogen enriched and heteroatom depleted products. In operations where hydroprocessing is used to decrease the amount of sulfur present, the practice better known as hydrodesulfurization (HDS). In the case of cracked naphtha the feed usually has an important amount of valuable olefins, compounds that help boosting the octane number. The problem of HDS is that while a decrease in the level of sulfur is achieved, large amounts of hydrogen are consumed and the octane number of the stream is compromised on account of the hydrogenation of olefins. Research regarding this matter is extensive; the type of catalyst, the operation conditions, and the nature of the compounds present in the feed have been studied to find the best possible way to do desulfurization minimizing olefin saturation. What is important to this work is the research done in that context with respect to reactivity of olefins.

Operations such as the HDS of fluid catalytic cracking (FCC) naphtha has received some attention in recent years. The reactivity of different olefins present in FCC gasoline was studied in the selective HDS over a sulfide CoMoP/Al_2O_3 catalyst in order to define how the reaction conditions, the type of active sites and the selectivity of HDS were related.[1] The study showed that the carbon-carbon double bond is isomerized from a terminal to an internal position; this double bond isomerization is favored at higher temperatures, but skeletal isomerization was not promoted by the catalyst under the range of working temperatures (220^{o}C -260^{o}C). Besides that, the reactivity of the olefins hydrogenation decreased with branching due to steric hindrance in the double bond. There were double bond isomerization and hydrogenation active sites and the sulfidation temperature of the catalyst proved to influence the active sites for hydrogenation but not double bond isomerization.

The reactivity of terminal olefins with carbon number between 4 and 7 present in FCC naphtha was studied under different reaction temperatures using a PtPd/USY catalyst. They proved that olefins with small carbon number react faster during hydrogenation.[2] A recent study had special interest for understanding the inhibition effects of olefins present in a model FCC naphtha on HDS process using CoMo-S/γ-Al_2O_3 as catalyst.[3] They showed that in general all olefins have an inhibiting effect in the operation, but the effect decreases when the steric hindrance of the molecule is higher, the non-branched olefins were the ones with a stronger inhibition effect.

Hydrogenation of alkene-alkyne mixed hydrocarbons over precious metal catalysts has been extensively studied as well. There are studies regarding the hydrogenation specifically of pentadienes over Palladium while other type of unsaturated structures such as alkynes were present in the reaction mixture.[4] The study showed the results in the reactivity of conjugated and isolated systems when competitive adsorption was taking place; reactivity of the conjugated 1,3-pentadiene based on the first order rate constant was decreased by the presence of the alkyne whereas the non-conjugated 1,4-pentadiene seemed to have a positive interaction with the alkyne, having a higher reactivity.

When dealing with olefins in light boiling fractions coming from thermal cracking processes, it is important not only to know the right strategy, but also to understand the chemical route taken by a specific molecule when the strategy has been devised. It is well known that mono-olefins along with diolefins are compounds that are more reactive than their corresponding saturated hydrocarbons. Between the two of them, diolefins are the most reactive ones. It has been shown that the presence of molecules with high reactivity like diolefins triggers undesired reactions e.g. coking, in important refining processes making them deleterious to product quality.[5]

The purpose of the study was to find a sequence in the reactivity of different olefins with special interest in conjugated diolefins, as they have been proved to be harmful if present in refining processes; having a better fundamental understanding of their reactivity helps to anticipate the outcome in a specific reaction. Having that in mind, an important refining reaction such as hydrogenation was used as reaction probe to compare the reactivity of a selected group of olefins. Ideally a wide range of catalyst should have been used to have a wider understanding of the reaction when molecules with olefinic functional groups are present; platinum, palladium, nickel and nickel molybdenum sulfide are typical catalyst used for hydrogenation in refining processes, but for the present study only platinum supported on activated carbon was used.

The main objective of the experiments was to collect information of the change in the concentration of the compound of interest with time, in order to find the reaction rate constant and stablish a reactivity sequence for the relative reactivity of the olefins studied. The progress of the reaction was followed by GC-MS and GC-FID, the first technique was used to identify the product distribution during the hydrogenation and the other to quantify the change in the concentration of the olefin studied. Competitive hydrogenation on the active sites of the catalyst was not studied here, each compound was hydrogenated one at the time.

2. Experimental

2.1 Materials

Table 6. 1. Materials description

Compound	Formula	CASRN [a]	Mass fraction purity [b]	Supplier
Materials for reactions				
decane	$C_{10}H_{22}$	124-18-5	≥99%	Sigma Aldrich
trans-1,3-Pentadiene	C_5H_8	2004-70-8	90%	Sigma Aldrich
3-Methyl-1,3-pentadiene (mixture of *cis* and *trans*)	C_6H_{10}	4549-74-0	98%	Sigma Aldrich
Cyclohexene	C_6H_{10}	110-83-8	99.7%	Sigma Aldrich
1-Methyl-cyclohexene	C_7H_{12}	591-49-1	97%	Sigma Aldrich
1,3-Cyclohexadiene	C_6H_8	592-57-4	97%	Sigma Aldrich
Vinylcyclopentane	C_7H_{12}	3742-34-5	99%	Sigma Aldrich
1,4-Pentadiene	C_5H_8	591-93-5	99%	Sigma Aldrich
1-Hexene	C_6H_{12}	592-41-6	97%	Sigma Aldrich
Cylinder gases				
Nitrogen	N_2	7727-37-9	0.999995 [c]	Praxair
Helium	He	7440-59-7	0.999995 [c]	Praxair
Compressed Air	Air	132259-10-0	0.999999	Praxair
Catalyst				
Platinum on activated charcoal	Pt/C		5% Pt basis	Sigma Aldrich

[a] CASRN = Chemical Abstracts Services Registry Number

[b] This is the purity of the material guaranteed by the supplier; material was not further purified.

[c] Mole fraction purity.

Molecules *trans*-1,3-pentadiene, cyclohexene and vinylcyclopentane were chosen because they were previously found in the thermally cracked naphtha sample. According to GC-MS, 2-methyl-1,3-pentadiene was a compound with a high chance of being present in the naphtha sample also, but due to its lack of commercial availability, 3-methyl-1,3-pentadiene, a molecule with similar structure was used instead. The isolated diolefin 1,4-pentadiene was included taking into account that some dienes similar to that were detected by Alberta Innovates-Technology Future analysis of the thermally cracked naphtha (i.e. 1,5-hexadiene and 1,7-octadiene). 1-Hexene was used as control molecule and it is present in the naphtha mixture as well. The other molecules are part of the study, because they have similar number of carbons in their structure, which would be good for comparison purposes.

2.2 Equipment and procedure

The employed conditions were similar to those for hydrogenation reactions during the diolefins characterization. The solvent selected was decane, due to its non-polar nature and long hydrocarbon chain guarantees the good solubility of the compounds and hence homogeneous liquid phase. The molar concentration used to do the reactions was defined based on the quantification results for the four molecules found in the thermally cracked naphtha. Thus, the value of the concentration of 1-methylcyclopentene was taken as reference to start the reactions (0.08M). During the partial hydrogenation reactions a mass of 2g of naphtha was used. In volume that corresponded to approximately 3ml of sample, volume used for decane. With the volume and molar concentration defined, the number of moles of each compound was fixed.

A 0.08M solution in decane of the compound of interest was prepared in a 50ml long neck graduated glass flask. The hydrogenation of each compound was studied at different reaction times. Reaction times 1, 2, 3, 4 and 5 minutes were studied; the experiment for each time was done always by triplicate. That meant that for the hydrogenation of each compound, 15 vials should have been ready to use. 7 ml glass vials were selected. The reaction volume was 3ml; to each vial an amount of catalyst corresponding to 2% wt Pt/wt olefin based on the mass of feed olefin present in 3ml of solution was added. Once the catalyst was inside the vial, the solution was loaded. A small magnetic stirrer was immerse into the vial previously loaded with the solution and catalyst, the vial was introduced into the reactor and the system was closed and purged with nitrogen 3 times. The reaction was carried out in a micro-batch reactor with a volume of 15ml, was manufactured by Swagelok and the material of tubing and fittings was 316 stainless steel. The reactor length, internal diameter and outside diameter were 8.6 cm, 2.1cm and 2.6cm respectively. The reactor served as pressure container. A schematic of the experimental setup is shown in Figure 6.1.

The reactor was heated up to 60°C by immersing it into a water bath supported on a hot plate with temperature controller. A thermocouple was fitted inside the micro-batch reactor to accurately measure the reaction temperature. After the internal temperature of the reactor reached the same temperature of the water bath, hydrogen was loaded into the system to a gauge pressure of 0.41MPa, measured at 21°C and a barometric pressure of 0.1MPa, i.e. the absolute pressure was 0.5 MPa. The reactor was operated as a batch reactor, so the pressure reported was the initial pressure, the system reduced the hydrogen pressure as the reaction progressed, but the exact final pressure was not recorded. The calculated molar concentration of hydrogen relative to the olefin in the liquid was 27:1 and the decrease in pressure was minor. The data of the reaction temperature versus time was not recorded, but during the process the temperature remained constant to around 60°C. The reaction time and stirring to 1400rpm started when Hydrogen was loaded. After completing the time, the reactor was removed from the water bath, the remaining gas released, let to cool down and opened. The vial containing the reaction products was closed, the sample filtered through a syringe filter of 0.2µm and transferred to a 4ml vial to be stored. A scheme of the experimental set up for the hydrogenation is illustrated in Figure 6. 1.

The liquid reaction product was quantified and identified by GC-FID and GC-MS respectively. For the GC-FID analysis, gas-chromatography vials of 1.5ml were filled with 50mg of 1-Nonene used as internal standard to quantify the amount of olefin remaining followed by 0.5ml of the reaction product.

2.3 Analyses

The GC-MS was used to identify the reaction products. The instrument used was the same described in Section 2.3 of Chapter 3. The temperature program started at 30 °C, holding that temperature for 2 min; the oven was ramped up to 70 °C at a rate of 2.5 °C/min, held for 2 min and then raised up until 130°C at a rate of 10°C/min. The transfer line was kept at 325 °C, the injection volume was 1µl and the split ratio was 100:1. The carrier gas was Helium at a flow rate of 1 ml/min. The product identification was done comparing the reaction products spectra with that of the NIST MS Search 2.0 – Mass Spectra Library.

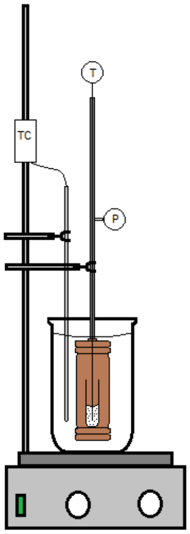


Figure 6. 1. Representation of the experimental set up used for the hydrogenation

2.4 Calculations

Taking as model reaction the following:

$$Olefin + H_2 \xrightarrow{Pt/C,60C} Alkane$$
$$A \quad + B \xrightarrow{Pt/C,60C} \quad C$$

The conversion was defined as:

$$X_A = \left[\frac{Moles\ of\ A\ reacted}{Moles\ of\ A\ fed}\right] \qquad \text{Equation 6. 1}$$

Taking into account that the type of reactor employed was a batch reactor, it is clear that the reagent will keep reacting inside the reactor as time goes, until is completely depleted or equilibrium is reached. Thus, conversion is a function of the time reagents are inside the reactor, then the moles of A reacted (consumed) can be expressed as:

$$Moles\ of\ A\ consumed = \left[Moles\ of\ A\ fed\right] \bullet \left[\frac{Moles\ of\ A\ reacted}{Moles\ of\ A\ fed}\right] \qquad \text{Equation 6. 2}$$
$$Moles\ of\ A\ reacted \ = \qquad \left[N_{A0}\right] \qquad \bullet \qquad X_A$$

Then, the moles of A remaining (unreacted) in the reactor after a time t, are:

$$\begin{array}{ccccc} \begin{matrix} Moles\ of\ A\ remaining \\ in\ a\ time,\ t \end{matrix} & = & \begin{bmatrix} Moles\ of\ A\ fed \\ in\ time,\ t=0 \end{bmatrix} & - & \left[Moles\ of\ A\ consumed \right] \\ \left[N_A\right] & = & \left[N_{A0}\right] & - & \left[N_{A0}\right]X_A \end{array} \quad \text{Equation 6. 3}$$

Rearranging Equation 6.3 to express the conversion in terms of the moles of A fed and the moles remaining in after a time t, one gets:

$$X_A = \frac{N_{A0} - N_A}{N_{A0}} \quad \text{Equation 6. 4}$$

Using the calibration curve of each analyte, the information for the number of moles fed and the moles remaining inside the reactor were calculated as a function of time. The instrument gave the amount in mg present in the sample and using the molecular weight, the mass in weight was transformed into mass in moles.

2.5 Calibrations

In this work calibration for the quantification of the identified reaction products was not done; instead calibrations to quantify the consumption of the feed olefin was performed. For such purpose, following the methodology explained in section 2.4 of Chapter 3 a calibration curve was developed for each compound studied. Based on that, the exhaustion of the compound of interest could be followed. Four calibration curves were done from the experimental work developed in that stage of the project, for this stage five calibration curves more were done. As was mentioned in the materials section, in the case of the branched conjugated diolefin the compound purchased was a mixture of stereoisomers perfectly distinguishable one from the other by chromatography. Calibration curves were developed for the individual species of 3-methyl-1,3-pentadiene stereoisomers that are present in a proportion 70-30 *trans* to *cis*. Same observation has to be made for *trans*-1,3-pentadiene that contained cyclopentene in a proportion of diolefins to cyclo-olefin of 90:10 approximately. All the calibration curves for the GC-FID can be seen in the Apendix A1, Figures A1.1 and Figure A1.2.

3. Results

3.1 Feed olefin concentration with time

To have comparable results, along with the pressure of hydrogen and the temperature, the concentration of the starting solution remained constant to an approximate value of 8.2×10^{-2}M. As was mentioned earlier in the chapter, the reactions for each time were performed in triplicate, those results were averaged and the value of concentration shown was obtained from that calculation together with the value of one sample standard deviation.

Table 6. 2 summarizes the change in concentration of the feed olefin during the five minutes of reaction for all the experiments carried out. For the first three compounds, the initial concentration feed olefin has a reported value for the standard deviation different than zero, because more than one mother solution was prepared to do those experiments, whereas a single mother solution was used for the other compounds.

Table 6. 2. Variation in the concentration in [mol/L] of olefins fed with time and their standard deviation. All the values in the table must be multiplied by 10^{-2}

	Reaction time [min]					
Feed Olefin	**0**	**1**	**2**	**3**	**4**	**5**
trans-1,3-Pentadiene	8.17±0.12	6.16±0.51	4.74±0.81	3.22±0.49	1.20±0.47	0.32±0.08
3-Methyl-1,3-pentadiene	8.19 ±0.02	7.34±0.10	6.61±0.10	6.22±0.13	5.65±0.20	4.56±0.33
cis-3-Methyl-1,3-pentadiene	2.45±0.02	2.20±0.03	2.09±0.12	1.93±0.06	1.78±0.07	1.37±0.17
trans-3-Methyl-1,3-pentadiene	5.74±0.01	5.13±0.07	4.52±0.20	4.26±0.18	3.87±0.14	3.19±0.17
Cyclohexene	8.21± 0.09	7.59±0.35	6.64±0.22	5.71±0.66	4.31±0.52	2.64±0.67
1-Methyl-cyclohexene	8.25 ±0.00	7.13±0.27	6.90±0.13	6.30±0.32	5.94±0.30	5.37±0.64
1,3-Cylclohexadiene	8.40 ±0.00	7.87±0.15	7.19±0.09	6.88±0.12	6.08±0.10	4.72±0.07
Vinylcyclopentane	8.04 ±0.00	7.71±0.06	7.52±0.08	7.37±0.12	6.97±0.08	6.61±0.18
1,4-Pentadiene	8.19 ±0.00	5.02±0.08	4.79±0.36	0.42±0.14	0.25±0.00	0.08±0.00
1-Hexene	8.29 ±0.00	6.11±0.11	4.79±0.41	3.02±0.49	1.15±0.19	0.67±0.26

In Figure 6.2 one can observe that except for the 1,4-pentadiene, the behavior of the concentration of all compounds with time appeared to be linear. During the first minute of the reaction according to Table 6.2, all the compounds except for the acyclic diolefins and the control olefin decreased their concentration by 4 to 13%, which was interpreted as having a moderate reaction rate.

Although it is possible to stablish an order numerically speaking, as a general observation the average values for the concentration of the feed olefin by that time are around the same (see Table 6.2). In the case of trans-1,3-pentadiene, 1,4 pentadiene and 1-hexene, initially the reaction was fast respect to the other compounds, after one minute of reaction conversions over 24% were seen. From that time a tendency can be seen and *trans*-1,3-pentadiene, 1,4-pentadiene and 1-hexene are molecules distinguished from the group, their concentration decreased rapidly, being 1,4-pentadiene the one with the fastest reaction rate among all and trans-1,3-pentadiene and 1-hexene with a similar reactivity. The standard deviation error bars show that there is a considerable scattering among the values collected for trans-1,3-pentadiene, cyclohexene and 1-hexene.

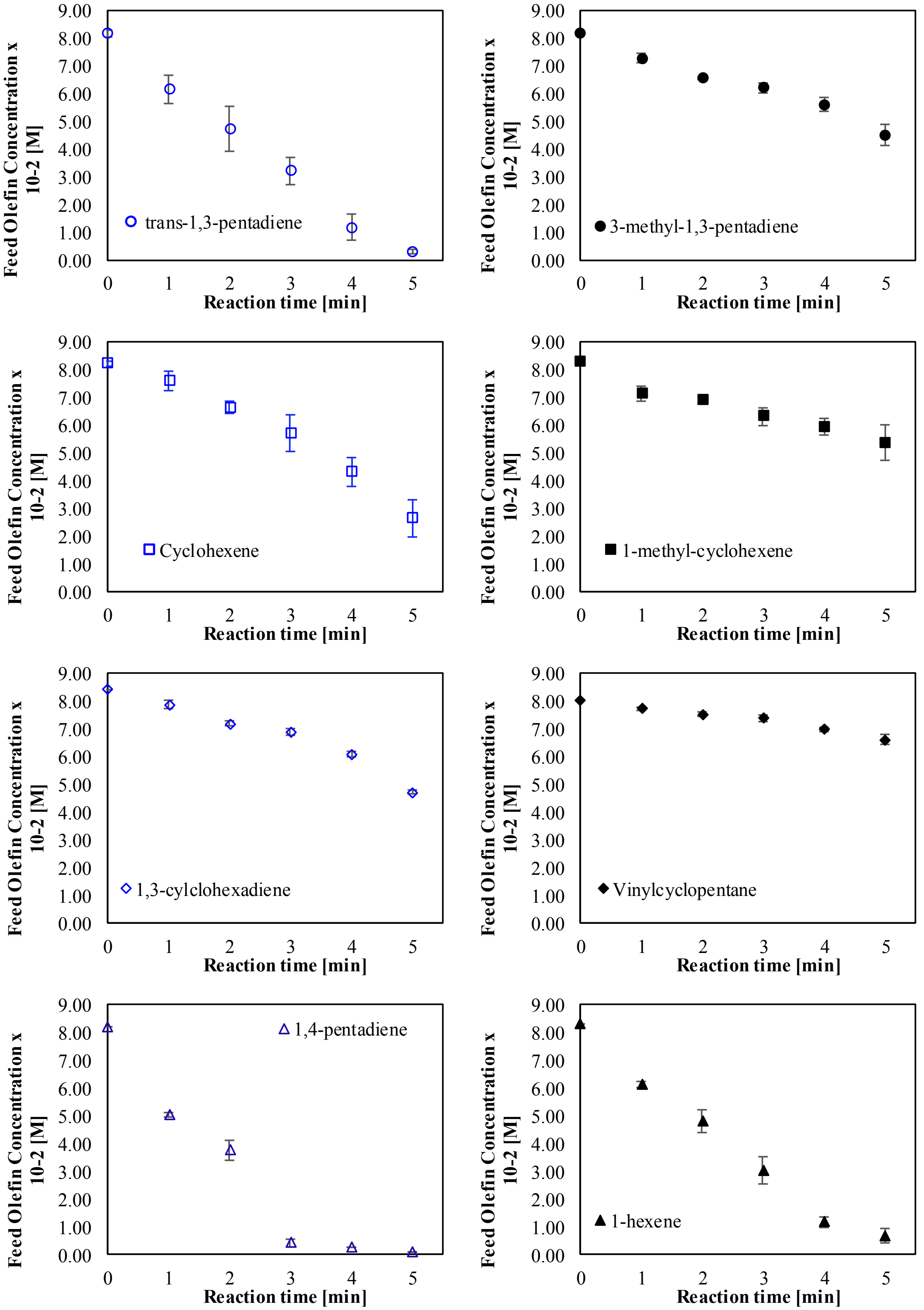


Figure 6. 2. Change in concentration of feed olefins as a function time.

3.2 Product distribution with time

The compounds produced during hydrogenation were identified by means of the GC-MS analysis. The products seen were not compared with analytical standards. The compounds taken as intermediates were the expected hydrogenated species. Comparison of the mass spectra of the obtained intermediate and the compound suggested by the NIST library supported the identification. Although their concentration was not rigorously determined (calibration curves for the intermediate and final products were not developed), using the information of the GC-FID the relative amount of reaction product was calculated based on the area of the peak of interest related to the sum of the areas of all peaks detected. Cyclohexene, 1-methyl-cyclohexene, vinylcyclopentane and 1-hexene did not give any other olefinic products, those molecules went from the olefin to the fully hydrogenated species. The remaining had more than one product as expected due to their nature (all of them have two double bonds in their structure). The plot of the relative product amount for all feed olefins is shown from Figure 6.3 to Figure 6.10. For more clarity a list of the identified products for all reactions and their relative amount versus time is given in Table 6. 3.

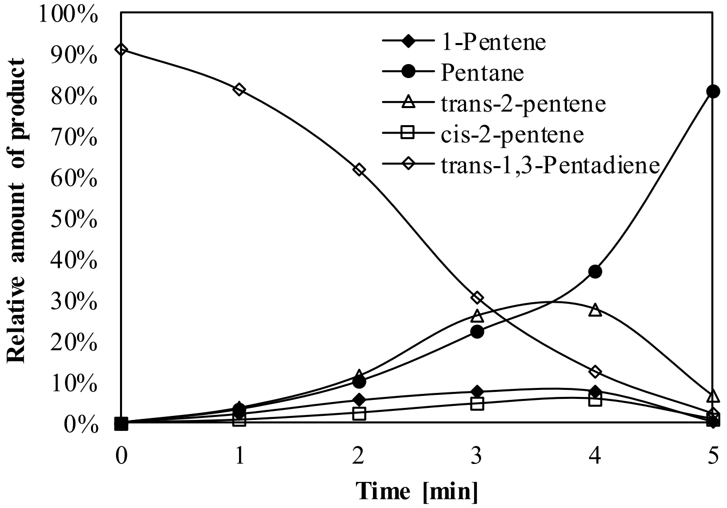


Figure 6. 3. Relative amount of product observed during hydrogenation of *trans*-1,3-pentadiene.

Table 6. 3. Relative amount of product (expressed as percentage) versus time for all olefins investigated.

Compound	**Product**	**Time [min]**					
		0	**1**	**2**	**3**	**4**	**5**
trans-1,3-pentadiene	1-Pentene	0.0±0.0	2.1±0.7	5.4±1.2	7.5±1.5	7.7±2.1	0.2±.1
	Pentane	0.0±0.0	3.3±1.3	10.0±0.7	21.7±2.7	36.9±5.9	80.9±6.1
	trans-2-pentene	0.0±0.0	3.6±0.6	11.2±0.2	26.2±4.0	27.8±2.3	6.6±5.3
	cis-2-pentene	0.0±0.0	0.7±0.2	2.4±0.7	4.6±0.9	5.8±0.7	0.9±0.9
	trans-1,3-pentadiene	91.0±0.0	81.1±0.1	61.8±5.6	30.7±6.5	12.6±4.8	2.2±2.7
Cyclopentene	Cyclopentene	9.0±0.0	9.2±0.1	8.6±0.0	7.0±1.6	5.7±1.2	0.0±0.0
	Cyclopentane	0.0±0.0	0.1±0.1	0.7±0.2	2.3±1.6	3.5±1.2	9.1±0.1
3-methyl-1,3-pentadiene	3-Methyl-1-Pentene	0.0±0.0	1.0±0.1	1.3±0.2	1.6±0.2	2.9±1.7	3.8±0.4
	3-Methyl-Pentane	0.0±0.0	2.9±0.1	5.0±1.3	9.9±0.4	13.4±3.7	19.3±0.9
	cis-3-methyl-2-pentene	0.0±0.0	0.7±0.1	1.4±0.5	1.6±0.3	3.5±2.0	3.3±0.4
	trans-3-methyl-2-pentene	0.0±0.0	2.8±0.2	3.9±0.4	8.0±0.7	12.0±6.9	16.5±1.0
	cis-3-Methyl-1,3-Pentadiene	30.2±0.0	28.6±0.7	26.3±0.6	24.4±0.4	19.2±1.1	16.0±0.5
	trans-3-Methyl-1,3-Pentadiene	69.8±0.0	63.9±0.4	62.2±2.3	54.6±0.8	49.1±4.8	41.0±0.3
Cyclohexene	Cyclohexane	0.0±0.0	7.6±1.3	24.0±5.9	31.6±5.0	45.8±3.4	70.3±6.9
	Cyclohexene	100.0±0.0	92.4±1.3	76.0±6.1	69.6±6.0	54.2±4.3	33.7±6.9
1-methyl-cyclohexene	Methylcyclohexane	0.0±0.0	2.1±0.4	6.1±1.0	10.8±0.7	18.7±0.4	26.2±2.5
	1-Methyl-Cyclohexene	100.0±0.0	97.9±0.4	93.9±0.9	88.8±0.6	81.3±0.4	73.8±2.5
1,3-cycloheptadiene	Cyclohexane	0.5±0.0	1.5±0.4	2.8±0.6	4.5±0.9	7.4±0.2	8.9±0.6
	1,3-Cyclohexadiene	98.2±0.0	94.5±1.7	88.3±0.9	83.1±3.0	74.6±0.5	68.3±0.4
	Cyclohexene	1.3±0.0	4.0±1.3	8.8±0.3	11.6±1.8	18.1±0.1	22.9±0.5
Vinylcyclopentane	Vinycyclopentane	100.0±0.0	96.5±0.8	94.2±0.5	92.5±0.9	87.5±0.2	82.2±1.7
	Ethylcyclopentane	0.0±0.0	3.5±0.8	5.8±0.4	7.6±0.7	12.5±0.2	17.8±1.6
1,4-pentadiene	1,4-Pentadiene	100.0±0.0	74.5±3.0	49.8±5.1	7.6±0.8	0.4±0.2	0.1±0.1
	1-Pentene	0.0±0.0	12.4±1.4	21.8±1.3	18.9±1.0	0.0±0.0	0.0±0.0
	Pentane	0.0±0.0	11.3±1.5	25.3±3.9	68.5±1.6	99.6±0.2	99.5±0.6
	trans-2-pentene	0.0±0.0	1.2±0.1	2.0±0.2	3.2±0.4	0.0±0.0	0.0±0.0
	cis-2-pentene	0.0±0.0	0.6±0.1	1.1±0.1	1.6±0.4	0.0±0.0	0.0±0.0
1-Hexene	1-Hexene	100.0±0.0	79.4±1.8	61.9±5.7	38.6±8.2	12.8±1.1	2.2±0.4
	n-Hexane	0.0±0.0	20.6±1.8	38.1±5.6	62.0±7.3	87.2±1.3	97.8±0.5

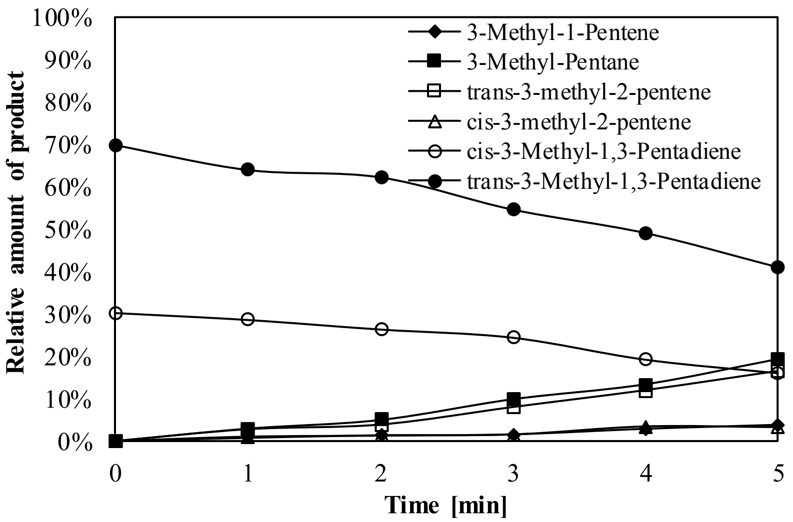


Figure 6. 4. Relative amount of product during hydrogenation of 3-methyl--1,3-pentadiene

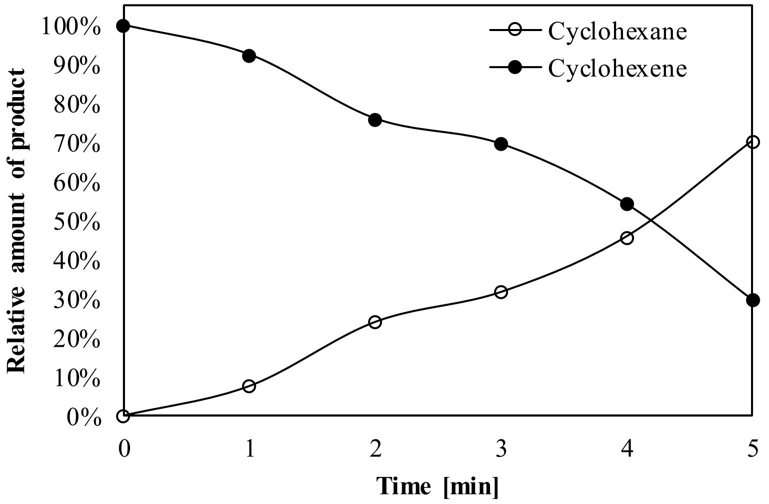


Figure 6. 5. Product selectivity during hydrogenation of cyclohexene.

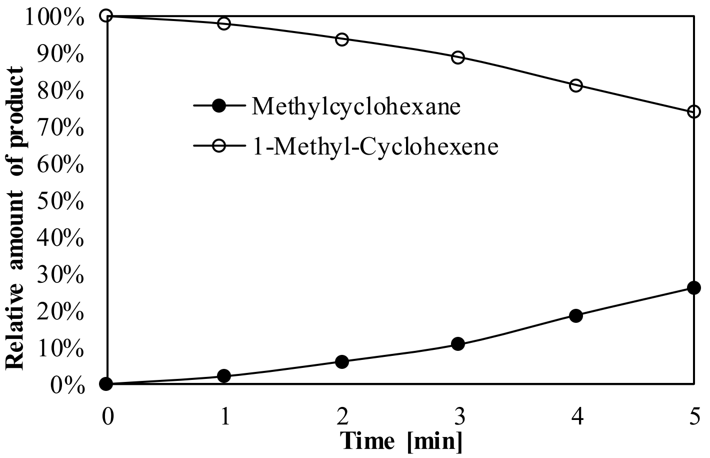


Figure 6. 6. Relative amount of product during hydrogenation of 1-methylcyclohexene.

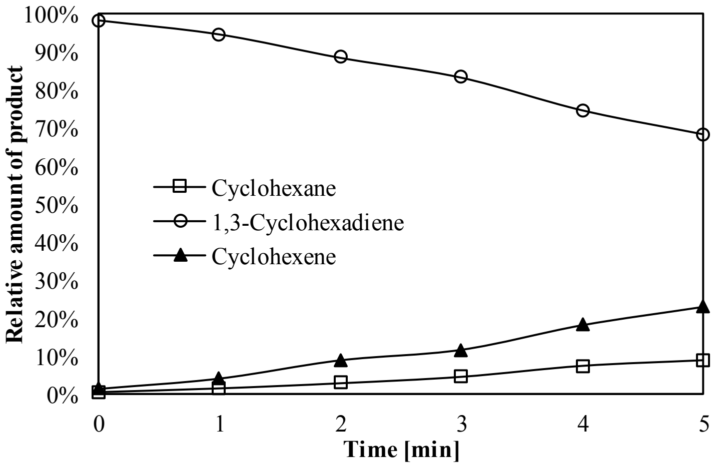


Figure 6. 7. Relative amount of product during hydrogenation of 1,3-cyclohexadiene.

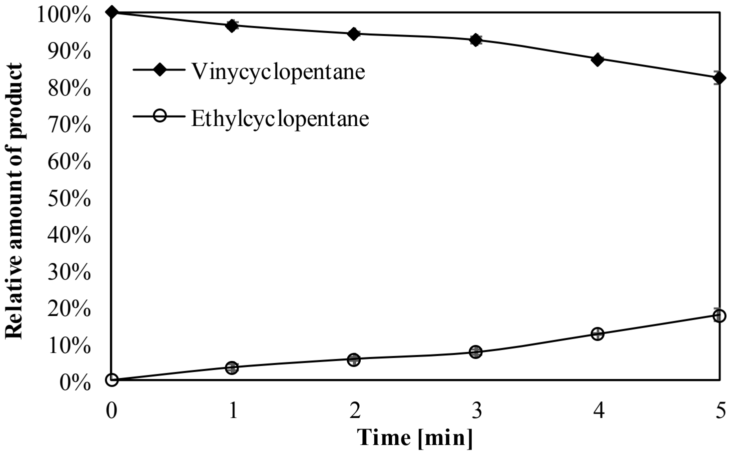


Figure 6. 8. Relative amount of product during hydrogenation of vinylcyclopentane.

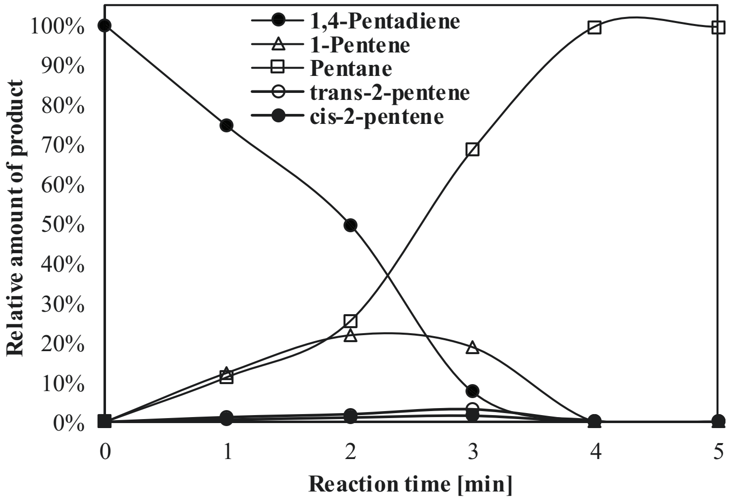


Figure 6. 9. Relative amount of product during hydrogenation of 1,4-pentadiene.

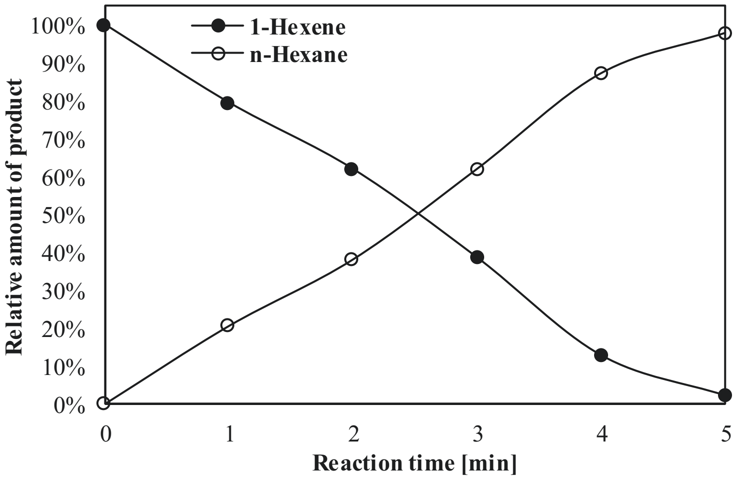


Figure 6. 10. Relative amount of product during hydrogenation of 1-hexene.

4. Discussion

4.1 Feed olefin conversion with time

With the information provided in Table 6.2, the conversion of feed olefin with time was calculated as indicated by Equation 6.4. The calculated data is given in Table 6.4. The information regarding the conversion as a function of time for each compound is illustrated in Figure 6.11. To compare, the compounds were grouped in two, those with an aliphatic chain and those with a cyclic chain. Among the open chain compounds are: *trans*-1,3-pentadiene, 3-methyl-1,3-pentadiene, 1,4-pentadiene and 1-hexene. If one looks at the plots of conversion versus time, several things are worth pointing out. 1,4-pentadiene (isolated diolefin) reaches almost complete conversion whereas *trans*-1,3-pentadiene (conjugated diolefin), 3-methyl-1,3-pentadiene and 1-hexene reached 96%, 45% and 92% conversion respectively after 5 minutes of reaction.

Table 6. 4. Conversion of feed olefins studied expressed as percentage through the reaction time and their corresponding standard deviation.

	Reaction time [min]					
Feed Olefin	**0**	**1**	**2**	**3**	**4**	**5**
trans-1,3-Pentadiene	0.0±0.00	24.59± 7.08	41.88±10.87	60.54±6.34	85.21±6.01	96.00±1.00
3-Methyl-1,3-pentadiene	0.0±0.00	10.92±1.92	19.81±0.52	23.41±2.37	31.18±3.16	44.65±4.37
cis-3-Methyl-1,3-pentadiene	0.0±0.00	9.69±0.96	14.39±5.19	19.36±3.04	26.93±2.21	43.82±6.52
trans-3-Methyl-1,3-pentadiene	0.0±0.00	10.21±0.28	20.97±3.90	25.39±2.70	32.07±2.13	44.27±2.72
Cyclohexene	0.0±0.00	7.66±3.99	19.19±3.257	30.46±8.76	47.48±6.84	67.75±8.51
1-Methyl-cyclohexene	0.0±0.00	13.48±3.29	16.33±1.52	23.58±3.84	28.00±3.61	34.91±7.83
1,3-Cylclohexadiene	0.0±0.00	6.37±1.81	14.45±1.03	18.07±1.39	27.58±1.22	43.87±0.81
Vinylcyclopentane	0.0±0.00	4.47±0.72	6.92±0.98	8.68±1.55	13.68±1.02	18.12±2.17
1,4-Pentadiene	0.0±0.00	38.64±1.04	54.30±4.39	95.08±1.66	97.00±0.00	99.00±0.00
1-Hexene	0.0±0.00	25.48±1.28	41.59±4.98	63.22±5.97	85.98±2.35	91.86±3.16

The isolated diolefin is almost totally converted within 3 minutes of reaction, showing a more reactive behavior than the conjugated diolefin, which was not expected, because usually conjugated diolefins are more reactive than their isolated counterparts. By including a branch in the structure of the *trans*-1,3-pentadiene, the conversion is greatly affected; after the 5 minutes of reaction, 3-methyl-1,3-pentadiene reached approximately half of *trans*-1,3-pentadiene conversion. 1-Hexene has similar behavior to *trans*-1,3-pentadiene, according to Table 6.4 the value of conversion for those compounds is almost overlapping.

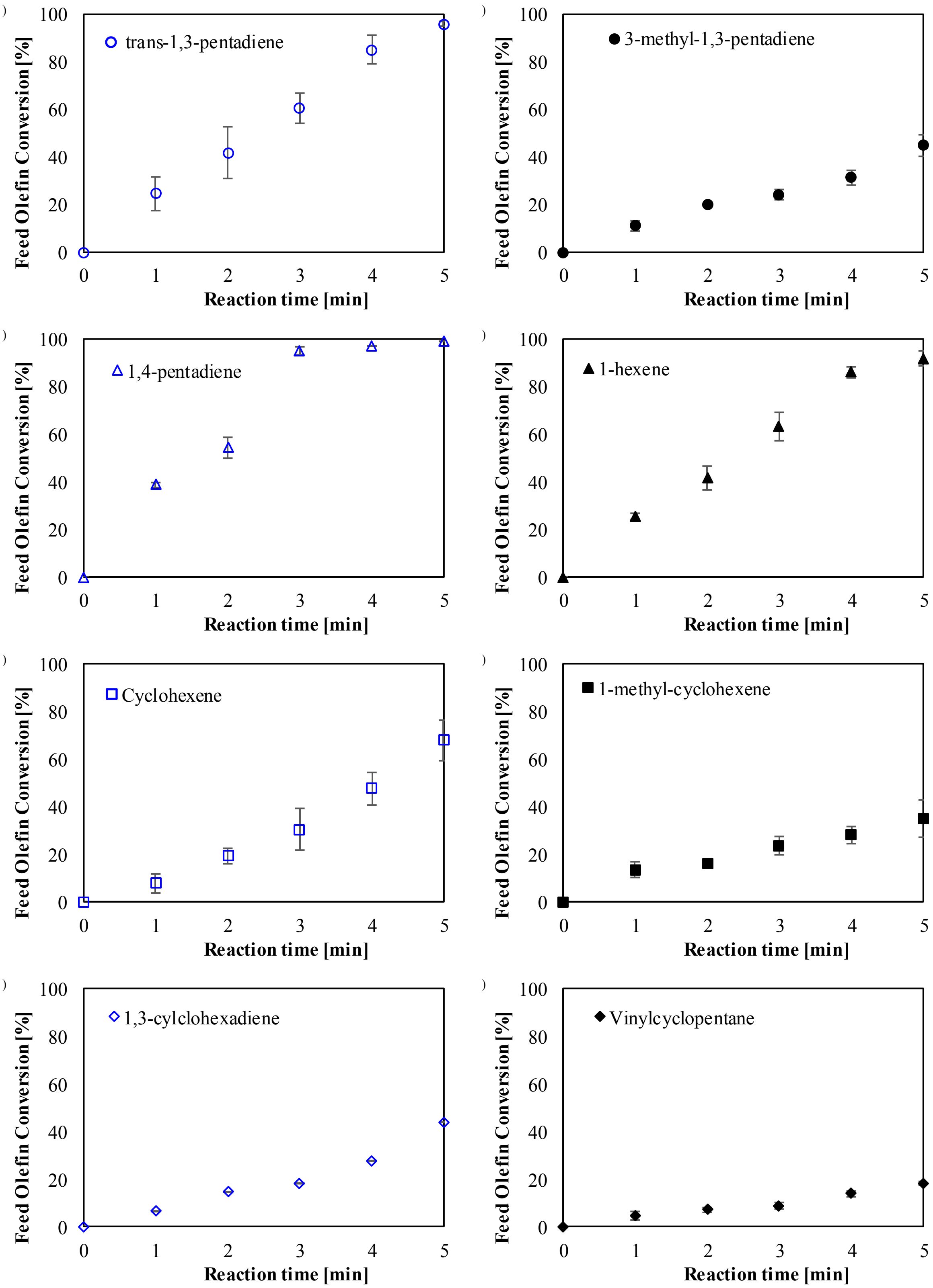


Figure 6. 11. Change in conversion of feed olefins as a function of time. Upper four plots correspond to the aliphatic chain olefins, the later four represent the compounds with a cycle in their structure.

In the case of the cyclic compounds, the figure shows that cyclohexene hydrogenation has the highest conversion among all; close to 68% of the compound is converted in the time range studied. Comparing the value of conversion of cyclohexene and 1-methyl-cyclohexene during the first minute of reaction, the first one is close to half of the later showing that initially the hydrogenation of the branched cycloalkene was faster. That behavior is then inverted and cyclohexene remains above the curve of 1-methyl-cyclohexene for the rest of the time. When an extra double bond is present in the six membered ring the conversion with respect to the mono-unsaturated species, decreases. 1,3-Cyclohexadiene converts slower compared to the 1-methyl-cyclohexene until four minutes, were the conversion of the later is lower than the diolefin. As seen in the plot of the acyclic olefins, there is also evidence of a strange shape when the data are plotted for 1-methyl-cyclohexene and 1,3-cyclohexadiene, is as if changing the structure of the base molecule (cyclohexene) had a marked influence in the way the reaction is taking place. Regarding to vinylcyclopentene it is obvious that it is the least reactive molecule. The highest conversion obtained when working with that molecule was around 18%.

4.2 Shape of conversion versus time plots

There is something particular about the shape of the curves of conversion versus time in Figure 6.11. In the case of *trans*-1,3-pentadiene the actively reacting period can be described by a line, as well as in the case of 1-hexene and vinylcyclopentane. In the case of 3-methyl-1,3-pentadiene, cyclohexene, 1-methyl-cyclohexene, 1,3-cyclohexadiene and 1,4-pentadiene, Figure 6. 11 shows some kind of s-shape between 2 and 3 minutes, that shape is subtle in the first four compounds mentioned. The s-shape is more pronounced in 1,4-pentadiene. The curve has a change in concavity that creates a staggered configuration. The figure shows that in the first 2 minutes the reaction was slow and after that time it accelerates.

Such behavior is described by the concept of induction period and has been reported in the hydrogenation of nitrobenzene on Au-ZrO_2; the researchers related the induction period to the amount of active sites available to chemisorb hydrogen molecules.[6] In the liquid-phase hydrogenation of carboxylic acids and ketones at room temperature, for different metal catalyst supported on nanoporous carbon there was also evidence of that phenomena; in the study was concluded that the rate determining step in the process was the adsorption of hydrogen on the metal or the activation of the metal hydride.[7] A concrete reason to explain the s-shape in the plot conversion versus time has not been stablished; mass transport limitations were considered.

The possibility of having external diffusion limitations was taken into account. To guarantee the effective delivery of the gas into the liquid phase, there are two aspects to consider: the hydrogen dissolution in the solvent and the diffusion into the liquid bulk. The hydrogen dissolution can be determined by Henry's Law; values for the Henry's constant of hydrogen in decane were not found, but literature reports the solubility of hydrogen in decane at different temperatures.[8] They found the molar fraction of the gas in the solvent for different pressures of hydrogen loaded and different temperatures. Using the information found in the cited reference, the molar fraction of hydrogen in decane was calculated at 50°C. The result was that at a hydrogen pressure of 0.41MPa, the molar fraction of the gas in the liquid is 0.3×10^{-2}. That molar fraction is equivalent to a molar concentration of 1.6×10^{-2}M. The reaction was done at 60°C, so the gas should have had a lower solubility. Although the approximate value of hydrogen concentration in the liquid is lower than the feed olefin (8.2×10^{-2} M) it cannot be taken as a bad solubility of the gas, still, there was a considerable amount of hydrogen available to migrate into the liquid phase as soon as the hydrogen dissolved was consumed. On the other hand, the diffusion of the gas to the liquid bulk can be measured by the gas-liquid mass transfer rate, which is proportional to the volumetric mass transfer coefficient. That coefficient is determined experimentally, but that was not done in the work developed in the laboratory. It depends in great part of the turbulence of the system and considering that the system was under constant and high stirring (1400 rpm) it is highly likely that the diffusion of the hydrogen through the solvent was effective.

Intra-particle diffusion limitations could be the reason for such shape in the conversion versus time curves, but the experimental procedures to verify that, were not the purpose of this work hence were not done to corroborate their presence. Another aspect that was taken into account was the diffusivity of each olefin in the solvent, decane. It is also important to take into consideration how fast each compound diffused through decane. The binary liquid diffusion coefficients for each compound and decane at infinite dilution were calculated according to the Hayduk and Minhas correlation[9] shown in Equation 5. 1:

$$D^{o}_{AB} = 13.3x10^{-8} * T^{1.47} * \frac{\eta_B^{\varepsilon}}{V_A^{0.71}} \quad where \quad \varepsilon = \left(\frac{10.2}{V_A}\right) - 0.791, \quad for \;\; normal \;\; parafin \;\; solvents$$

Equation 5. 1

and, D_{AB}^{o} [cm^2/s] is the mutual diffusion coefficient of solute A at very low concentrations in solvent B; T [K] is the temperature of the solution; V_A [cm^2/mol] is the molar volume of solute A at its normal boiling temperature and η_B [cP] is the viscosity of solvent B.

Based on the results of the calculation, shown in Table 6. 5, the diffusion coefficients have the same order of magnitude and are relatively close one to another, which is a confirmation that differences in the reaction rate of the compounds studied are not related with the facility of each compound to diffuse through the solvent, but their intrinsic reactivity.

Table 6. 5. Diffusion coefficient of solute A in decane

-	**A**	**D_{AB}^{o}**
1	*trans*-1,3-pentadiene	2.77E-05
2	3-methyl-1,3-pentadiene	2.44E-05
3	cyclohexene	2.54E-05
4	1-methylcyclohexene	2.27E-05
5	1,3-cyclohexadiene	2.65E-05
6	vinylcyclopentane	2.27E-05
7	1,4-pentadiene	2.77E-05
8	1-hexene	2.35E-05

Another aspect that has to be taken into account is the competitive adsorption between the feed olefin and the mono-olefins produced after reaction, if the catalyst surface is preferentially covered by the mono-olefins, their formation could decrease the amount of active sites available to adsorb new molecules of the feed olefin reaching the catalyst surface, causing a slower reaction rate. That form of competitive adsorption leading to apparent inhibition of diolefin hydrogenation could have continued until the full hydrogenation of the mono-olefin, which was desorbed allowing the feed olefin to adsorb.

4.3 Reaction network

Based on the plots of relative amount of product shown in Figure 6.3 to Figure 6.10 the following observations were made. During the reaction of *trans*-1,3-pentadiene the products formed were: *trans*-2-pentene, *cis*-2-pentene, 1-pentene and the fully saturated hydrocarbon, pentane; there was no evidence of double bond migration or skeletal rearrangement. In Figure 6.3 it can be seen that the product formation is oriented towards the most thermodynamically stable product, *trans*-2-pentene as can be verified, by heat of hydrogenation for that molecule. The information regarding the heat of hydrogenation of the studied compounds and the heat for some of the intermediates formed in the reactions carried is reported in the literature and compiled in Table 6.6.

Table 6. 6. Heats of hydrogenation of studied olefins and some others of interest.

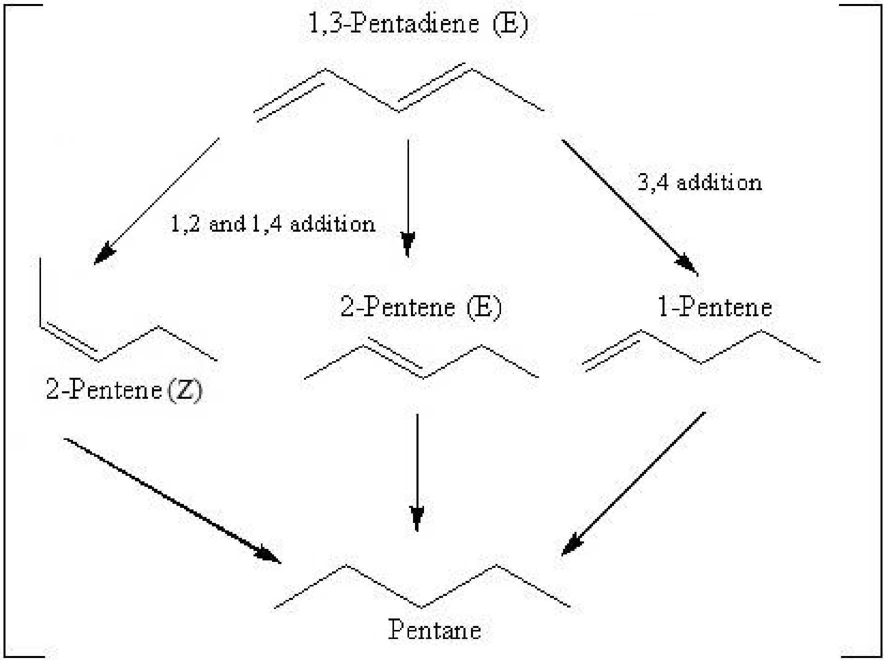
Compound	**-ΔH_r**[kJ/mol]
trans-1,3-pentadiene	226.4 ± 0.63[10]
Cyclohexene	118.6 +2.5[11]
1-methyl-cyclohexene	106.3 ± 0.46[12]
1,3-cylclohexadiene	224.4 ± 1.2[13]
Vinylcyclopentane	118.8 +0.8[11]
1,4-pentadiene	252.0 ± 0.63[14]
1-Hexene	125. ± 3.[15]
Cyclopentene	109.6±0.8[11]
1-Pentene	122.6 ± 2.4[16]
cis-2-Pentene	119.2±.8[17]
trans-2-Pentene	113.8±.8[17]
trans-3-methyl-2-pentene	110.1 ± 0.56[18]
cis-3-methyl-2-pentene	110.6 ± 0.44[18]
3-methyl-1-pentene	124.6 ± 0.54[18]

According to Table 6.3 after 1 min of reaction, that was already the product present in higher proportion; the amount of 1-pentene, pentane, *trans*-2-pentene and *cis*-2-pentene was 2.1, 3.3, 3.6 and 0.7% respectively. The product of the 3,4 addition, 1-pentene is produced in greater proportion respect to *cis*-2-pentene, but during the reaction time studied, its relative amount never goes higher than 8%. Regarding to the formation of Pentane, Figure 6.3 shows that almost until four minutes of reaction, the relative amount of that product is lower than that of *trans*-2-pentene. After that time, it rapidly increases. That matches with the decrease in the concentration of diene that by that time has a conversion of 85%. Previous works on the hydrogenation of *trans*-1,3-pentadiene using Platinum as catalyst have postulated that there is a competitive adsorption between the diene and the half hydrogenated species, the catalyst surface is covered by more molecules of the polyunsaturated compound which causes the desorption of the mono-olefin formed; when the concentration of diene on the metal drops to a low value, complete hydrogenation can be achieved.[19] It has also been reported that when conjugated diolefins are hydrogenated on Palladium, the isomerization typically observed when working with that catalyst is not seen until the diene concentration on the catalyst surface is lower to a point where it does not displace the olefins formed.[20] Maybe that is the explanation for the rapid formation of pentane after 3 minutes.

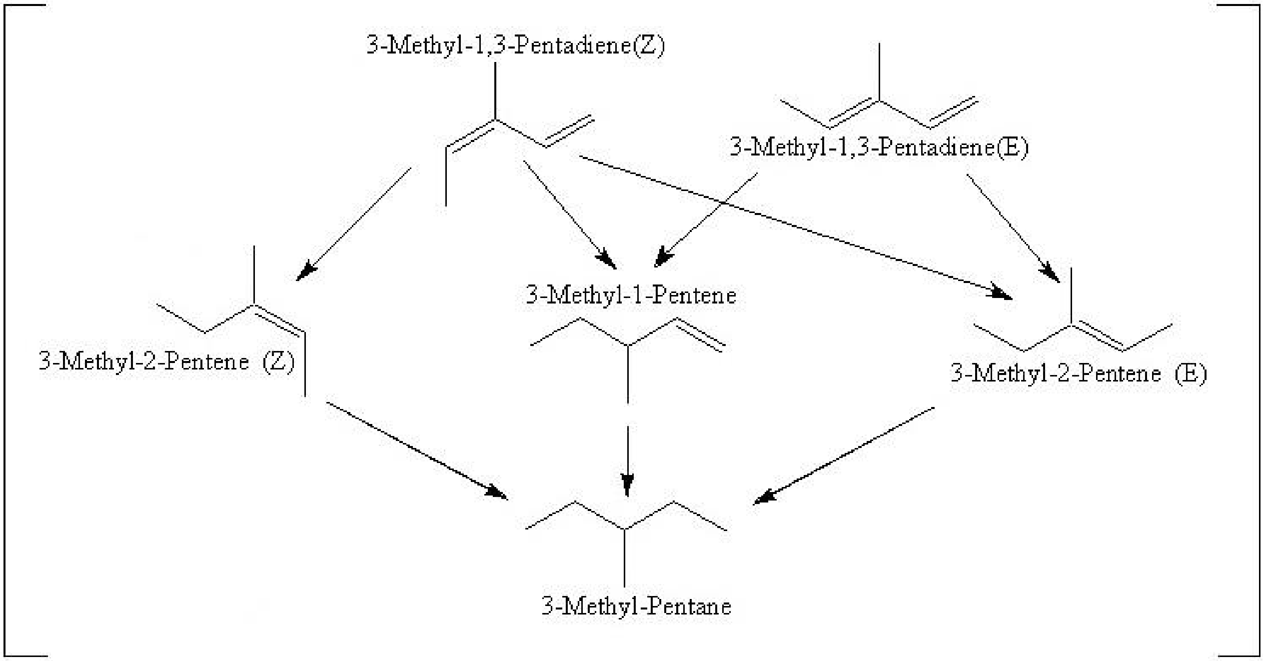
Figure 6. 4 shows the relative amount of product for 3-methyl-1,3-pentadiene. The intermediate products formed during the hydrogenation of that compound are the anticipated from 1-2, 1-4 and 3-4 addition of hydrogen, *cis*-3-methyl-2-pentene, *trans*-3-methyl-2-pentene, 3-methyl-1-pentene along with the fully hydrogenated alkane 3-methyl pentane. Among those four compounds two groups can be distinguish in Figure 6.4, based on their similar relative amount. 3-methyl-1-pentene, the product from the 3-4 hydrogen addition to *trans* and *cis*-3-methyl-1,3-pentadiene, has similar selectivity to *cis*-3-methyl-2-pentene, the product from the 1-2 hydrogen addition to *cis*-3-methyl-1,3-pentadiene. The other two compounds with similar proportion are 3-methyl-pentane (fully hydrogenated product) and *trans*-3-methyl-2-pentene (1-2 and 1-4 addition products of *trans* and *cis*-3-methyl-1,3-pentadiene respectively). The proportion of the first group is small, their relative amount never goes higher than 3.8%; whereas the compounds in the second group have a relative amount as high as 19.3%, with the completely hydrogenated compound being present since the beginning of the reaction. That is showing that the most stable species, *trans*-3-methyl-2-pentene is formed; it is known that *trans* isomers are more stable than *cis* configurations, which is corroborated with the heat of hydrogenation (taken as a measure of the stability of the molecule) provided in Table 6.6.

In this work, cyclohexene was hydrogenated to cyclohexane without the formation of other reaction products as can be seen in Figure 6.5. In the case of that compound, it has been reported that has propensity to aromatize when hydrogenation is taking place.[21] However, if the reaction temperature is low, which was the case of the present study, the hydrogenation reaction prevails and the product will be mainly the saturated cyclic hydrocarbon, as corroborated here. 1-Methylcyclohexene, vinylcyclopentane and 1-hexene, all compounds produced their corresponding saturated species, without the formation of isomers or other kind of compounds that could indicate an ongoing side reaction. Regarding to the cyclic conjugated diolefin the intermediate was the cyclohexene.

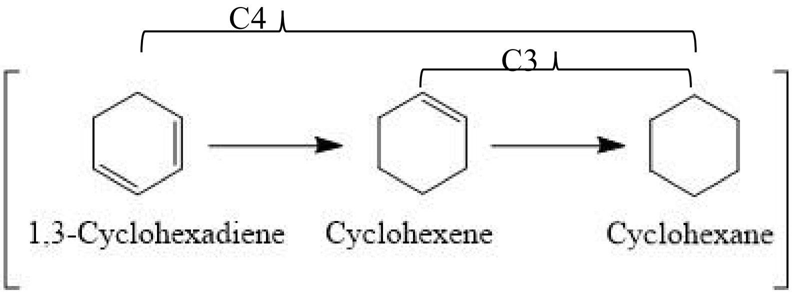
As could be predicted for the hydrogenation of 1,4-pentadiene, the main product was 1-pentene. It is well known that the nature of the catalyst has a major impact in the hydrogenation products, thus, when such reaction is carried out using Palladium as catalyst, the finding of products coming from isomerization of the double bond as well as hydrogenation is expected.[22,23] Evidence shows that isomerization of the double bond in the mono-alkene formed was present to a less extent. By the increase of conversion, the relative amount of the isomerization products also increased; the highest amount of the products *trans*-2-pentene and *cis*-2-pentene was 3.2 and 1.6% after three minutes of reaction. After that, all the intermediates went to pentane. There was no evidence of the formation of the more stable diene, 1,3-pentadiene, so isomerization of the double bond in the initial molecule was not present. Using the information extracted about the intermediates and final products of hydrogenation, a reaction network was proposed for each compound. The reaction networks developed are illustrated in Scheme 6. 1 to Scheme 6. 7.



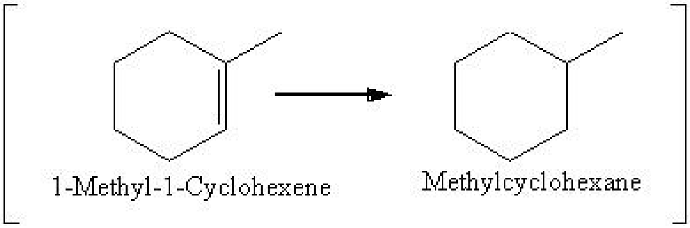
Scheme 6. 1. Proposed reaction network for hydrogenation of *trans*-1,3-pentadiene.



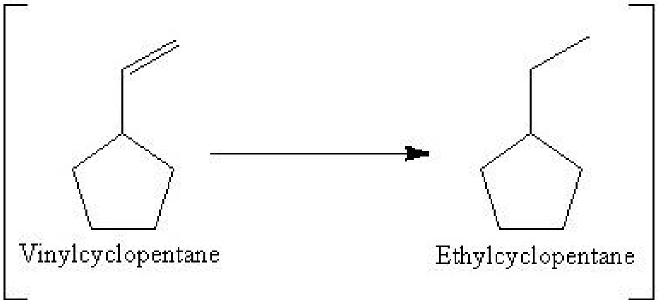
Scheme 6. 2. Proposed reaction network for hydrogenation of 3-methyl-1,3-pentadiene.



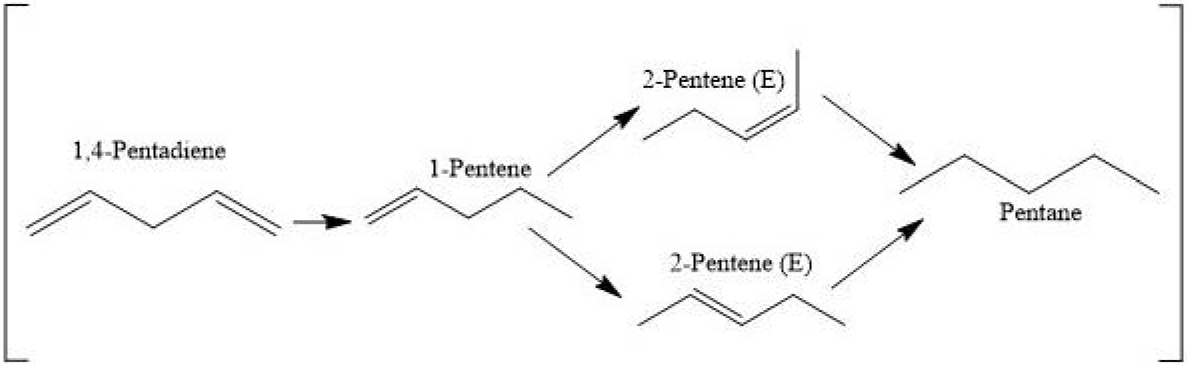
Scheme 6. 3. Proposed reaction network for hydrogenation of cyclohexene and 1,3-cyclohexadiene.



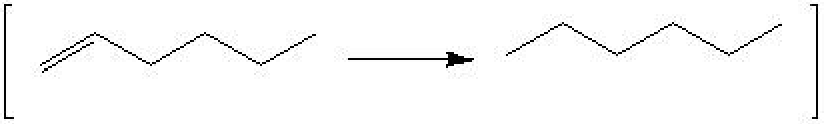
Scheme 6. 4. Proposed reaction network for hydrogenation of 1-methyl-cyclohexene.



Scheme 6. 5. Proposed reaction network for hydrogenation of vinylcyclopentane.



Scheme 6. 6. Proposed reaction network for hydrogenation of 1,4-pentadiene.



Scheme 6. 7. Proposed reaction network for hydrogenation of 1-hexene.

4.4 Relative reactivity sequence

Using the collected information for the change in concentration versus time, the initial reaction rate was calculated for all the compounds, to stablish an order in the reactivity between the olefins studied. Table 6.7 shows the results of such calculation.

Table 6. 7. Observed initial reaction rate for all compounds studied.

i	Compound	r_0 x10^{-2} [M*min^{-1}]
1	*trans*-1,3-Pentadiene	2.0
2	3-Methyl-1,3-pentadiene	0.9
3	Cyclohexene	0.6
4	1-Methyl-cyclohexene	1.1
5	1,3-Cylclohexadiene	0.5
6	Vinylcyclopentane	0.4
7	1,4-Pentadiene	3.2
8	1-Hexene	2.1

Taking into account the results shown in Table 6.7, the reactivity sequence based on the observed initial reaction rate in this specific study done at 0.5MPa (absolute) of hydrogen, 60°C and initial concentration of 0.08M was: 1,4-pentadiene > 1-hexene > *trans*-1,3-pentadiene > 1-methyl-cyclohexene > 3-methyl-1,3-pentadiene > cyclohexene > 1,3-cylclohexadiene > vinylcyclopentane.

An order in stability can be defined by comparing heats of hydrogenation (Table 6.6).[24] A small heat of hydrogenation is an indication of a more stable compound; if the starting alkene released less energy during the reaction, it was a low energy reactant. Molecules *trans*-1,3-pentadiene, 1,3-cylclohexadiene and 1,4-pentadiene have the highest value of heat of hydrogenation which makes sense if one takes into account that during hydrogenation of diolefins two double bonds are broken, hence more energy is liberated.

Conjugated olefins are well known for their higher thermodynamic stability compared to non-conjugated systems; that, due to the resonance structure that pi orbitals provide.[25] However being thermodynamically stable cannot be interpreted as being less reactive. Generally there is a rough relationship between stability seen from the enthalpy of hydrogenation and the relative rates of hydrogenation of unsaturated hydrocarbons.[26] When the diolefins are being hydrogenated, the energy released during reaction does not give information about the rate of the chemical reaction, is the energy of the transition states respect to the reagents what can give information of that matter. [27]

Previous studies done under mild conditions as well, but using Pd/alumina showed that hydrogenation of *trans*-1,3-pentadiene was faster than hydrogenation of 1,4-pentadiene with an initial first order rate constant of 0.028 min^{-1} compared to 0.016 min^{-1} for the isolated diolefin.[4] Having that in mind, it was expected for *trans*-1,3-pentadiene to be more reactive than 1,4-pentadiene and yet the acyclic isolated diolefin reacts faster than *trans*-1,3-pentadiene (see Figure 6.11).

Now if the purity of *trans*-1,3-pentadiene is brought into the picture an explanation can be given. The conjugated diolefin has a purity of 90%, having cyclopentene as the main impurity. It could be that the cycloalkene present slows down the reaction through competitive adsorption, which has happened in systems diolefins-cycloalkene. The reactivity of 2,5-dimethyl-2,4-hexadiene in the presence of cyclohexene under HDS conditions over CoMo-S/γ-Al2O3 catalyst was studied at several temperatures;[3] the study showed a strong inhibition effect caused by cyclohexene since the conversion for the hydrogenation of the diolefin decreased from 100% to 54% when done without and with the cyclo-olefin respectively. In that study it was also demonstrated that cyclohexene not only reduced the reaction rate, but changed the product distribution of 2,5-dimethyl-2,4-hexadiene. As was mentioned earlier in this study (see Figure 6.4) *trans*-2-Pentene and 1-Pentene were the two intermediate products formed in greater proportion during *trans*-1,3-pentadiene hydrogenation; it is reported in the literature that the selectivity towards those same products was 49 and 38% respectively[28] and in this study those two compounds had the highest selectivity as well (see Table 6.3). The interpretation given is that although cyclopentene could have inhibited the rate of saturation of the pentadiene, it did not affect the product distribution of the reaction.

Despite the influence of cyclopentene, *trans*-1,3-pentadiene is evidently more reactive than 3-methyl-1,3-pentadiene. It is known that the methyl group bonded to the olefinic carbon in position 3 reduces the reactivity of the diolefin[1] because that substitution in the double bond is stabilizing[27] and steric hindrance due to the methyl group is the cause of such a decrease in the reactivity. There was not a value in the literature for the heat of hydrogenation of the discussed compound.

Some of the important aspects regarding the hydrogenation of 1,4-pentadiene have already been discussed in previous paragraphs. However it is considered important to compare the reactivity of that molecule with 1-hexene. Based on the plots of conversion versus time, it is clear that 1,4-pentadiene is faster than 1-hexene. In previous investigations was corroborated that the isolated diolefin, 1,4-pentadiene reacts in a manner similar to 1-pentene[4] which is one of the characteristics of isolated diolefins; they have a reactivity similar to simple alkenes.[29] Once the first double bond is hydrogenated, the intermediate is a terminal alkene, in this case 1-pentene. The intermediate 1-pentene reacts faster than 1-hexene, because that extra methyl group in the hexene has an inductive effect on the molecule. In experiments done under HDS conditions over PtPd/USY zeolite of a full boiling range FCC gasoline, the results showed that reaction rate of hydrogenation of *n*-alkenes decreases when the carbon number of the olefin increases.[2]

It is evident that the structure of the olefins plays an important role understanding why one compound is hydrogenated faster than other. According to Table 6.7 the carbon number of the molecule has an effect on the reaction rate. The molecules with 5 carbon atoms would have been more reactive if cyclopentene would not have been present with *trans*-1,3-pentadiene. Also, how bulky is the molecule, affects the reaction; as a group, the cyclic olefins showed a smaller value for the observed initial reaction rate, respect to the acyclic olefins.

5. Conclusions

Having in mind the importance of generating fundamental understanding to deal with diolefins when they are present in complex mixtures along with other type of molecules presenting unsaturations in their structure, this work was done with the purpose of finding a reaction sequence when different types of olefins are being hydrogenated under the same conditions. Some of the following are the most significant aspects of tis work:

1. Under the working conditions, hydrogenation was the preferred reaction, isomerization of the double bonds did not take place.

2. Acyclic diolefins have a more reactive nature than other type of olefins regardless of where the unsaturation is found in the structure of the other olefins (within an open or close chain or forming part of a cycle or not).

3. The final conversion of the linear diolefins after 5 minutes at 60 °C and 0.5 MPa H_2 pressure was close to 100%; 1,4-pentadiene showed 99% of conversion and *trans*-1,3-pentadiene 96%.

4. For this specific study the conjugated nature of diolefins did not imply the highest diolefin reactivity. Based on the observed initial reaction rate, the isolated diolefins exhibited a more reactive behavior than its conjugated counterpart.

5. If branches are included next to a double bond in linear olefins, the result is that the substituent decreases the reactivity, suggesting that steric hindrance causes a slower hydrogenation of the double bond.

6. The observed initial reaction rate was higher in 1-methylcyclohexene than cyclohexene, showing that initially the branch does not have the same type of hindering effect in the reactivity of the cyclic olefin as it does in the acyclic compound.

7. There is not enough experimental information to be absolutely sure about the influence of the cyclopentene in the hydrogenation of *trans*-1,3-pentadiene, but the reduction of the reaction rate in the conjugated diolefin, despite its nature could be explained by inhibition of diolefin hydrogenation by competitive adsorption.

8. The reactivity sequence found in this work was: 1,4-pentadiene > 1-hexene > *trans*-1,3-pentadiene > 1-methyl-cyclohexene > 3-methyl-1,3-pentadiene > cyclohexene > 1,3-cylclohexadiene > vinylcyclopentane.

References

(1) Toba, M.; Miki, Y.; Matsui, T.; Harada, M.; Yoshimura, Y. Reactivity of olefins in the hydrodesulfurization of FCC gasoline over CoMo sulfide catalyst. *Appl. Catal. B Environ.* **2007**, *70* (1-4), 542–547.

(2) Magyar, S.; Jeno, H.; Dénes, K. Reactivity of several olefins in the HDS of full boiling range FCC gasoline over PtPd/USY. *Fuel Process. Technol.* **2008**, *89* (8), 736–739.

(3) Morales-Valencia, E. M.; Baldovino-Medrano, V. G.; Giraldo, S. a. Reactivity of olefins and inhibition effect on the hydrodesulfurization of a model FCC naphtha. *Fuel* **2015**, *153*, 294–302.

(4) Jackson, S. D.; Monaghan, A. Hydrogenation of unsaturated hydrocarbons-40 years on: Hydrogenation of 1,3-pentadiene over Pd/alumina. *Catal. Today* **2007**, *128* (1-2 SPEC. ISS.), 47–51.

(5) Gray, M. R.; McCaffrey, W. C. Role of chain reactions and olefin formation in cracking, hydroconversion, and coking of petroleum and bitumen fractions. *Energy Fuels* **2002**, *16* (3), 756–766.

(6) Gómez, S., Torres, C.; García Fierro, J., Apesteguía, C.R., Reyes, P. Hydrogenation of nitrobenzene on Au/ZrO2 catalysts. *J. Chil. Chem. Soc.* **2012**, *57* (2), 1194–1198.

(7) Lee, D.; Kim, H.; Kang, M.; Ji, M. K.; Lee, I. M. Efficient hydrogenation catalysts of Ni or Pd on nanoporous carbon workable in an acidic condition. *Bull. Korean Chem. Soc.* **2007**, *28* (11), 2034–2040.

(8) Brunner, E. Solubility of Hydrogen in 10 Organic Solvents at 298.15, 323.15, and 373.15 K. *J. Chem. Eng.* **1985**, *30*, 269–273.

(9) Poling, B. E.; Prausnitz, J. M.; O'Connell, J. P. *Properties of Gases and Liquids*, Fifth.; McGraw-Hill Education: New York, 2001.

(10) Gresham, T. L.; Stiakowsky, G. B. K. Heats of Organic Reactions . V . Heats of

Hydrogenation of Various Hydrocarbons. *J. Am. Chem. Soc.* **1937**, *59*.

(11) Roonns, D. W.; Mclafferty, F. J. A new Hydrogen calorimeter. Heats of hydrogenation of allyl and vinyl unsaturation adjacent to a ring. *Tetrahedron* **1971**, *27* (16), 3765–3775.

(12) Turner, R. B.; Garner, R. H. Heats of hydrogenation. V. Relative stabilities in certain exocyclic-endocyclic olefin pairs. *J. Am. Chem. Soc.* **1958**, *80* (1424-1430).

(13) Turner, R. B.; Mallon, B. J.; Tichy, M.; Doering, W. V. E.; Roth, W. R.; Schroeder, G. Heats of hydrogenation. X. Conjugative interaction in cyclic dienes and trienes. *J. Am. Chem. Soc.* **1973**, *95* (26), 8605.

(14) Ruhoff, J. R.; Smith, H. A.; Vaughan, W. E.; Smith, A.; Vaughan, W. E. Heats of Organic Reactions. IV. Hydrogenation of some dienes and of Benzene. *J. Am. Chem. Soc.* **1935**, *58*, 146–153.

(15) NIST. 1-Hexene http://webbook.nist.gov/cgi/cbook.cgi?ID=C592416&Units=SI&Mask=8#Thermo-React (accessed Jun 16, 2016).

(16) Rachforo, R. Heats of hydrogenation by a simple and rapid calorimetric method. *Appl. Catal.* **1984**, *9*, 219–223.

(17) Egger, K. W.; Benson, S. W. Nitric oxide and iodine catalyzed isomerization of olefins. VI. Thermodynamic data from equilibrium studies of the geometrical and positional isomerization of n-pentenes. *J. Am. Chem. Soc.* **1966**, *88* (2), 236–240.

(18) Rogers, D. W.; Crooks, E.; Dejroongruang, K. Enthalpies of hydrogenation of the hexenes. *J. Chem. Thermodyn.* **1987**, *19*, 1209–1215.

(19) Litvin, F. Hydrogenation of stereoisomers of piperylene on metallic catalysts. *Pet. Chem. U.S.S.R.* **1963**, *3* (2), 139–143.

(20) Chemistry, O.; Kazanskii, B. A. Hydrogenation mechanism of dienes with conjugated double bonds on a palladium catalyst. *Pet. Chem. U.S.S.R.* **1964**, *4* (2), 111–116.

(21) Bond, G. C. Hydrogenation of alkenes and related processes. In *Metal-Catalysed reactions*

of hydrocarbons; Springer: New York, 2005; pp 292–356.

(22) Hubert, A. J.; Reimlinger, H. The Isomerization of Olefins Part II. Thermal and Catalytic Isomerization of Olefins using Acids, Metals, Metal Complexes, or Boron Compounds as Catalysts. *Synthesis*. 1970, pp 405–430.

(23) Augustine, R. L. *Catalytic hydrogenation*; Marcel Dekker: New York, 1965.

(24) Vollhardt, P.; Schore, N. *Organic Chemistry: Structure and Function*; W.H. Freeman: New York, 2007.

(25) Rappoport, Z. Thermochemistry of dienes and polyenes. In *The chemistry of dienes and polyenes*; 1997; pp 67–110.

(26) Siegel, S. Stereochemistry and the Mechanism of Hydrogenation of Unsaturated Hydrocarbons. *Adv. Catal.* **1966**, *16*, 123–177.

(27) Carey, F. a.; Sundberg, R. J. Structural Effects on Stability and Reactivity. In *Advanced Organic Chemistry: Part A. Structure and Mechanisms*; Springer, 2007; pp 253–388.

(28) Bond, G. C. *Metal-Catalysed Reactions of Hydrocarbons*; Springer, 2005.

(29) Cagogan, J. I.; Cais, M. *The chemistry of alkenes*; Interscience Publishers: London, 1964.

CHAPTER 7. CONCLUSIONS

The goals of this project included the development of a strategy for the characterization of diolefins in complex mixtures, the exploration of alternative low temperature treatment strategies different to the conventional hydrogenation of unsaturated compounds and the definition of a reactivity sequence of representative olefinic and diolefinic species in thermally cracked naphtha. The following are the most relevant findings of this study:

a) The identification of individual diolefinic species in a thermally cracked naphtha sample showed that molecules with conjugated double bonds are present in greater proportion compared to compounds with isolated or cumulated double bonds in their structure. The results of the University of Alberta and those of Alberta Innovated Technology Futures (AITF) showed that diolefins of open and closed chain are present.

b) In the University of Alberta study, the carbon number of the diolefins detected in thermally cracked naphtha ranged between 5 and 7; the compounds identified in the mixture were: *trans*-1,3-pentadiene, *cis*-1,3-pentadiene, 2-methyl-1,3-pentadiene and a branched cyclic conjugated diolefin of 5 or 6 carbons. In the case of AITF, the compounds detected had chains of 6 to 8 carbons; their analysis showed the presence of *trans*-1,4-hexadiene, 2,3-dimethyl-1,3-butadiene, 3-methyl-1,3-pentadiene, tetramethylallene, and 1,7-octadiene, but the presence of lower or higher carbon number cannot be ruled out.

c) The characterization of diolefins was influenced by the highly matrix interference of the sample. Thermal cracking products range from alkanes, cycloalkanes, alkenes and cycloalkenes to aromatics along with all the isomers in those categories and several times peaks initially thought to be diolefins ended up being cycloalkenes. Such was the case of 1-methylcyclopentene and cyclohexene.

d) There is evidence about a change in the organic function of compounds treated (diolefins) by reaction with water, however all those changes did not correspond entirely to modifications due to hydration of the molecules. The chemistry of the hydration reaction proved to be more complex. The formation of oxygenates was seen (not necessarily alcohols), but acid cracking, double bond shift, *cis-trans*-isomerization and addition, reactions were also present.

e) In the case of the reaction with water only with 2,5-dimethyl-2,4-hexadiene, the reaction products with all the catalysts were distributed in three distinctive groups: (1) cracking products and oxygenates with a smaller carbon chain and/or lower boiling point than the feed, (2) oxygenated products with nearly the same carbon number as the feed, (3) heavy products with longer carbon chain and/or higher boiling point than the feed, possibly due to acid catalyzed addition reactions.

f) The conversion of the hydration reaction of 2,5-dimethyl-2,4-hexadiene varied with respect to the catalyst used and as is known, it was limited by the equilibrium constraint of the water addition to the alkene. The catalyst that showed a closer conversion to the maximum equilibrium conversion was sulfuric acid, which was chosen as catalyst for the hydration of the diolefins mixture.

g) The model mixture hydration reaction, showed that linear conjugated and isolated diolefins with no branches have a tendency to double bond shift and *cis-trans* isomerization. Conjugated cyclic diolefins did not show reactivity towards the formation of alcohols, but it is speculated that addition reactions took place and that branched diolefins were hydrated and then reacted further by cyclization to give ethers under acid catalyzed reaction conditions.

h) The Diels-Alder cycloaddition was carried out with diolefins of different nature and it showed that the formation of a Diels-Alder product can be achieved, using a Lewis acid catalyst at low temperatures (60°C).

i) The reactivity of a molecule towards the reaction depended strongly on their structure. Acyclic diolefins were the most prone to undergo the cycloaddition; whereas cyclic molecules did not show high conversions under the same reaction conditions. Stereoisomerism plays an important role in the reaction. The place where the substituents of a molecule are located, limits the reactivity of the compound. Stereoisomers with a *cis* configuration are more reactive in the cycloaddition reaction.

j) The selection of dienophile is an important factor to take into account when doing the reaction because it affects the reaction rate. In this specific case, methyl vinyl ketone was more reactive to the cycloaddition than 3-buten-2-ol.

k) According to the product selectivity stablished for the eight molecules studied during the relative reactivity experiments, the hydrogenation of the olefins at 60°C over Pt/C as catalyst, was preferred over other type of reactions such as double bond isomerization. Only during the hydrogenation of 1,4-pentadiene, products coming from the isomerization of the double bond were seen and in small proportion.

l) The structure influences greatly the rate of hydrogenation. In general, acyclic olefins are more reactive than cyclic olefins and the inclusion of branches in the structure of the olefin decreases its reactivity due to steric hindrance. It was expected that conjugated diolefins had the highest reactivity, but in this study, the conjugated nature of a molecule did not imply that it had the highest reactivity. Based on the observed initial reaction rate, the isolated diolefin exhibited a more reactive behavior than its conjugated counterpart.

m) Using the information collected for the change in the concentration versus time, for all compounds, an observed initial reaction rate was calculated to define the relative reactivity sequence. The order in reactivity found in this work from the most reactive to the least was: 1,4-pentadiene > 1-hexene > *trans*-1,3-pentadiene > 1-methyl-cyclohexene > 3-methyl-1,3-pentadiene > cyclohexene > 1,3-cylclohexadiene > vinylcyclopentane.

Future work

According to the results obtained in the experimental work, the following are some recommendations for future work in the subject that could give a broader knowledge about the application of the strategies here proposed to deal with diolefins:

- The hydration reaction was done with only one model compound and then with the mixture of diolefins and it proved to render a variety of products, which showed that the reaction was far more complex. It would be useful to repeat the reaction with each diolefin forming the mixture separately to check the individual behavior and make better predictions respect to the products that would be formed, depending on the structure of the diolefin.
- The reactivity sequence can be expanded by changing variables such as the type of catalyst used, the reaction temperature and the pressure. That to have a clearer idea of how those variables affect the reactivity of the olefinic and diolefinic compounds present in the thermally cracked naphtha.
- During the experiments to stablish the reactivity sequence, the isolated diolefin reacted faster than the conjugated diolefin. According to literature, the behaviour is usually inverse. One of the explanations was the presence of cyclopentene when *trans*-1,3-pentadiene was being hydrogenated. Therefore it is suggested to do some hydrogenation reactions with 1,4-pentadiene when cyclopentene is present approximately in the same proportion as for the conjugated diolefin to check if the reactivity remains the same or changes.
- The proposed mitigation strategies were applied to model compounds and a model mixture of diolefins. As future work, it would be useful to run reactions using a naphtha sample to check how the other compounds present in the mixture are affected and what is the change in the naphtha composition.

BIBLIOGRAPHY

Altbach, M. I.; Fitzpatrick, C. P. Identification of conjugated diolefins in fossil fuel liquids by H-n.m.r. two-dimensional correlated spectroscopy. *Fuel* **1994**, *73* (2), 223–228.

Altshuller, A. P.; R., C. I. Spectrophotometric methods for olefins- Colorimetric determination of conjugated diolefins. *Anal. Chem.* **1960**, *32* (13), 1843–1848.

Anderson, J.; McAllister, S. H.; Derr, E. L.; Peterson, W. H. Diolefins in Alkylation Feedstocks. *Ind. Eng. Chem.* **1948**, *40* (12), 2295–2301.

Andrade, D. F.; Azevedo, D. A. Comparison of UOP-326, voltammetric and gas chromatographic/mass spectrometric methods for the determination of conjugated dienes in Brazilian Naphtha. *Fuel* **2006**, *85* (7-8), 1024–1031.

Augustine, R. L. *Catalytic hydrogenation*; Marcel Dekker: New York, 1965.

Badoni, R. P.; Bhagat, S. D.; Joshi, G. C. Analysis of olefinic hydrocarbons in cracked petroleum stocks: a review. *Fuel* **1992**, *71* (5), 483–491.

Bond, G. C. *Metal-Catalysed Reactions of Hydrocarbons*; Springer, 2005.

Brunner, E. Solubility of Hydrogen in 10 Organic Solvents at 298.15, 323.15, and 373.15 K. *J. Chem. Eng.* **1985**, *30*, 269–273.

Cagogan, J. I.; Cais, M. *The chemistry of alkenes*; Interscience Publishers: London, 1964.

Carbognani, L.; Lopez-Linares, F.; Trujillo, M.; Wu, Q.; Carbognani, J.; Pereira-Almao, P. Olefin content estimation in heavy oil, bitumen and their upgraded products. *Prepr. Pap.-Am. Chem. Soc., Div. Energy Fuels* **2013**, *58* (2), 507–508.

Carey, F. a.; Sundberg, R. J. Structural Effects on Stability and Reactivity. In *Advanced Organic Chemistry: Part A. Structure and Mechanisms*; Springer, 2007; pp 253–388.

Cheremisinoff, N. P. *Industrial Solvents Handbook, Revised And Expanded*; Marcel Dekker: New York, 2003.

Clark, J. J. J. tert-Butyl Alcohol: Chemical Properties, Production and Use, Fate and Transport, Toxicology, and Detection in Groundwater and Regulatory Standards. *Oxyg. Gasol.* **2001**, *799*, 92–106.

Clayden, J.; Greeves, N.; Warren, S. Pericyclic reactions 1: cycloadditions. In *Organic chemistry*;

Oxford University press: New York; pp 877–908.

Cortiñas, F. Determination of conjugated dienes in petroleum products by supercritical fluid chromatography and ultraviolet detection. *J. Sep. Sci.* **2003**, *26* (15-16), 1403–1406.

D1159-07. Standard Test Method for Bromine Numbers of Petroleum Distillates and Commercial Aliphatic Olefins by Electrometric Titration 1. *Astm* **2010**, *20* (Reapproved 2012), 1–10.

De Andrade, D. F.; Fernandes, D. R.; Miranda, J. L. Methods for the determination of conjugated dienes in petroleum products: A review. *Fuel* **2010**, *89* (8), 1796–1805.

De Andrade, D. F.; Figueiredo, E. Proposal of a voltammetric method for the determination of conjugated dienes in Brazilian naphtha. *Fuel* **2006**, *85* (17-18), 2578–2585.

De Klerk, A. *Fischer-Tropsch refining*; Weinheim: Wiley-VCH: Weinheim, 2011.

De La Puente, G.; Sedran, U. Formation of gum precursors in FCC napthas. *Energy & Fuels* **2004**, *18* (2), 460–464.

Edwards, K. E.; Qian, K.; Wang, F. C.; Siskin, M. Quantitative analysis of conjugated dienes in hydrocarbon feeds and products. *Energy Fuels* **2005**, *19* (5), 2034–2040.

Egger, K. W.; Benson, S. W. Nitric oxide and iodine catalyzed isomerization of olefins. VI. Thermodynamic data from equilibrium studies of the geometrical and positional isomerization of n-pentenes. *J. Am. Chem. Soc.* **1966**, *88* (2), 236–240.

Ehwald, H.; Fiebig, W.; Lischke, G.; Parlitz, B.; Reich, P. High pressure catalytic hydration of olefins over various proton-exchanged zeolites. *Appl. Catal.* **1987**, *34*, 275–287.

Freidlin, L.; Litvin, Y. Hydrogenation mechanism of dienes with conjugated double bonds on a palladium catalyst. *Pet. Chem. U.S.S.R.* **1964**, *4* (2), 111–116.

Fringuelli, F.; Taticchi, A. *Dienes in the Diels-Alder reaction*; John Wiley & Sons, Inc.: New York, 1990.

Froment, G. F.; Bernard, D.; Grange, P. *Hydrotreatment and hydrocracking of oil fractions*; Elsevier, Ed.; Amsterdam, 1997.

Funel, J.-A.; Abele, S. Industrial applications of the diels-alder reaction. *Angew Chem Int Ed* **2013**, *52* (14), 3822–3863.

Garcia, J.; do Prado, I. *Olefin conversion for field upgrading*; Edmonton, 2014.

Gómez, S., Torres, C.; García Fierro, J., Apesteguía, C.R., Reyes, P. Hydrogenation of nitrobenzene on Au/ZrO2 catalysts. *J. Chil. Chem. Soc.* **2012**, *57* (2), 1194–1198.

Gray, M. R. Hydrotreating Processes. In *Upgrading Oilsands Bitumen and Heavy Oil*; The University of Alberta Press: Edmonton, 2015.

Gray, M. R.; McCaffrey, W. C. Role of chain reactions and olefin formation in cracking, hydroconversion, and coking of petroleum and bitumen fractions. *Energy & Fuels* **2002**, *16* (3), 756–766.

Gresham, T. L.; Stiakowsky, G. B. K. Heats of Organic Reactions . V . Heats of Hydrogenation of Various Hydrocarbons. *J. Am. Chem. Soc.* **1937**, *59*.

Hengstebeck, R. J. *Petroleum Processing, Principles and Applications*; McGraw-Hill: New York, 1959.

Hsu, C. S.; Robinson, P. R. *Practical advances in Petroleum Processing*; Springer: New York, 2006; Vol. 1.

Hubert, A. J.; Reimlinger, H. The Isomerization of Olefins Part II. Thermal and Catalytic lsomerization of Olefins using Acids, Metals, Metal Complexes, or Boron Compounds as Catalysts. *Synthesis*. 1970, pp 405–430.

Hunter, Shawn E.; Ehrenberger, Carolyn E.; Savage, P. E. Kinetics and Mechanism of Tetrahydrofuran Synthesis via 1,4-butanediol dehydration in high temperature water. *J. Org. Chem.* **2006**, *71* (3), 6229–6239.

Jackson, S. D.; Monaghan, A. Hydrogenation of unsaturated hydrocarbons-40 years on: Hydrogenation of 1,3-pentadiene over Pd/alumina. *Catal. Today* **2007**, *128* (1-2 SPEC. ISS.), 47–51.

Jense, J.; Uaprasert, V.; Fujii, C. Acid-Catalyzed hydration of dienes. 2. Changes in activity coefficient ratios, enthalpy and entropy as a function of sulfuric acid concentration. *J. Org. Chem.* **1976**, *41* (10), 1675–1680.

Kamínski, M.; Kartanowicz, R.; Gilgenast, E.; Namieśnik, J. High-Performance Liquid Chromatography in Group-Type Separation and Technical or Process Analytics of Petroleum Products. *Crit. Rev. Anal. Chem.* **2005**, *35* (3), 193–216.

Kawahara, F. K. Composition of gum in cracked naphtha. *Ind. Eng. Chem.* **1965**, *4* (1), 7–9.

Kissin, Y. V. Chemical Mechanism of Hydrocarbon Cracking over Solid Acidic Catalysts. *J. Catal.* **1996**, *163* (1), 50–62.

Lee, D.; Kim, H.; Kang, M.; Ji, M. K.; Lee, I. M. Efficient hydrogenation catalysts of Ni or Pd on nanoporous carbon workable in an acidic condition. *Bull. Korean Chem. Soc.* **2007**, *28* (11), 2034–2040.

Levandowski, B. J.; Houk, K. N. Theoretical analysis of reactivity patterns in Diels-Alder reactions of cyclopentadiene, cyclohexadiene, and cycloheptadiene with symmetrical and unsymmetrical dienophiles. *J. Org. Chem.* **2015**, *80* (7), 3530–3537.

Litvin, F. Hydrogenation of stereoisomers of piperylene on metallic catalysts. *Pet. Chem. U.S.S.R.* **1963**, *3* (2), 139–143.

Magyar, S.; Jeno, H.; Dénes, K. Reactivity of several olefins in the HDS of full boiling range FCC gasoline over PtPd/USY. *Fuel Process. Technol.* **2008**, *89* (8), 736–739.

Maxxam-CAPP. Test Method for Determination of Olefin Content of Crude Oils, Condensates and Diluents by H-NMR. Edmonton 2005, pp 1–11.

Mckay, F. High Performance Liquid Chromatographic Separation of Olefin, Saturate, and Aromatic Hydrocarbons in High-Boiling Distillates and Residues. *Anal. Chem.* **1980**, *52* (11), 1618–1621.

Minachev, K.; Mortikov, Y. Hydration of Olefins on Zeolite Catalysts. *Pet. Chem. U.S.S.R.* **1976**, *16* (4), 216–223.

Mitsui, S.; Kasahara, A. Hydrogenation of Alkenes. In *The chemistry of alkenes. Vol 2*; Interscience Publishers: London, 1970.

Morales-Valencia, E. M.; Baldovino-Medrano, V. G.; Giraldo, S. a. Reactivity of olefins and inhibition effect on the hydrodesulfurization of a model FCC naphtha. *Fuel* **2015**, *153*, 294–302.

NIST. 1-Hexene http://webbook.nist.gov/cgi/cbook.cgi?ID=C592416&Units=SI&Mask=8#Thermo-React (accessed Jun 16, 2016).

Ortega, L. C.; Lopez-, F. Analysis of Olefins in Heavy Oil, Bitumen, and Their Upgraded Products. In *Analytical methods in petroleum upstream applications*; CRC press, 2015; pp 81–109.

Paez, N. Y.; De Klerk, A. *Diolefin characterization in thermally cracked naphtha*; Edmonton, 2016.

Pereira, R. C. C.; Pasa, V. M. D. Effect of mono-olefins and diolefins on the stability of automotive gasoline. *Fuel* **2006**, *85* (12-13), 1860–1865.

Poling, B. E.; Prausnitz, J. M.; O'Connell, J. P. *Properties of Gases and Liquids*, Fifth.; McGraw-Hill Education: New York, 2001.

Pradelle, F.; Braga, S. L.; Martins, A. R. F. A.; Turkovics, F.; Pradelle, R. N. C. Gum Formation in Gasoline and Its Blends: A Review. *Energy & Fuels* **2015**, *29* (12), 7753–7770.

Rachforo, R. Heats of hydrogenation by a simple and rapid calorimetric method. *Appl. Catal.* **1984**, *9*, 219–223.

Rappoport, Z. Thermochemistry of dienes and polyenes. In *The chemistry of dienes and polyenes*; 1997; pp 67–110.

Raseev, S. *Thermal and catalytic processess in petroleum Refining*; Marcel Dekker: New York, 2003.

Reger, D.; Goode, S.; Ball, D. *Chemistry: Principles and practice*; Brooks/Cole: Belmont, 2010.

Richard, K. Process improvements in the direct hydration of olefins to alcohols. *Digital refining, processing, operations and maintenance*. May 2014.

Roberts, J.; Caserio, M. *Basic principles of organic chemistry*, Second.; W. A. Benjamin, Inc: Menlo Park, 1977.

Rogers, D. W.; Crooks, E.; Dejroongruang, K. Enthalpies of hydrogenation of the hexenes. *J. Chem. Thermodyn.* **1987**, *19*, 1209–1215.

Roonns, D. W.; Mclafferty, F. J. A new Hydrogen calorimeter. Heats of hydrogenation of allyl and vinyl unsaturation adjacent to a ring. *Tetrahedron* **1971**, *27* (16), 3765–3775.

Ruhoff, J. R.; Smith, H. A.; Vaughan, W. E.; Smith, A.; Vaughan, W. E. Heats of Organic Reactions. IV. Hydrogenation of some dienes and of Benzene. *J. Am. Chem. Soc.* **1935**, *58*, 146–153.

Rylander, P. Hydrogenation of Olefins. In *Catalytic Hydrogenation in Organic Syntheses*; Academic Press: New York, 1979; pp 31–63.

Schug, K. a.; Sawicki, I.; Carlton, D. D.; Fan, H.; McNair, H. M.; Nimmo, J. P.; Kroll, P.; Smuts, J.; Walsh, P.; Harrison, D. Vacuum ultraviolet detector for gas chromatography. *Anal. Chem.* **2014**, *86* (16), 8329–8335.

Schwartz, F. G.; Whisman, M.; Allbright, C.; Ward, C. *Storage stability of gasoline-Fundamentals of Gum Formation Including a Discussion of Radiotracer Techniques.*; Washington, D.C, 1964.

Siegel, S. Stereochemistry and the Mechanism of Hydrogenation of Unsaturated Hydrocarbons. *Adv. Catal.* **1966**, *16*, 123–177.

Speight, J. G. *Heavy and Extra-heavy Oil Upgrading Technologies*; Gulf professional publishing: Oxford, 2013.

Speight, J. G. *Heavy Oil Production Processes*; Gulf professional publishing: Oxford, 2013.

Stunnenberg, F.; Niele, F. G. M.; Drent, E. Hydration of conjugated dienes to produce ketones catalyzed by ruthenium complexes. *Inorganica Chim. Acta* **1994**, *222* (1-2), 225–233.

Toba, M.; Miki, Y.; Matsui, T.; Harada, M.; Yoshimura, Y. Reactivity of olefins in the hydrodesulfurization of FCC gasoline over CoMo sulfide catalyst. *Appl. Catal. B Environ.* **2007**, *70* (1-4), 542–547.

Turner, R. B.; Garner, R. H. Heats of hydrogenation. V. Relative stabilities in certain exocyclic-endocyclic olefin pairs. *J. Am. Chem. Soc.* **1958**, *80* (1424-1430).

Turner, R. B.; Mallon, B. J.; Tichy, M.; Doering, W. V. E.; Roth, W. R.; Schroeder, G. Heats of hydrogenation. X. Conjugative interaction in cyclic dienes and trienes. *J. Am. Chem. Soc.* **1973**, *95* (26), 8605.

Undeela, S.; Ramchandra, J. P.; Menon, R. S. A sequential synthesis of substituted furans from aryl alkynes and ketones involving a cerium (IV) ammonium nitrate (CAN) -mediated oxidative cyclization. *Tetrahedron Lett.* **2014**, *55* (41), 5667–5670.

Vollhardt, P.; Schore, N. *Organic Chemistry: Structure and Function*; W.H. Freeman: New York, 2007.

Vollhardt, P.; Schore, N. *Organic Chemistry: Structure and Function*; W.H. Freeman: New York, 2007.

Von Zanier, a.; Jäckle, H. W. Thermal-oxidative stability of motor gasolines. *Erdoel Erdgas Kohle*

2000, *116* (3), 109–115.

Wassermann, A. *Diels-Alder reactions organic background and physico-chemical aspects*; Elsevier publishing company, 1965.

Yuhan, X. Acid Catalyzed Aromatic Alkylation in the Presence of Nitrogen Bases MSc thesis, University of Alberta, Edmonton, AB, Canada, 2012.

APPENDIX A1. QUANTIFICATION OF OLEFINS

The quantification of nine olefins was done by means of the GC-FID; for such purpose a calibration curve for each compound was determined by the internal standard (ISTD) calibration method, where errors caused by sample preparation or the variability inherent in the GC system can be diminished. Four compounds were calibrated as part of the olefins identification in the thermally cracked naphtha sample (Chapter 3). Those compounds being: *trans*-1,3-pentadiene, 1-methylcyclopentene, cyclohexene, and vinylcyclopentane. Cyclopentene was also calibrated, because it was present as an impurity in the *trans*-1,3-pentadiene purchased. During the hydrogenation over Pt/C for the relative reactivity study (Chapter 6) five olefins were quantified, curves were developed for: 3-methyl-1,3-pentadiene, 1-methylcyclohexene, 1,3-cyclohexadiene, 1,4-pentadiene and 1-hexene. The temperature program created for the GC-MS during the identification of diolefins present in the naphtha sample was reproduced to work in the GC-FID. The following are some important aspect in the development of the calibration curves and the results obtained.

Calibration standards preparation: The analyte to use was dissolved in n-decane (solvent). Except for *trans*-1,3-pentadiene, all reagents were analytical standards with a purity higher than 99%. The addition of the analyte to the solvent was done by mass, using a Mettler-Toledo, Model XS105 Dual Range Analytical Balance with 4 decimal places. The solution prepared was dilluted several times, 1 ml of the initial solution was taken to a separate vial and 2 ml of solvent added. That process was repeated 2 or 3 times more to obtain 4 or 5 points in the calibration curve. At this point there were 4 or 5 solutions. A graphic description of this process is shown in Figure A1.1.

During the preparation of calibration standards, the same amount of ISTD was added (~50mg) to a vial for chromatography and the exact weight was recorded. The internal standard used was 1-nonene. Afterwards a volume of 0.5ml was taken from each solution and added to different chromatography vials that already contained the ISTD. From that process 4 or 5 chromatography vials were ready to run in the GC-FID. Each sample run three times and the final value for the area of the peaks was taken as an average of those measurements. The details regarding the range of concentrations used and the retention time of each compound are shown in Table A1.1. while the amount of analyte and solvent varied depending on the dilution.

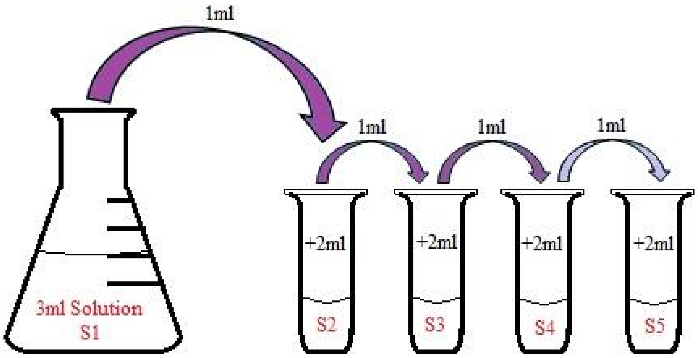


Figure A1. 1. Methodology for calibration samples preparation.

Table A1. 1. Retention time of analytes and concentration range of the calibration standards prepared.

Compound		Cocentration (ppm)				
	RT (min)	S1	S2	S3	S4	S5
trans-1,3-pentadiene	2.938	6919	2309	767	256	84
1,4-Pentadiene	2.673	12320	3939	1395	460	155
Cyclopentene	3.153	769	257	85	28	9
1-Hexene	3.486	14295	4570	1619	534	179
cis-3-methyl-1,3-pentadiene	4.339	2618	873	291	97	32
trans-3-methyl-1,3-pentadiene	4.450	6108	2037	679	226	75
1-methylcyclopentene	4.458	27955	8561	2854	951	-
1,3-cyclohexadiene	4.820	8940	2996	1018	337	114
Cyclohexene	5.053	14477	4827	1609	536	-
Vinylcyclopentane	6.343	6792	2268	751	252	-
1-methyl-1-cyclohexene	7.945	12106	3935	1338	447	150

Calibration curves and correlation coefficient: After running all standards by triplicate the data was mathematically treated to generate the calibration curve. Part of that treatment was calculating the areas and amounts ratio of analyte to ISDT, better known as relative response and relative amount of analyte as shown in (1) and (2), where the subindex *i*, represents the analyte.

$$rsp_i = \left(\frac{A_i}{A_{IS}}\right) \quad (1) \qquad amt_i = \left(\frac{w_i}{w_{IS}}\right) \quad (2)$$

This is done for each calibration standard and then a plot of rsp_i vs amt_{IS}, is generated for each analyte. The plot should be linear and will give the calibration curve for which the slope is also known as the response factor (*RF*$_i$). That analysis of data was done automatically with the software Agilent 7890 which is useful to avoid human errors and increases the numerical precision. After getting the corresponding trend line, the amount of analyte can be calculated as shown in (3). Although the amount of analyte was provided by the instrument and the operator did not have to do calculations.

$$\begin{gathered} rsp_i = RF_i * (amt_i) + \mathrm{y} \\ \mathrm{w}_i = \left(\frac{rsp_i - y}{RF_i}\right) * w_{IS} \qquad (3) \end{gathered}$$

Table A1. 2. Linear correlation coefficients and response factors for the compounds calibrated using the ISTD calibration method.

Compound	R^2	RF*i*	Compound	R^2	RF*i*`
trans-1,3-pentadiene	1.000	0.915	1-methylcyclopentene	1.000	2.809
1,4-Pentadiene	0.999	0.964	1,3-cyclohexadiene	1.000	0.907
Cyclopentene	1.000	0.808	Cyclohexene	1.000	1.124
1-Hexene	0.999	0.985	Vinylcyclopentane	0.996	0.896
cis-3-methyl-1,3-pentadiene	0.999	0.836	1-methyl-1-cyclohexene	0.999	0.985
trans-3-methyl-1,3-pentadiene	0.999	0.851			

The calibration curves obtained can be seen in Figure A1.2 and Figure A1.3.

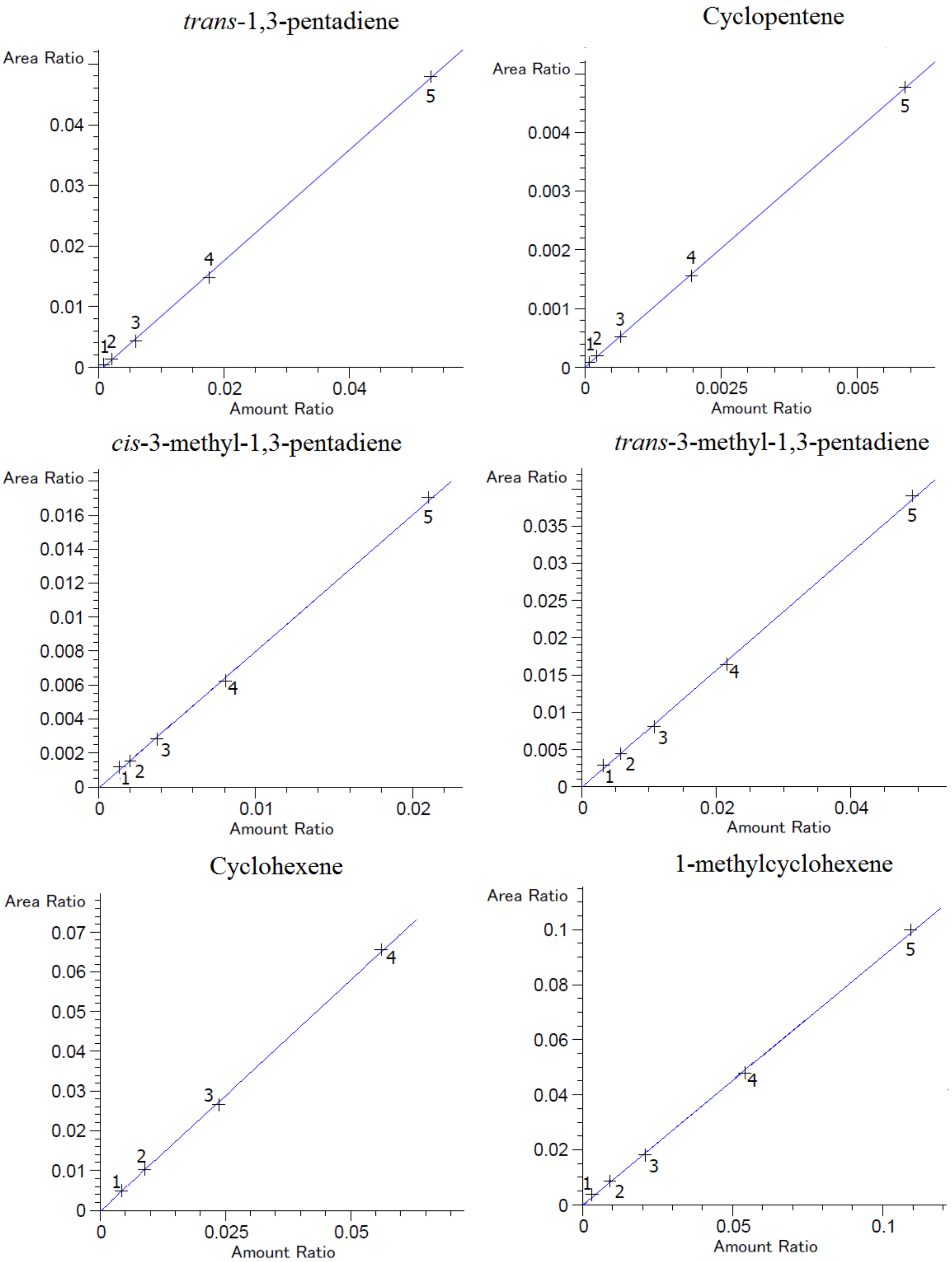


Figure A1. 2. Calibration curves for *trans*-1,3-pentadiene, cyclopentene, 3-methyl-1,3-pentadiene (*cis* and *trans* conformation), cyclohexene and 1-methylcyclohexene.

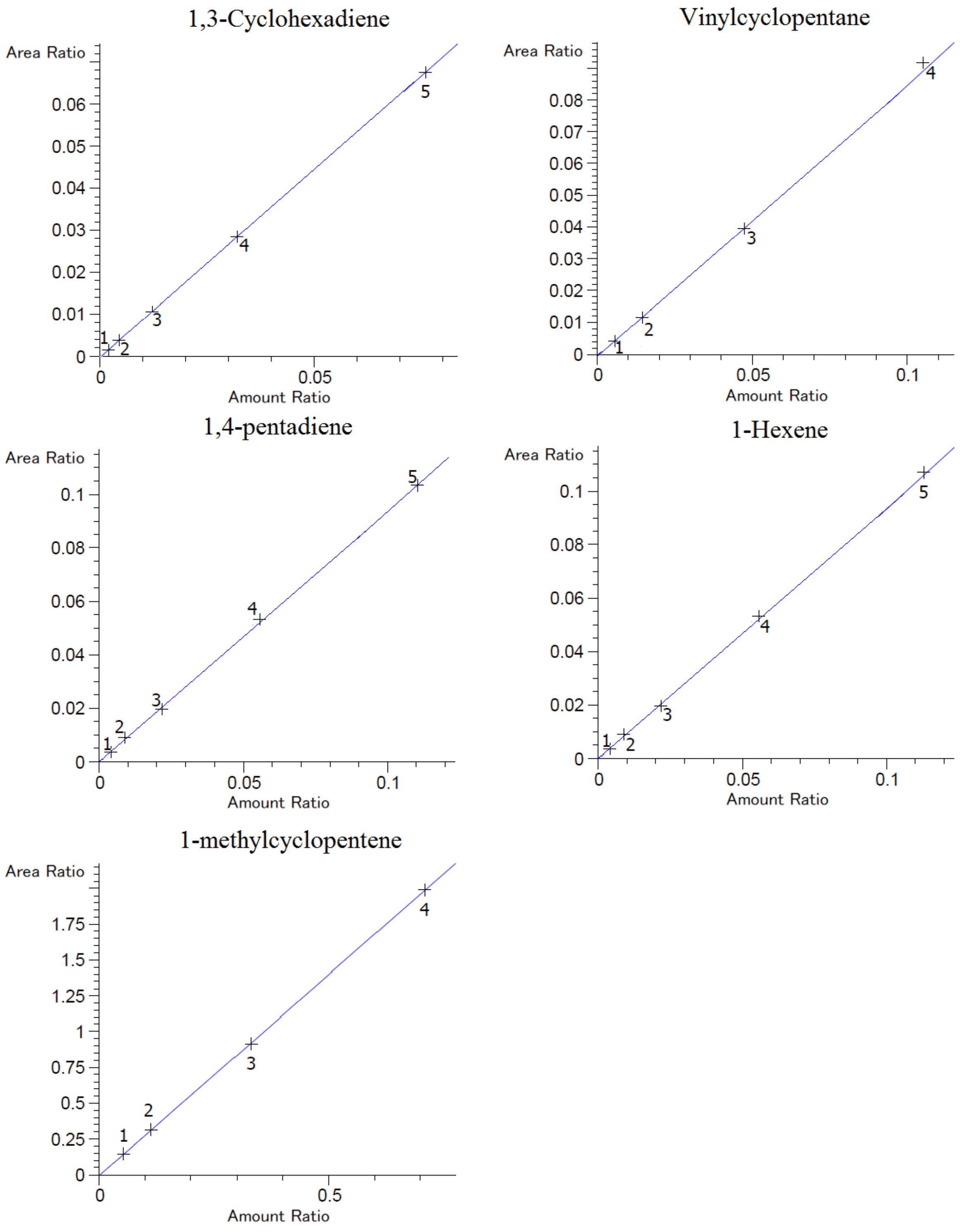


Figure A1. 3. Calibration curves for 1,3-cyclohexadiene, vinylcyclopentane, 1,4-pentadiene, 1-hexene and 1-methylcyclopentene.