An exploration towards a more sustainable process for dimethyl naphthalene-2,6-dicarboxylate over acidic zeolites

Christophe Bouvier

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An exploration towards a more sustainable process for dimethyl naphthalene-2,6-dicarboxylate over acidic zeolites

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Christophe Pierre BOUVIER

Ingénieur Chimiste de l'Ecole Nationale Supérieure de Chimie de Mulhouse (Frankrijk)
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Dit proefschrift is goedgekeurd door de promotor:
Prof. dr. W. Buijs

Samenstelling promotiecommissie:

Rector Magnificus	voorzitter
Prof. dr. W. Buijs	Technische Universiteit Delft, promotor
Prof. em. dr. J.A. Moulijn	Technische Universiteit Delft
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Prof. dr. ir. S. Walter	Université de Haute-Alsace, Frankrijk
Dr. G. Mul	Technische Universiteit Delft

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Shoot for the Moon. Even if you miss, you'll land among the stars...

Preface and thesis outline

This thesis describes the results obtained in Friedel-Crafts alkylation of naphthalene over zeolitic catalysts and presents a discussion of these results. A new type of catalysts is tested and evaluated with respect to society and industry considerations. As it often happens with specialised work, some topics presented in this thesis may not be familiar to all readers. To circumvent that, chapters begin with an introduction where background information is supplied. Besides this, even though this thesis is intended to give a broad description, all chapters have been written in such a way that they can be read independently.

Thesis outline:

- Chapter 1 gives an introduction to the background of this work in terms of sustainability and economics. The choice of the model reaction is explained as well.
- Chapter 2 compiles data over nomenclature, diisopropylnaphthalenes characterisation, Friedel-Crafts reactions and information derived from modelling such as isomer distribution, molecular dimensions and zeolite characteristics.
- Chapter 3 presents the results obtained over classical commercial zeolites and gives some conclusions on shape-selectivity in the isopropylation of naphthalene.
- Chapter 4 covers the performance of first generation BImodal POrous Materials (BIPOMs) and offers a comparison with the best classical commercial zeolite.
- Chapter 5 presents the influence of temperature on activity and selectivity for the best classical and BIPOM catalysts in a process perspective.
- Chapter 6 summarises results obtained in separation of one specific diisopropylnaphthalene out of the isomer mixture and the possible industrial interest.
- Chapter 7 describes a possible industrial process for the production of 10 000 tons per year of dimethyl naphthalene-2,6-dicarboxylate from naphthalene. Economics are compared with those available for the Amoco production from *ortho*-xylene.
- The Appendix presents the way molecular dimensions were obtained for each isomer and indicates which less stable conformers were found to be smaller.

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Sustainability: from theoretical concepts to practical approaches

Abstract

In the past decades, the academic world has proposed a series of recommendations such as the E factor and the 12 principles of Green Chemistry to address sustainability in industrial chemistry. The Integrated Pollution and Prevention Control document issued by the European Commission has turned them into legislative constraints for the industry, transforming theoretical concepts into practical approaches. Friedel-Crafts alkylations are among the most unsustainable processes according to this document and also correspond to an important industrial production capacity. Zeolite catalysis might help overcoming this but is often hindered by low reaction rates. The development of specific super-microporous zeolites, called BImodal POrous Materials (BIPOMs), is expected to fill this gap. Diisopropylation of naphthalene was chosen as a model reaction to evaluate their performances both for scientific and process economical reasons. Different selectivity issues can also be considered. Moreover a direct comparison with the similar industrial process of Kureha and the economic evaluation of the Amoco process by the former Stanford Research Institute (now SRI International) will be possible.

1.1. Sustainability and Chemistry

Defining when considerations on how to deal with economics and environment together have been first proposed is not easy. In 1968, the so-called “Club of Rome” might have been the first international organisation to address this issue. The report to the “Club of Rome” predicted that economic growth could not continue indefinitely because of the limited availability of natural resources, particularly oil, and the 1973 oil crisis increased public concern about this problem. The report, *Limits to Growth*, is considered to be the first best-seller environmental book. In the 1980s, increasing concern about the effects of economic development on health, natural resources and the environment led the United Nations to release the Brundtland Report [1] in 1987. It defines sustainable development as "development which meets the needs of the present without compromising the ability of future generations to meet their own needs." It stresses the point that apart from the limitation in the resources and the technological challenges, social factors (rich/poor division in the world) are equally important.

It was however not until 1992 at the Rio Earth Summit that nations around the world came together to push for concerted action to try and reach an agreement on the best way to slow down, halt and reverse environmental deterioration. Out of Rio came Agenda 21 [2], the Framework Convention on Climate Change and the Convention on Biological Diversity.

Finally, Al Gore presented in 2006 his “*Inconvenient Truth*”, a documentary film about global warming and shared the Nobel Peace Prize in 2007 for his ”efforts to build up and disseminate greater knowledge about man-made climate change, and to lay the foundations for the measures that are needed to counteract such change”.

Sustainability recognises the interdependence of environmental, social and economic systems and promotes equality and justice through people empowerment and a sense of global citizenship. Whilst we cannot be sure what the future may bring, a sustainable future is a more preferable one.

If society wants to keep on developing in the way it has done in the past, more attention needs to be paid to our environment. How this is best achieved is often a matter of opinion rather than fact, dependent upon different perspectives of the environment and views of nature. Recently, a concept has emerged that has attempted to bring together the best aspects of these different viewpoints and to harmonise the development of mankind with the protection of nature. This is the concept of "sustainable development".

Sustainable development involves maintaining as far as possible our current rate of development while leaving suitable resources behind for later generations to continue to develop. In this context, environmental problems must be tackled by considering their relationship with the state of the economy and the wellbeing of society. In fact, the environment, the economy and society taken together, include everything that we need to consider for a healthy, prosperous and stable life.

Our basic requirements - air, food and water - come from the environment, as do the energy and natural resources for housing, transportation and the products we depend on. Protection of the environment, therefore, resides at the core of sustainable development.

Securing economic development, environmental protection and social equity and justice is the goal of sustainable development. Although these three factors can work in harmony, they are often found to conflict with one another. During the last century, economic development for a better standard of living has been instrumental in damaging the environment. We are now in a position whereby we are consuming more resources than ever, and polluting the Earth with waste products. However, even if a lot has still to be done, many major improvements have been achieved by industry in the last decades regarding emission abatement and energy consumption. This is for example the case of bulky inorganic compound syntheses or cracking processes where only very few wastes are produced. More recently, society has grown to realise that we cannot live in a healthy society or economy with so much poverty and environmental degradation. Economic wealth will remain the basis for human development, but it must change and become less environmentally destructive. The challenge of sustainable development is to put this understanding into practice, changing our unsustainable ways into sustainable ones. Sustainable development consists of a long-term integrated approach to developing and achieving a healthy community by jointly addressing economic, environmental and social issues, while avoiding the over-consumption of key natural resources.

United Nations Programme's GEO-2000 [3] reported in 2000 that:

- Around 2 billion ha of soil, equal to 15% of the Earth's land, was classed as degraded because of human activities. About one sixth of this, a total of 305 million ha of soil, was either "strongly or extremely degraded". Extremely degraded soils are so badly damaged that they cannot be restored.
- Around half of the world's rivers were seriously depleted and polluted.
- Depletion of the ozone layer had reached record levels. In September 2000, the ozone layer hole over Antarctica covered more than 28 million km^2.
- Concentrations of carbon dioxide stood at 367 ppm or 25% higher than those 150 years ago. Concentrations of other greenhouse gases, such as methane and halocarbons, had also risen.

This clearly shows that our current development is not sustainable. It has become obvious that economic development that disregards environment and social impacts can bring unintended and unwanted consequences, as evidenced by the threat of climate change, over-use of freshwater resources, loss of biological diversity and raising inequalities.

According to the Johannesburg Plan of Implementation [4] adopted at the 2002 World Summit on Sustainable Development "fundamental changes in the way societies produce and consume are indispensable for achieving global sustainable development".

As more natural resources are being consumed and more pollution is generated, it is becoming clear that decoupling economic growth from adverse environmental impacts, such as emissions of greenhouse gases, waste production and use of hazardous materials holds one of the keys to sustainable development. To achieve this, companies and industries must become more "eco-efficient". Eco-efficiency includes:

- Reducing the material requirements (total mass consumed).
- Reducing the energy intensity (energy consumed during every phase of production).
- Reducing toxic dispersion.

- Enhancing material recyclability and reducing waste production.
- Maximising sustainable use of renewable resources.
- Extending product durability.

Global environmental threats, such as poor air quality or the Asian Brown Cloud, resulting from open combustion of work wood in developing countries, must be reduced to protect human and environmental health. The use of non-renewable resources such as fossil fuels should not be stopped overnight, but they must be used efficiently and the development of alternatives should be encouraged to help phasing them out.

As far as chemistry is concerned, the impulse for developing new, more efficient and selective catalysts and the realisation of new process technology are strongly related to environmental compatibility and are a possible answer for this issue. The goals must be to give a positive answer in several of the above topics such as to reduce the total mass consumed, the amount of energy needed, to decrease toxicity, to improve recyclability, to lessen waste production, particularly by-products and salts formation, which means to go closer to "100% selectivity" and "0 emission".

Only very few chemical reactions lead to the formation of a desired compound with a 100% yield or no purification step. A corollary to this is that most of the time a reaction produces wastes that can be as various as air pollutants, water pollutants, by-products, salts as a result of the neutralisation part of the process or coming from the catalyst destruction when it cannot be recovered. These aspects are linked to drawbacks such as loss of productivity, extra costs for separation and treatment, loss of time or pollution issues.

Many types of waste are encountered in a classical reaction. They are contaminants from the raw materials and their degradation products during storage, stabilisers and auxiliary agents used for the storage of raw materials, side-products generated during the reaction, unreacted feedstock, products made while the work-up part of the process is operating (gas emissions in particular if air is used as an oxidant, salts produced to neutralise the reaction mixture, etc), solvents used during the reaction, work-up and separation or refining steps as in neutralisation, distillation, liquid-liquid extraction or recrystallisation processes and heat emissions. In addition to this, for a given reaction, some other factors may influence the character and scale of emissions such as plant age, variation of the raw material composition depending on the provider, different process conditions, possibility to value by-products, etc.

A typical example to understand this issue could be to consider two possible routes for the acylation of anisole with acetic anhydride [5]. The first one is a classical Friedel-Crafts protocol with up to two equivalents of $AlCl_3$ as a "catalyst" whereas the second one uses H-Beta zeolite. Even if the classical route provides far better yields, it really becomes economically no longer feasible when the use of resources and the production of wastes are taken into consideration. The work-up is actually easier with the H-Beta zeolite [6-7] in a way that it is only needed in catalytic amounts, that the catalyst can be recovered and that separation between the reaction mixture and the catalyst is easier and does not need important amounts of solvents. In the end, the reduction of sweet water consumption and corrosion waste in an heterogeneous process makes it economically much more attractive. The loss of productivity it creates is easily compensated and this is even more evident if the comparison is made on several runs.

The main air pollutants from large volume organic chemicals processes are Volatile Organic Compounds (VOCs) but emissions of combustion gases (CO_2), acid gases (NO_x, SO_2) and particulate matter may also be significant. Waste gas treatment units are specifically designed for a certain waste gas composition and may not provide treatment for all pollutants. VOCs from processes are where possible re-used within processes. An alternative is to recover the VOC calorific content as fuel.

The main water pollutants from large volume organic chemicals processes are mixtures of oil/organics, biodegradable, recalcitrant or volatile organics, heavy metals, acid or alkaline effluents, suspended solids and heat.

The main soil pollutants from large volume organic chemicals processes are heavy metals like lead, quicksilver, cadmium and arsenic from catalysts, as well as metal wastes generated by mining exploitations.

In the past decades, the academic world has proposed several approaches to address sustainability.

The so-called E factor first presented by Sheldon [8] stressed the amount of waste generated for the production of a given amount of a desired product. Table 1.1 shows the E factor values in the chemical industry in the early 90s. Interestingly, the parameter obtained by multiplying the volume and the E factor is always within the same order of magnitude. When dealing with catalysis and aiming for optimised selectivity, it seems easier to impact industries with a limited volume but a high waste capacity and efforts should, therefore, be focused on bulk and fine chemicals.

Industry Segment	**Volume (tons/annum)[a]**	**E Factor (kg waste/kg product)**
Oil refining	10^6-10^8	ca. 0.1
Bulk chemicals	10^4-10^6	<1-5
Fine chemical industry	10^2-10^4	5->50
Pharmaceutical industry	10-10^3	25->100

[a]: Annual production of the product world-wide or at a single site.

Table 1.1: E factors in the chemical industry

Anastas and Warner [9] summarised their recommendations in the so-called 12 principles of Green Chemistry. They are:

1. **Prevent waste:** Design chemical syntheses to prevent waste, leaving no waste to treat or clean up.
2. **Design safer chemicals and products:** Design chemical products to be fully effective, yet have little or no toxicity.
3. **Design less hazardous chemical syntheses:** Design syntheses to use and generate substances with little or no toxicity to humans and the environment.
4. **Use renewable feedstocks:** Use raw materials and feedstocks that are renewable rather than depleting. Renewable feedstocks are often made from agricultural products or are the wastes of other processes; depleting feedstocks are made from fossil fuels (petroleum, natural gas, or coal) or are mined.

5. **Use catalysts, not stoichiometric reagents:** Minimize waste by using catalytic reactions. Catalysts are used in small amounts and can carry out a single reaction many times. They are preferable to stoichiometric reagents, which are used in excess and work only once.
6. **Avoid chemical derivatives:** Avoid using blocking or protecting groups or any temporary modifications if possible. Derivatives use additional reagents and generate waste.
7. **Maximise atom economy:** Design syntheses so that the final product contains the maximum proportion of the starting materials. There should be few, if any, wasted atoms.
8. **Use safer solvents and reaction conditions:** Avoid using solvents, separation agents, or other auxiliary chemicals. If these chemicals are necessary, use innocuous chemicals.
9. **Increase energy efficiency:** Run chemical reactions at ambient temperature and pressure whenever possible.
10. **Design chemicals and products to degrade after use:** Design chemical products to break down to innocuous substances after use so that they do not accumulate in the environment.
11. **Analyse in real time to prevent pollution:** Include in-process real-time monitoring and control during syntheses to minimise or eliminate the formation of by-products.
12. **Minimise the potential for accidents:** Design chemicals and their forms (solid, liquid, or gas) to minimise the potential for chemical accidents including explosions, fires, and releases to the environment.

These principles can be found expressed slightly differently in the relevant literature [10].

In 2003, the Integrated Pollution Prevention and Control document [11] was obtained by a joint action between the European Union governments and the chemical industry. It takes into account academic addresses such as the 12 principles of Green Chemistry and the E factor and summarises the Best Available Techniques (BAT) that have to be matched to achieve a high level of protection of the environment as a whole. It lays down a framework requiring member states to issue operating permits for certain installations carrying on industrial activities. For numerous processes it shows that zeolites are frequently considered as BAT and therefore they seem to be an obvious choice when dealing with catalysis.

A new type of zeolitic catalysts [12] has been recently invented at the Catholic University of Leuven by the group of Profs. Jacobs and Martens. Nanoslabs with MFI zeolite framework topology and having aluminosilicate composition were assembled into nanosize crystals and Zeogrid materials. Nitrogen adsorption revealed the presence of two types of porosity: ultra-microporosity characteristic of MFI type framework and super-microporosity consisting of interlinked parallelepipedic voids occurring in between individual nanoslabs.

Interesting results are expected with such a well-organised structure of the catalysts, particularly regarding to internal mass transfer limitations and/or diffusion and a collaboration was therefore set up. Delft University of Technology’s input in this project was related to the evaluation of these catalysts in catalysis along with their potential impact regarding sustainability. Other partner groups were in charge of synthesis, characterisation, membrane applications, adsorptive separation and multiscale modelling.

Even though the catalyst structure has no direct impact on sustainability, it could allow, in this case, faster reactions and therefore ease the transition between homogeneous and heterogeneous catalysis for processes currently applied.

1.2. Choice of a model reaction

As it is impossible to improve the sustainability of all reactions in a general way, it has been decided to focus on basic and very common reactions where the improvement could be done in a chemical way. Unless finding a new synthetic route this means that the improvement of the investigated reactions has to be linked with a modification of the catalyst. All others factors are indeed very specific to a precise reaction and their generalisation would surely be very difficult.

Industrial organic chemistry has a very particular structure, as presented in Figure 1.1. Starting from only three fossil sources i.e. gas, coal and oil, it is possible to get a wide range of complex compounds with only a few operations.

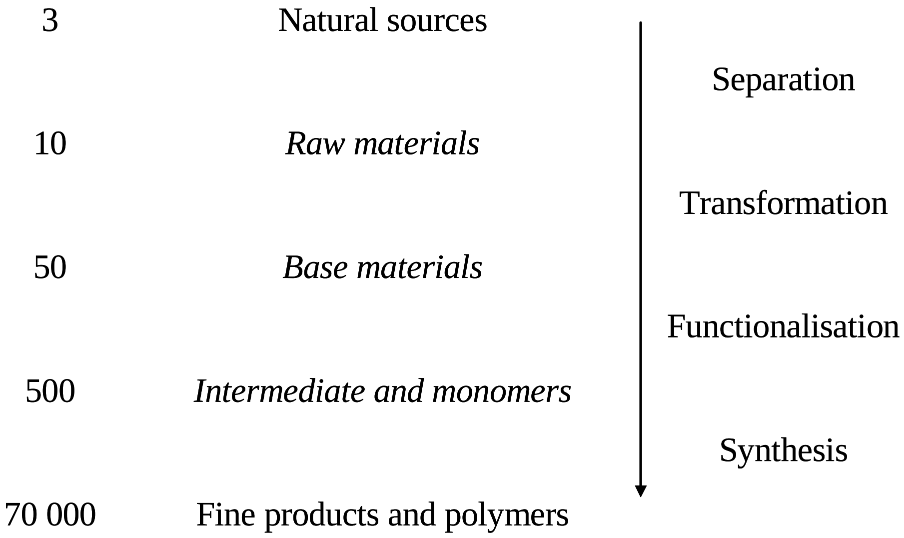

Figure 1.1: Structure of industrial organic chemistry

An important work has already been performed in the first step to get very pure raw materials. The economic aspect is so important that numerous specialised research groups already work on these topics. Moreover, the last step, organic synthesis itself, allows getting very specific and valuable compounds, such as drugs, dyes or plastic. The production capacity for these compounds is however generally very low compared to bulk chemicals. There is no special need, at this time, to try to get these processes more sustainable as long as bulk chemical processes are still operated in an unsustainable way.

To combine this approach and the academic recommendations, it was decided to focus on the most common organic compounds, that is to say base materials, intermediates and monomers. These compounds are produced in a large enough scale and an improvement in sustainability will certainly be possible and will have a significant impact.

According to Figure 1.1, there are still hundreds of processes that can be investigated. In order to narrow the number of compounds to study, it was decided to consider only acid-catalysed reactions and oxidations, which are among the most industrially important reactions in terms of occurrence and production capacities. Furthermore, many industrial processes using these two types of reactions are still using homogeneous catalysts such as $AlCl_3$ and other common Lewis acids or sulfuric, nitric, phosphoric and hydrochloric acids as Brønsted acids. These reactions consist of nitration, sulfonation, esterification, alkylation and acylation, many (de)protection reactions, epoxide ring openings, many rearrangements, alcohols and thiols syntheses. Processes linked to them are often environmental unfriendly and an important effort has still to be done regarding sustainability. Moreover, introduction of acidity in zeolites is very frequent and working on reactions requiring acid catalysis is therefore fully compatible with the type of catalysts developed within this project.

An excellent example to show the interest of this choice is the alkylation of aromatics. In former days, such processes have mainly been carried out in the presence of homogeneous Lewis or Brønsted acid catalysts such as $AlCl_3$, $FeCl_3$, BF_3 or HF, using a Friedel-Crafts type protocol. The already stated drawbacks of such homogeneously catalysed processes can be overcome by applying heterogeneous catalysis. Therefore, much industrial research effort has already been invested to develop alternative solid-acid technologies free of drawbacks, such as low yields, environmental impacts throughout air and water pollutions, use of corrosive catalysts leading to handling and disposal problems, production of large amounts of salts due to neutralisation, necessity of high amounts of catalyst and its relatively poor life-time, high heat consumption to achieve a good separation between products and catalyst, formation of oligomers and impurities.

By checking the abundant literature, it has been possible to find many important industrial processes and reactions that are still using homogeneous acid catalysts [11, 13-15] and that may be relevant for a heterogeneous acid catalyst switch. However, in 1999, more than 100 industrial processes were already described with a heterogeneous acid catalyst and 40% of them were of the zeolite type [16].

Products	**Catalysts**	**Remarks**
1,2-dichloroethane	$CuCl_2$ (chlorinating agent)	oxychlorination
Acetone	H_2SO_4	by-product of cumene process, BAT=zeolites
Acrylate esters	H_2SO_4	esterification
Adiponitrile	H_3PO_4	vapour phase reaction exists
Alkylbenzene	HF, HBF_4, $AlCl_3$	Friedel-Crafts alkylation
Allyl chloride	$PdCl_2$-$CuCl_2$	oxychlorination
Bisphenol acetone	H_2SO_4, dry HCl - MeSH	*ortho/para* isomers possibility
Butanol (*sec*, *tert*)	from butenes, H_2SO_4, acidic ion exchanger	sulfate process
n-butyl acetate		esterification
Caprolactam	H_2SO_4	Beckmann rearrangement
Chlorobenzene	$FeCl_3$ or $CuCl_2$	direct chlorination or oxychlorination
Chloroform	$CuCl_2$, KCl	CH_4 oxychlorination: all $CH_xCl_{(4-x)}$ products
Chloromethane	$ZnCl_2$, $FeCl_3/ZnCl_2$, $CuCl_2$, H_3PO_4, SiO_2	mainly with radical chain reaction
Chloroprene	CuCl	isomerisation
Cumene	H_2SO_4, $AlCl_3$, H_3PO_4/SiO_2 or zeolites	Friedel-Crafts alkylation, BAT=zeolites
DDT	acid-catalysed condensation	decreasing because of toxicity
Dioxane	H^+	
Dioxolane	H^+	unstable in strong acids

Products	**Catalysts**	**Remarks**
Diphenylmethane diisocyanate		not used commercially
Ethanol	H^+	mostly by fermentation
Ethyl acetate	H^+, $Al(OEt)_3$ + Zn^{2+}, Cl^- as promoter	esterification
Ethylbenzene		Friedel-Crafts alkylation
Ethyl chloride	$AlCl_3$, $FeCl_3$	reagent for the manufacture of $PbEt_4$
Ethylene glycol	H_2SO_4	ethylene oxide hydrolysis, mostly uncatalysed
Formic acid	H_2SO_4	acid used to avoid an equilibrium
Higher linear olefins	$AlEt_3$	Ziegler process
Higher branched olefins	H_3PO_4/SiO_2, H_2SO_4, acidic ion exchanger	non biodegradable
2-propanol	from propene, H_2SO_4, HPA, ion exchanger	sulfate process
Methyl *t*-butyl ether		production decreasing, carcinogenic
Phenol	H_2SO_4	cumene process only, BAT=zeolites
Tetrachloroethylene	$CuCl_2$, $FeCl_3$, $AlCl_3$	with C_2HCl_3, oxychlorination
Tetrachloromethane	Fe, $FeCl_3$, no catalyst	main process for CCl_4
Trichloroethylene	$CuCl_2$, $FeCl_3$, $AlCl_3$	with C_2Cl_4, oxychlorination

Table 1.2: European most important industrial products in terms of capacity and requiring an acid catalyst, according to the IPPC document [11].

According to the 2003 Integrated Pollution Prevention and Control document [11], the European production capacity of most of the compounds described in Table 1.2 was above 100 kt/y. Some industrially important processes like cationic polymerisation have not been considered relevant for this study as it seems unrealistic to handle them on a solid catalyst.

The synthesis of all the products listed in Table 1.2 involves, at least for one of the possible routes, a homogeneous acid-catalysed reaction. Homogeneous acid-catalysed processes are often linked to many environmental unfriendly issues. Many Lewis or Brønsted acids are highly corrosive, react violently with water and lead to a substantial formation of salts during neutralisation in the work-up part of the process. Moreover, separation of products from the catalyst by extraction and/or distillation leads to high-energy consumption. Furthermore, in many cases, the catalysts cannot be recovered and/or have to be used in stoichiometric amounts to give reasonable yields as in the case of Friedel-Crafts alkylation where aluminium trichloride is destroyed and has to be present sometimes in more than one equivalent to allow full conversion.

For these reasons, trying to replace these catalysts by heterogeneous catalysts is an important issue when dealing with sustainability, as it may solve many problems in the same time.

Concerning sustainability, the main improvements carried by heterogeneous catalysts in acid-catalysed reactions or oxidations may be:

- An increase of the reaction selectivity and/or yield due to shape-selectivity induced by the support.
- An easier reaction work-up leading to a decrease of the amounts of solvents and energy used for purification.
- Less waste or useless side-products.
- A decrease of gas emission (CO_2, NO_x, SO_2, volatile organic compounds, …) and water pollutants (salts, unreacted feedstock, side-products).
- Catalysts recovery instead of destruction.
- A reduction of the catalyst amount.
- Better handling and storage conditions, regarding both the catalyst and the products.

Next to these straightforward improvements, heterogeneous catalysts have intrinsic interesting properties and shape-selectivity is frequently targeted when using zeolites. Shape-selectivity can be achieved through three different ways, namely selectivity at the feedstock, at the transition state or at the product level, which will be discussed in more details in Chapter 2. In all three cases, access is allowed to a restricted amount of species due to steric constraints generated by the zeolite framework.

For some of the compounds listed in Table 1.2, such as phenol and acetone produced through the cumene process, there is already an emerging heterogeneous acid-catalysed process [11, 15] that is considered as BAT. These new processes are not only more sustainable but also often more competitive. Yield and selectivity have already been improved in a really interesting way and for this reason they may not be relevant for this study anymore.

Regarding to several processes, the acid-catalysed route is not the main one and is only justified through some law dispositions. This is for example true for the production of ethanol, which is preferably done in Europe by fermentation whenever possible, essentially because of tax legislation.

In some other cases, products presented in Table 1.2 have to be seen as valuable by-products and this route is not the one dedicated to their aimed production, as for the chlorination of alkanes, which is usually a radical chain reaction using chlorine and initiated by light. The acid-catalysed route takes here advantage of the fact that the Lewis acid is also the chlorinating agent.

Among the reactions using Lewis or Brønsted acids, a combination between acidic reactions and oxidations can occur as in the oxychlorination reactions. As it is planned to investigate only the acidic properties of the new catalysts at this time, all these processes should be let aside to be sure to avoid an interpretation due to oxidation or to a combination of acidic and oxidising properties of the catalysts.

Furthermore, some products presented in Table 1.2 are not environmental friendly themselves, (this is the case of DDT, chloroprene and tetrachloromethane for example) or are used as intermediates for environmental unfriendly compound syntheses like tetraethyl lead which production is decreasing considerably. It does not seem pertinent to work on improving this kind of processes either, as it is assumed that they will have less and less importance in the future and that industry is already trying to replace them by more environmental friendly compounds. A very recent study [17] suggests, however, that DDT may play again a role as it is by far the cheapest and most effective pesticide to fight malaria which is again at the origin of a lot of deaths in under-developed countries.

Finally, some types of reactions are already investigated by other groups in this project, even if sustainability is not the main concern. This concerns the catalytic cracking, the Beckmann rearrangement and the epoxidation of hexene. These processes will not be investigated either, in order to widen the exploration of the potential range of the new catalysts.

By considering all these observations, it is possible to considerably reduce the number of relevant processes for this study. Those remaining can easily be linked to few common organic reactions. Some other basic organic reactions may also be added because they are widely used, even if the production figures for a specific compound are not industrially significant. As presented in Table 1.3, a particular reaction that may introduce position selectivity, isomers formation issues or with a particular environmental issue may be investigated for each of these remaining reactions or processes as it is an important aspect of the catalyst evaluation.

Reaction type	**Example**	**Interest**
Friedel-Crafts alkylation	alkylation of naphthalene	α/β selectivity [18-19], 2,6/2,7 selectivity [20-21], isomerisation and transalkylation [22].
Friedel-Crafts acylation	2-acetyl-6-methoxynaphthalene, intermediate for Naproxen® (anti-inflammatory drug)	α/β selectivity [13], $AlCl_3$ in stoichiometric amount.
C-C coupling	bisphenol A	*ortho/para* isomers [23].
Protection/deprotection reactions	dioxane, dioxalane	formation and hydrolysis of acetals.

Reaction type	**Example**	**Interest**
Aldol reaction	from acetaldehyde towards butadiene	without elimination (aldol condensation).
Electrocyclic reaction	butadiene + cyclopentadiene	non-activated substrates for Diels-Alder reaction, endo/exo products.
Hydroxyalkylation		often bis-arylmethane type by-products.
Alcohols from olefins	Cyclohexanol from cyclohexene	sulfate process = important amounts of salts.
Olefin dimerisation	propylene	high octane number gasoline.
Olefin isomerisation	hexane isomerisation	linear/branched olefins.

Table 1.3: Interesting reactions for the evaluation of the catalysts.

For some of these examples, TU Delft has previous knowledge. Some work has already been performed on naphthalene isopropylation, hexene hydration, aldol condensation and olefin dimerisation and/or isomerisation. These reactions are consequently the most interesting starting points for this study as they allow the use of some previous analysis techniques. Moreover some potential problems are known. Other interesting points like isomerisation issues can easily be linked to these reactions.

Naphthalene alkylation is interesting for many chemical reasons:

- A comparison between different alkylating agents (alcohol, alkyl halide, alkene) can be made.
- The selectivity towards the industrially relevant 2,6-isomer can be investigated.
- Isomerisation or transalkylation are described as reaction pathways to the 2,6- and 2,7-dialkylnaphthalenes [22], resulting in a complex system.
- If the alkyl group is big enough (at least an isopropyl), isomerisation of the alkyl chain may also occur.
- Shape-selectivity is claimed over some zeolites such as H-Mordenite.

Naphthalene alkylations are already performed on heterogeneous catalysts but it is still impossible to get one specific compound in very high yields, even if many catalysts and reaction conditions have already been investigated, making it possible to still consider that reaction as needing further improvement regarding to sustainability.

Finally, the existence of a process for the isopropylation of naphthalene in Germany (Duisburg) and in Japan allows anchoring this work into industrial reality. Rütgers Kureha Solvents is running this process for a total of 10,000 tpa [24] using a silica-alumina catalyst. The flow diagram is presented on Figure 1.2.

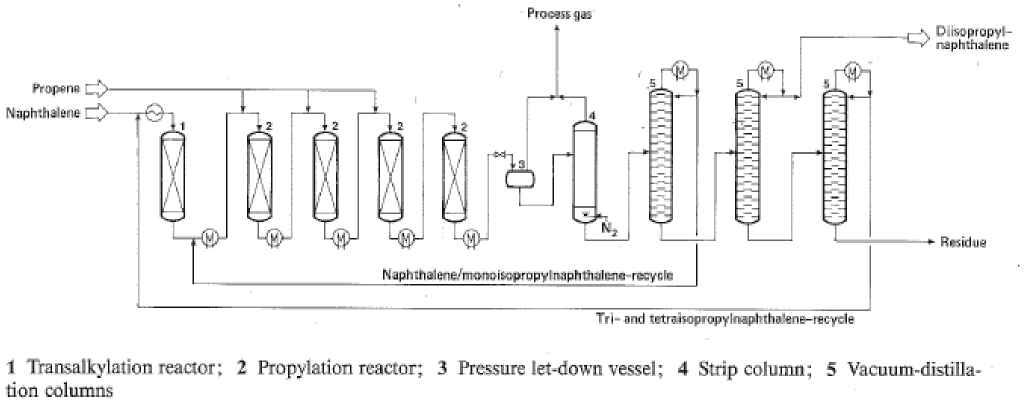

Figure 1.2: Flow diagram of the Kureha process

Naphthalene and recycled over-alkylated species are fed into a reactor over an aluminosilicate catalyst to undergo transalkylation. The product is then fed together with under-alkylated recycled species into a series of alkylation reactors. Propene is fed in order to bring the alkylation degree towards diisopropylation. The reaction mixture is then split by vacuum distillation to provide the diisopropylnaphthalene mixture. The reaction is performed at 7 bars and 200°C.

Even if the selective formation of 2,6-diisopropylnaphthalene appears to be challenging, the isomer mixture in itself has an industrial application as solvent for carbonless copy paper and selectivity towards diisopropylation in general would already be of great interest. 2,6-DIPN on the other hand is one of the possible intermediates to reach 2,6-naphthalenedicarboxylic acid needed by the polymer industry to generate PolyEthylene Naphthalate (PEN), presented in Figure 1.3. An SRI report, issued in 1993, presents the full process developed by Amoco (Figure 1.4) for the production of 2,6-naphthalene dicarboxylic acid (NDA), the intermediate. Applications for this advanced polymer are so far hindered by the monomer production costs, but its properties outperform those of PolyEthylene Terephthalate (PET), suggesting that the potential market is important.

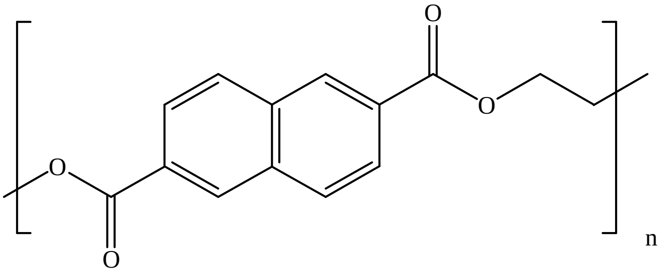

Figure 1.3: Structure of the PolyEthylene Naphthalate

The process proposes a route to 2,6-dimethylnaphthalene from toluene and butadiene in order to avoid the issue of the selectivity towards the positions 2 and 6 on naphthalene. The oxidation part to yield NDA and further 2,6-dimethylnaphthalene dicarboxylate (NDC) is performed in an analogue way than the oxidation of *p*-xylene towards terephthalic acid, that is in an acetic acid liquid phase, over a catalyst containing cobalt, manganese and bromine. The data provided in this review could be applied as well for 2,6-diisopropylnaphthalene therefore allowing a full economic description.

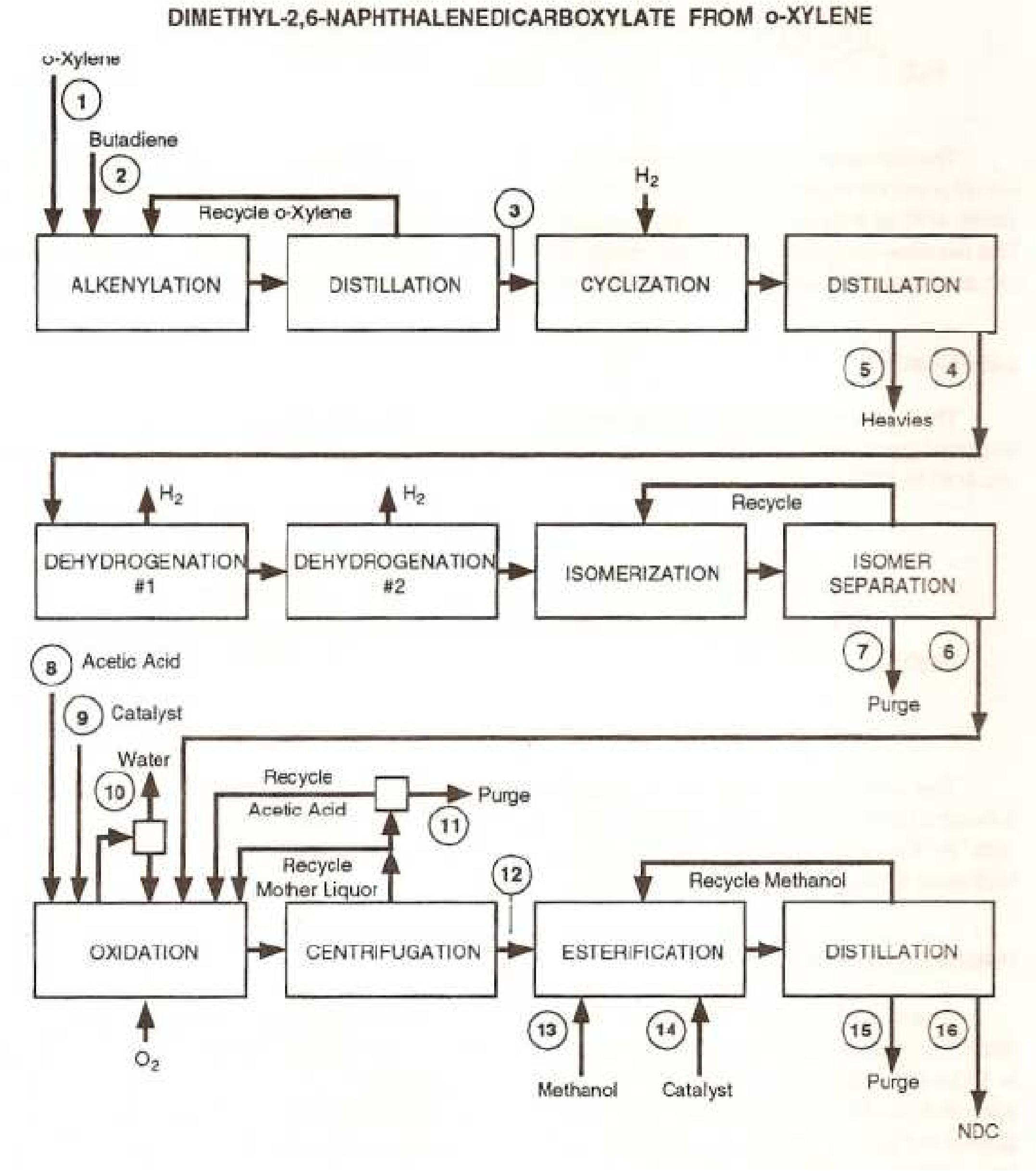

Figure 1.4: Block diagram from the Amoco process as presented in the SRI report [25]

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2

Diisopropylnaphthalenes and catalysis in Friedel-Crafts alkylation

Abstract

Basic concepts of diisopropylation of naphthalene with respect to nomenclature, analysis, catalysts, synthesis and modelling are provided. Furthermore, analytical techniques are discussed and a more accurate system for analysis is presented. Finally, general aspects of shape-selectivity are discussed and illustrated by a comparison with the disproportionation of xylenes over ZSM-5 zeolites.

2.1. Nomenclature

Naphthalene substitution positions are very precisely numbered in order to ease communication between chemists [1]. The central organisation IUPAC (International Union of Pure and Applied Chemistry) recommends the numbering presented in Figure 2.1.

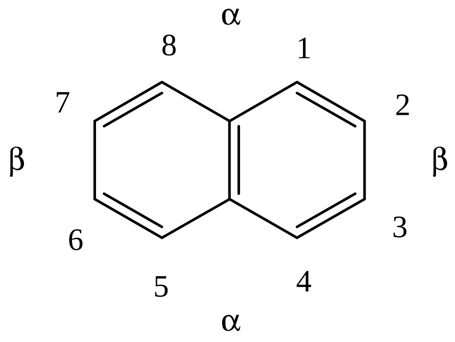


Figure 2.1: Nomenclature for substituent positions of naphthalene.

Due to symmetry reasons, naphthalene has two types of chemically different substitution positions. Carbons denoted 1, 4, 5 and 8 are called α while carbons 2, 3, 6 and 7 are called β. α-positions are the kinetically favoured ones for substitution while β-positions are the thermodynamically ones. The two carbons of the fused ring system cannot undergo any substitution and are therefore usually not considered.

For the same symmetry reasons, the total number of diisopropylnaphthalene (DIPN) isomers is only 10 and not 28. Following the IUPAC rules, they should be named 1,2-DIPN, 1,3-DIPN, 1,4-DIPN, 1,5-DIPN, 1,6-DIPN, 1,7-DIPN, 1,8-DIPN, 2,3-DIPN, 2,6-DIPN and 2,7-DIPN. Intermediates compounds are 1-isopropylnaphthalene (1-IPN) and 2-isopropylnaphthalene (2-IPN). Products with a substitution degree higher than 2 will be referred to in this work as polyisopropylnaphthalenes (PIPNs).

2.2. Characterisation

Commercial products like 1-IPN, 2-IPN, 2,6-DIPN and 2,7-DIPN were used as references. Non-commercially available products were isolated with preparative gas chromatography and identified with ^{1}H-NMR and ^{13}C-NMR, in agreement with the relevant literature [2].

2.2.1. Gas Chromatography

Position isomers can have different liquid vapour data and different interactions with the support so Gas Chromatography (GC) can yield separation between the IPN / DIPN systems and between isomers themselves. These differences are however very small and a precise analysis has to be carried out in order to avoid misinterpretation or bad separation as stated by Brzozowski *et al.* [3].

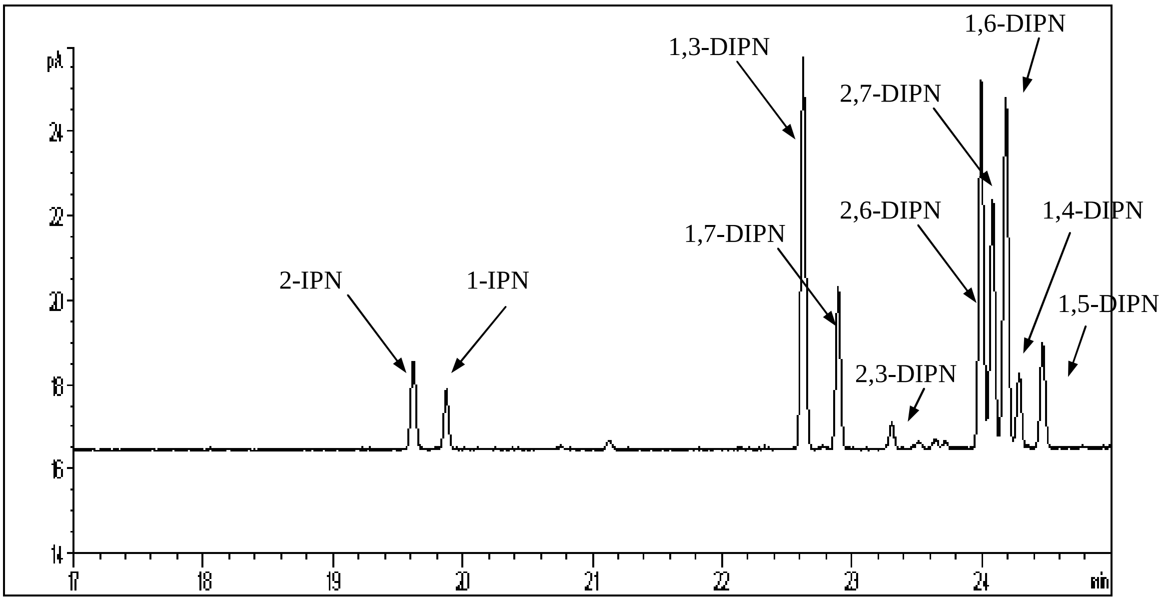


Figure 2.2: Typical chromatogram displaying the 2 IPNs and the main DIPNs.

As can be seen in Figure 2.2, baseline separation is not always achieved with concentrated samples and one should be very careful when presenting selectivity towards one specific isomer. In order to circumvent this problem, several columns and temperature programs have been tested. In addition, when samples are too diluted it becomes difficult to make a clear distinction between the baseline variation and a small peak. Therefore the signal-to-noise ratio was set at 10 to avoid huge relative errors. This means that at low conversion, some peaks, though detectable, are deliberately not integrated.

When nitrogen is used as carrier gas instead of helium, analysis time required is more than doubled and the separation of the DIPN isomers is less efficient. Hydrogen might have allowed an even better separation than helium but was not used due to internal safety regulation.

2.2.1.1 Wax column

A CP-Wax-52 column with dimensions of 25 m x 0.25 mm, film thickness 0.25 µm was used. Helium was used as carrier gas and the flow was kept constant at 1 ml/min. The split ratio was 1:100. The injection volume was 1 µl. The front detector temperature was 250°C and the temperature program was as follows: 1 min at 70°C and a ramp at 5°C/min till 250°C. The chromatograms obtained for a 2,6-DIPN/2,7-DIPN 1:1 mixture and for the commercial DIPN mixture provided by Fisher Scientific are presented in Figures 2.3 (a) and 2.3 (b) respectively.

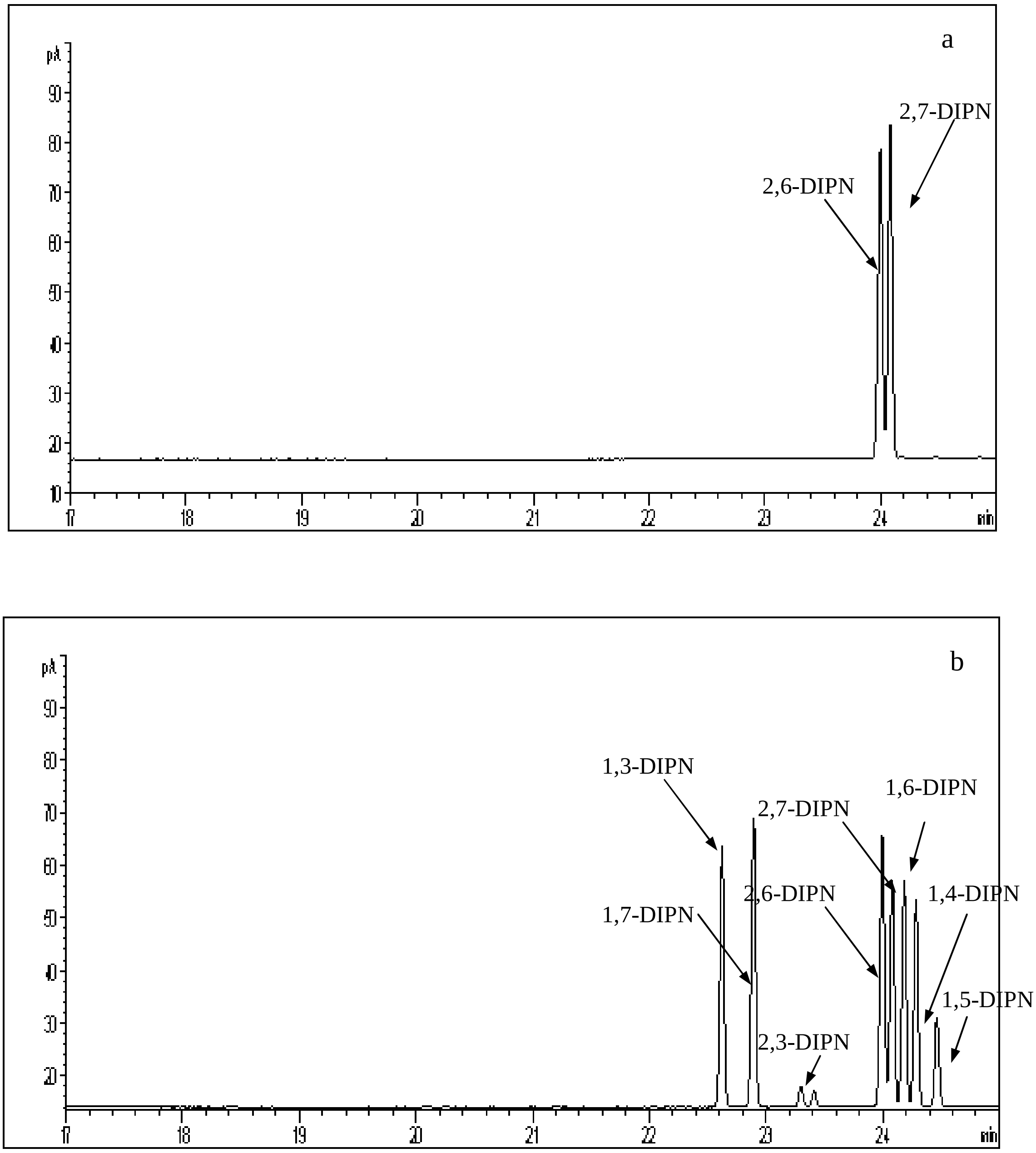
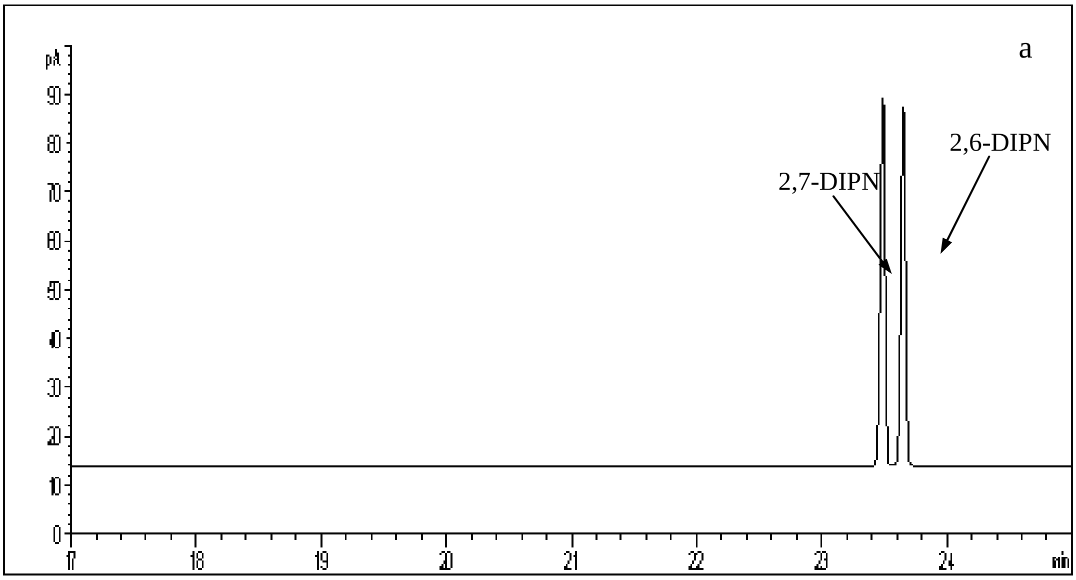


Figure 2.3: Chromatogram of a 2,6-DIPN/2,7-DIPN 1:1 mixture (a) and of the commercial DIPN mixture (b) on the CP-Wax-52 column.

2.2.1.2 CP-Sil-8 column

A CP-Sil-8 column with dimensions of 25 m x 0.25 mm, film thickness 0.25 µm was used. Helium was used as carrier gas and the flow was kept constant at 1 ml/min. The split ratio was 1:100. The injection volume was 1 µl. The front detector temperature was 250°C and the temperature program was as follows: 1 min at 70°C and a ramp at 5°C/min till 250°C. The chromatograms obtained for a 2,6-DIPN/2,7-DIPN 1:1 mixture and for the commercial DIPN mixture are presented in Figures 2.4 (a) and 2.4 (b) respectively.



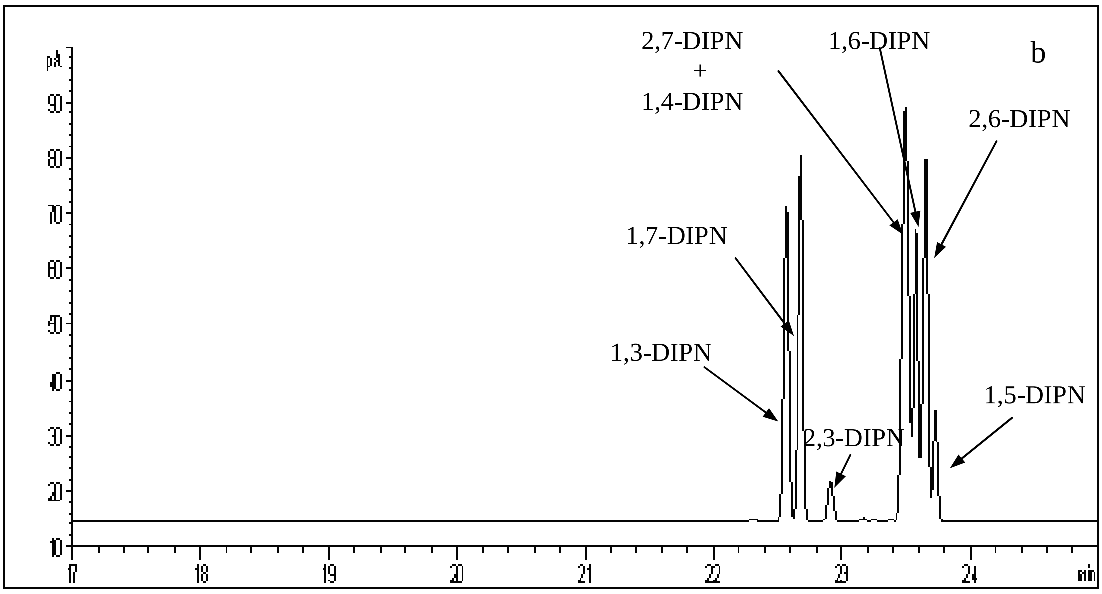
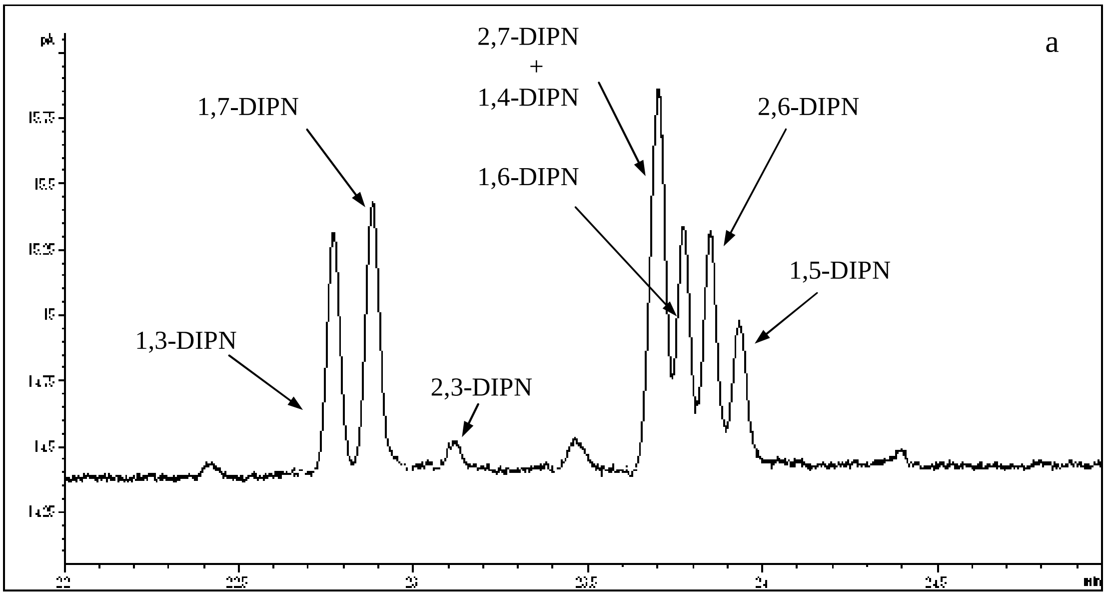


Figure 2.4: Chromatogram of a 2,6-DIPN/2,7-DIPN 1:1 mixture (a) and of the commercial DIPN mixture (b) on the CP-Sil-8 column.

As can be seen, the order of elution with respect to 2,6-DIPN and 2,7-DIPN is opposite to the one obtained on the CP-Wax-52 column. Peak intensity is comparable but some isomers are clearly better separated on one specific column. For example, separation of the latest isomers is reasonably good on the CP-Wax-52 column while the CP-Sil-8 displays one peak less. On the other hand, baseline separation of the binary mixture is obtained with the CP-Sil-8 column, but not with the CP-Wax-52.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15.5
15.25
15
14.75
14.5
14.25
22
22.5
23
23.5
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min
1,3-DIPN
1,7-DIPN
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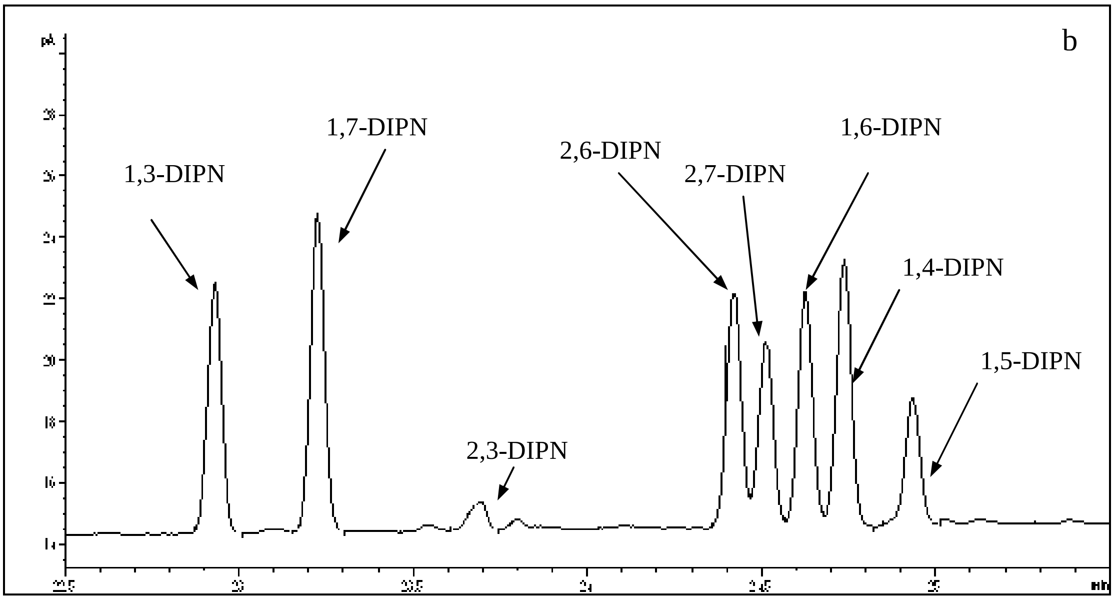
2,6-DIPN
1,5-DIPN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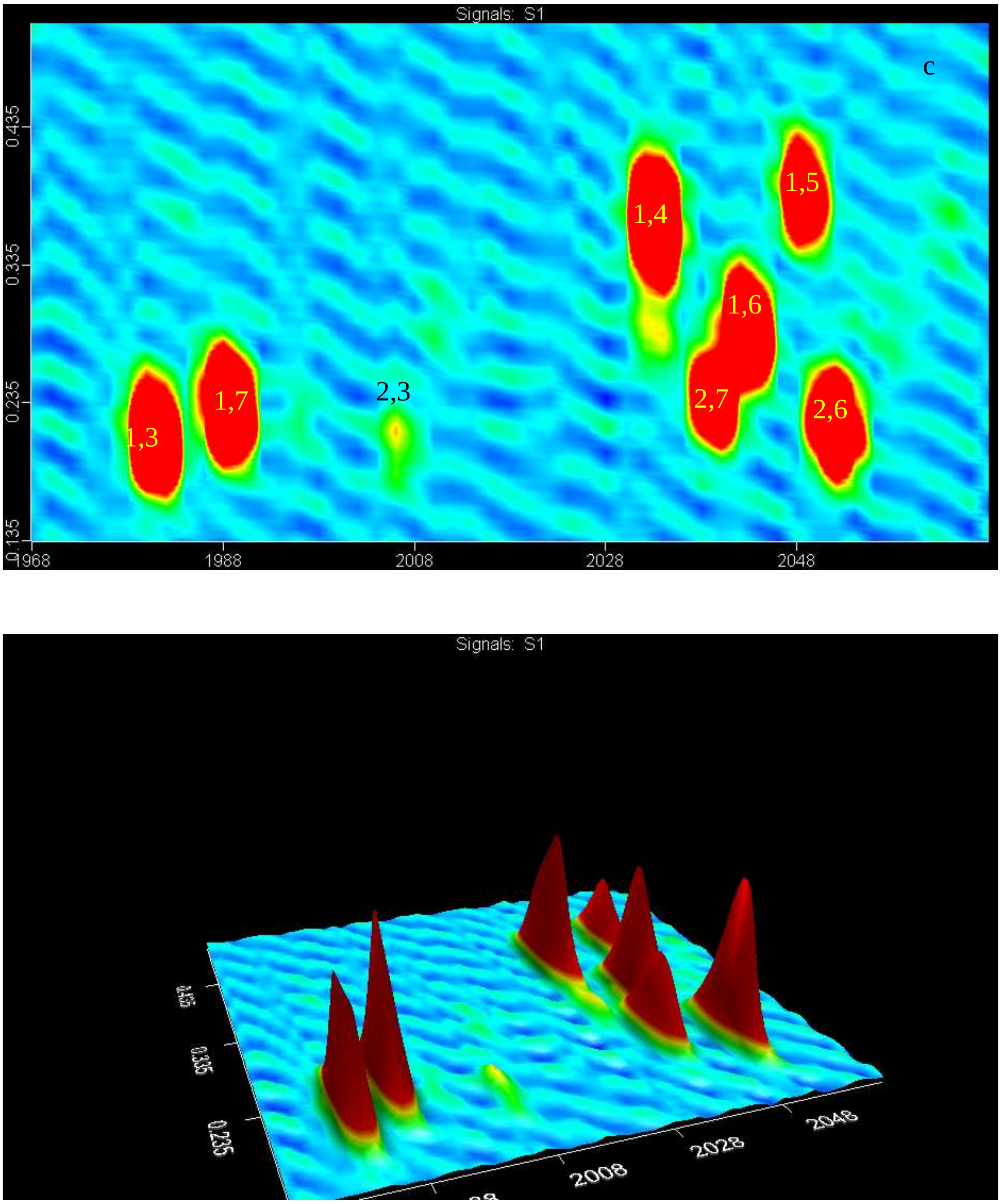

Figure 2.5: Experimental mixture of DIPNs over CP –Sil-8 (a), over CP–Wax-52 (b) and with GCxGC (c).

Figures 2.5 (a) and 2.5 (b) show part of chromatograms obtained for an experimental mixture of DIPNs over a CP-Sil-8 and a CP-Wax-52 column, respectively, while Figure 2.5 (c) shows the chromatogram obtained when using GCxGC. Conventional single column capillary gas chromatography offers much separation but often suffers from coeluting compounds or (unknown) interferences. In comprehensive two-dimensional gas chromatography (GCxGC) two independent separations are applied to an entire sample. The sample is first separated on a capillary column under programmed-temperature conditions. The effluent of this column then enters a thermal (or cryo) modulator, which traps each subsequent small portion of eluate, focuses these portions and releases the compounds into a second column for further separation. The second separation is made to be fast enough (e.g. 5 – 10 s) to permit the continual introduction of subsequent, equally small fractions from the first column without mutual interference.

In this particular application, comparing the chromatograms obtained over two different columns enables a better discrimination of some peaks due to the inversion in the order of elution. In this example, accuracy for peaks of 1,4-DIPN and 1,5-DIPN is clearly improved when the CP-Wax-52 column is used. Attribution of non-commercially available DIPNs is therefore eased when analysis is performed over several columns. Considering that α substituted isomers are more present when kinetic conditions are applied, and β-isomers under thermodynamic conditions, comparing chromatograms obtained under different operating conditions and with different separation pattern can lead to a full assignment of all isomers.

However, these important differences also lead to the conclusion that one should be really careful with peak assignment in this isomeric system and that working over several GC columns, either in parallel or in series, may be very interesting as they provide complementary information. Working with only one column, even with separation similar to the best examples described in the literature [3], is not generating accurate enough results, as peaks may be either not baseline separated or show some overlap. An alternative to GCxGC could be the use of deconvolution techniques but this supposes an ideal peak pattern, which is not always the case for the reaction products considered in this thesis.

2.2.1.3 Internal Standard and adsorption

Methyl benzoate was used as an internal standard to obtain calibration lines for naphthalene, 2,6-DIPN and 2-propanol. Considering the complexity of the samples to analyse and the amount of potential components, it was considered more accurate and easier to establish calibration lines on several key components and to check if the derived response factors were matching computed ones that could therefore allow other computed values to be extrapolated for non commercial compounds. Theoretical response factors (RF) were calculated using Equation 2.1 described by Scanlon *et al.* [4] with parameters described by Poole *et al.* [5], where MW stands for the molecular weight of either the component studied or the reference and ECN stands for Effective Carbon Number and its value is determined with literature data.

$$RF = \frac{MW(comp) x ECN(ref)}{MW(ref) x ECN(comp)} \qquad (2.1)$$

Theoretical response factors obtained this way were identical to experimental ones and therefore assigned accordingly. In order to increase the accuracy, naphthalene was considered to be a better internal standard at low naphthalene conversions for data work-up and was therefore used as reference for the expression of response factors. In some 2,6-DIPN isomerisations, conversion was very low and therefore 2,6-DIPN was used as internal standard to gain accuracy.

Choosing a naphthalene type of internal standard allows a better differentiation between product families compared to methyl benzoate as it widens the differences between response factors. In addition, linear fitting was forced to the origin in order to allow more meaningful results at low naphthalene contents.

Furthermore, to ensure the validity of mass balances, adsorption studies have been performed for naphthalene, 2,6-DIPN and 2-propanol. It appears that naphthalene and its derivatives are not absorbed at all in the zeolites at room temperature in the presence of cyclohexane as solvent while up to 30% of the 2-propanol is adsorbed overnight. These results justify the expression of mass balances based on naphthalene or one of its derivatives.

2.2.2. Gas Chromatography - Mass Spectroscopy

As DIPNs are position isomers, no difference can be expected in terms of fragmentation pathways. The only variation lays in the fragment abundances due to small variations of the fragment stability, but in order to identify the products without any doubts high reproducibility and high sample purity are required. For these reasons, GC-MS was solely used to identify families of compounds and not the compounds themselves.

2.2.3. Nuclear Magnetic Resonance

In ^{1}H-NMR, neighbouring groups have an influence on the value of the chemical shift δ and on the fine structure. This may lead to differences between isomers in terms of both peak positions and coupling patterns. It allows making a clear distinction between isopropyl groups carried by one or two aromatic rings.

In ^{13}C-NMR, the amount of peaks for quaternary carbons will provide very useful information. Depending on the substitution positions on naphthalene, DIPNs may be mirror symmetric (1,4-DIPN, 1,8-DIPN, 2,3-DIPN and 2,7-DIPN), point symmetric (1,5-DIPN and 2,6-DIPN) or show no symmetry at all (1,2-DIPN, 1,3-DIPN, 1,6-DIPN and 1,7-DIPN).

DIPNs without symmetry properties reveal 4 different quaternary carbons, mirror symmetric ones show 3 and point symmetric ones only 2, as can be seen in Figure 2.6.

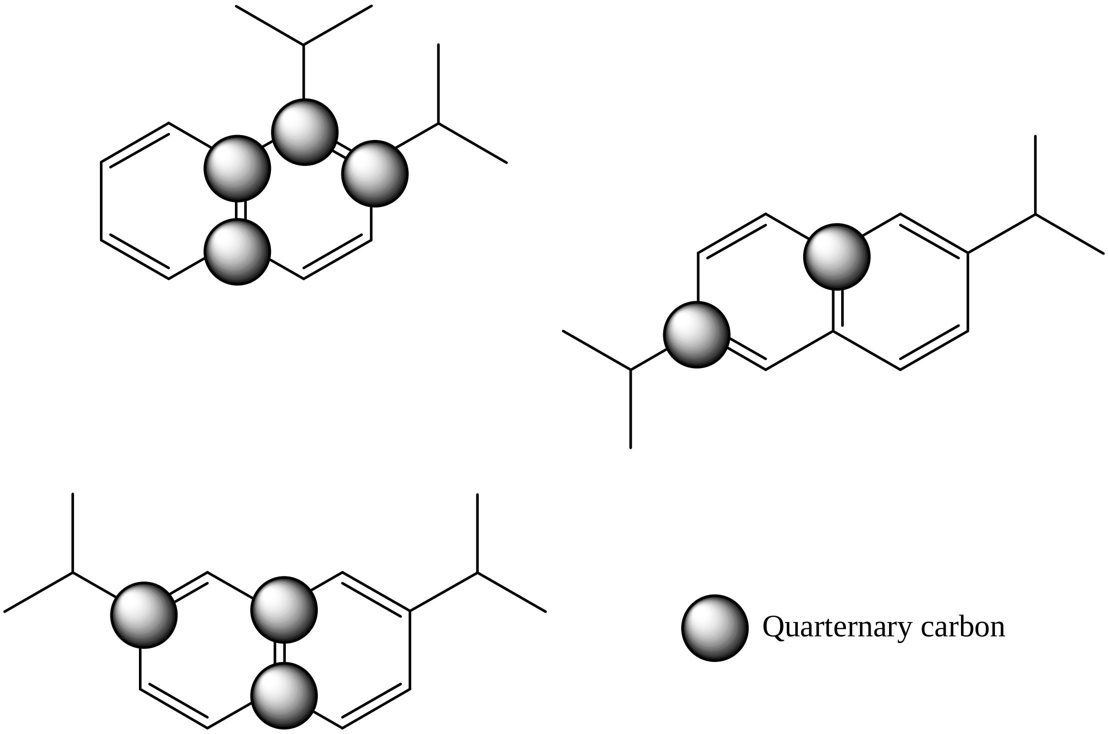

Figure 2.6: The different quaternary carbons with respect to symmetry.

One should however not forget that chemical shifts of all isomers will be very similar. Combining ^{1}H-NMR and ^{13}C-NMR allows the structural identification of all 10 isomers. The only requirement is that samples must be very pure, as peak overlapping from different isomers will make the spectrum interpretation considerably more difficult if not impossible.

2.3. Experimental set-up

All test reactions were performed in a 50 mL stirred stainless steel Parr autoclave (Figure 2.7) using the following standard procedures.

For alkylation reactions, 320 mg of naphthalene (2.5 mmol), 500 mg of catalyst (powder) and 0.38 ml (5.0 mmol) of 2-propanol were stirred at 150-200 rpm for 24 h at

200°C in 25 mL of cyclohexane. At the beginning of a catalytic run, samples were taken hourly. For isomerisation reactions, 530 mg of 2,6-DIPN (2.5 mmol) and 500 mg of catalyst in 25 mL of cyclohexane were introduced into the reactor vessel and heated at 200°C for 24 h. Pressure was built up autogenously and was set by the reaction temperature.

In both cases, temperature was changed when performing optimisation experiments.

Catalysts applied and their characteristics are described in Chapters 3 and 4. They were calcined prior to use under a static air atmosphere according to the following procedure: 3°C/min from room temperature to 550°C and kept at that temperature for 5 h before cooling to room temperature. Relatively high amounts of catalyst were used to reach a significant conversion, even with poorly active catalysts. The catalyst was removed from the reaction mixture by filtration over cotton and the reaction samples were analysed directly. Generally, the mass balance was about 95% based on naphthalene and about 70% based on C_3.

These operating conditions are close to what is generally described in the literature. Temperatures are usually between 200°C and 250°C with few articles mentioning higher temperatures but in gas phase reactions. Cyclohexane is generally used as a solvent even though some research groups prefer to use mesitylene despite its aromatic character that may lead to solvent alkylation! No more than three samples per run where taken and only in prospective experiments in order to ensure that sampling remained without influence on the outcome of the reaction.

Figure 2.7: Experimental set-up

2.4. Alkylation, dealkylation, transalkylation and isomerisation in Friedel-Crafts reactions

The Friedel-Crafts reaction was first described by Charles Friedel and James Crafts in 1877 [6-7]. Organic textbooks [8-9] usually describe Friedel-Crafts alkylation of benzene with Lewis acids such as $AlCl_3$ as catalyst according to the mechanism presented in Figure 2.8. It is clearly not the aim of this work for reasons presented in Chapter 1 but the mechanism explaining the reactivity and the selectivity is very similar in the case of acidic zeolites as described by Sauer *et al.* [10].

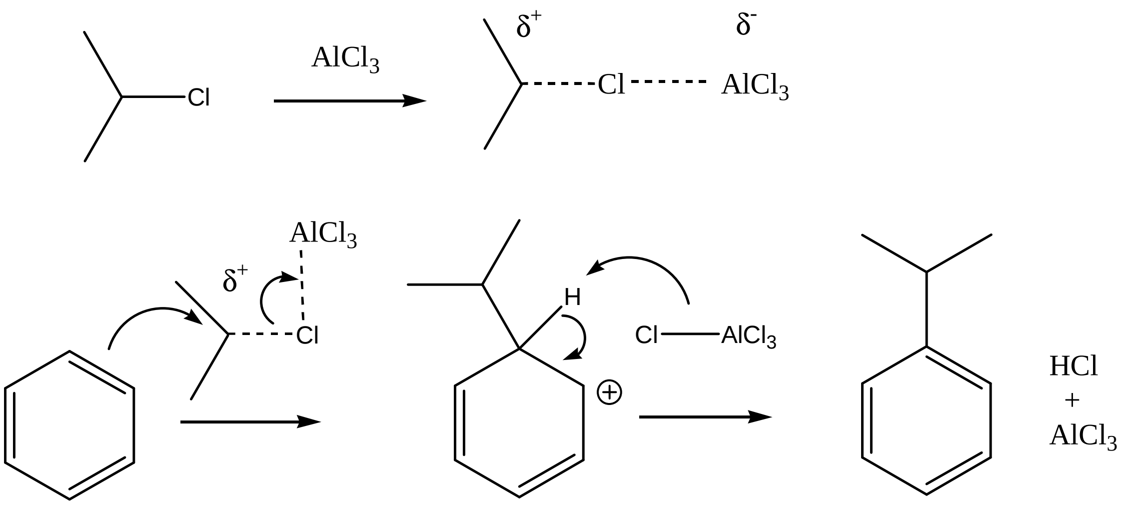

Figure 2.8: Friedel-Crafts classical alkylation mechanism with $AlCl_3$ as catalyst and isopropyl chloride as reactant.

Friedel-Crafts reactions show a peculiar behaviour. Upon alkylation with an electron donating group, the substituted substrate becomes more reactive than the original substrate. This leads very easily to over-alkylation, unless it is prevented by steric constraints. Besides this, when dealing with naphthalene, rules that are valid for benzene derivatives must be adapted. It is no longer a question of ortho, meta and para substitution but of α or β substitution, as described in paragraph 2.1. But Friedel-Crafts alkylations have other drawbacks. Dealkylation, transalkylation and isomerisation reaction can also take place, as strong acids as well as high temperature also allow the cleavage of the alkyl group. Whether the cleaved alkyl group is simply removed or contributes to alkylation at another position, or on another substrate, is mainly related to temperature, operating conditions and the type of catalyst applied. If the catalytic system is fast enough, any Friedel-Crafts system will reach a thermodynamic equilibrium, as well in terms of substitution degree as in terms of position of the alkyl groups. A general representation of such a system, in the case of isopropylation, is presented in Figure 2.9. For isopropylation, n is usually limited to 3, as higher substitution degree is very unlikely due to steric reasons.

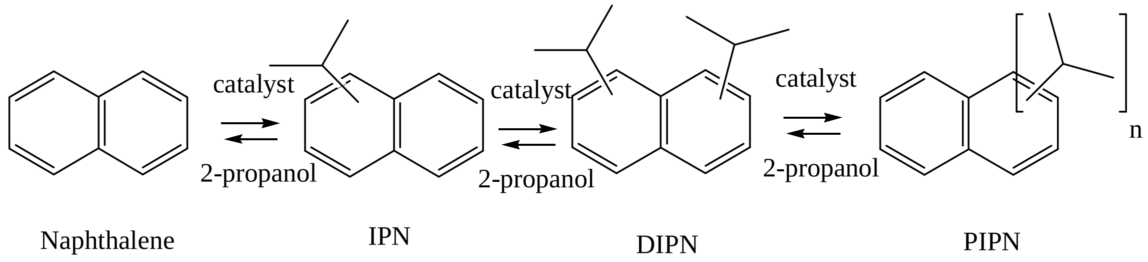

Figure 2.9: The different reaction steps in catalytic naphthalene isopropylation.

When it comes to industrial production, PIPNs and IPNs can simply be recycled to the reactor and other DIPNs isomerised to yield extra desired product, as described with the Kureha process in Chapter 1. One should, however, keep in mind that this recycling steps require high energy consumption and should therefore still have a negative impact on the sustainability of the process.

Aluminium chloride is nowadays widely described as the worst catalyst to use, but few data sustaining that do exist. For all the reasons listed in Chapter 1, this criticism is obvious when environmental aspects are taken into account. What research groups usually do not show is whether it still has to be considered as a good catalyst when chemical issues such as conversion and selectivity are concerned. Industry can only change its habits and its processes for overall economic reasons, not just to avoid paying a pollution tax, as implementing a complete new process will definitely cost much more.

Isopropylation over $AlCl_3$ was therefore studied in the liquid phase, at 200°C for 5 hours using 2-propanol as alkylating agent. Catalyst loading was 1 g. The product distribution obtained is presented in Figure 2.10.

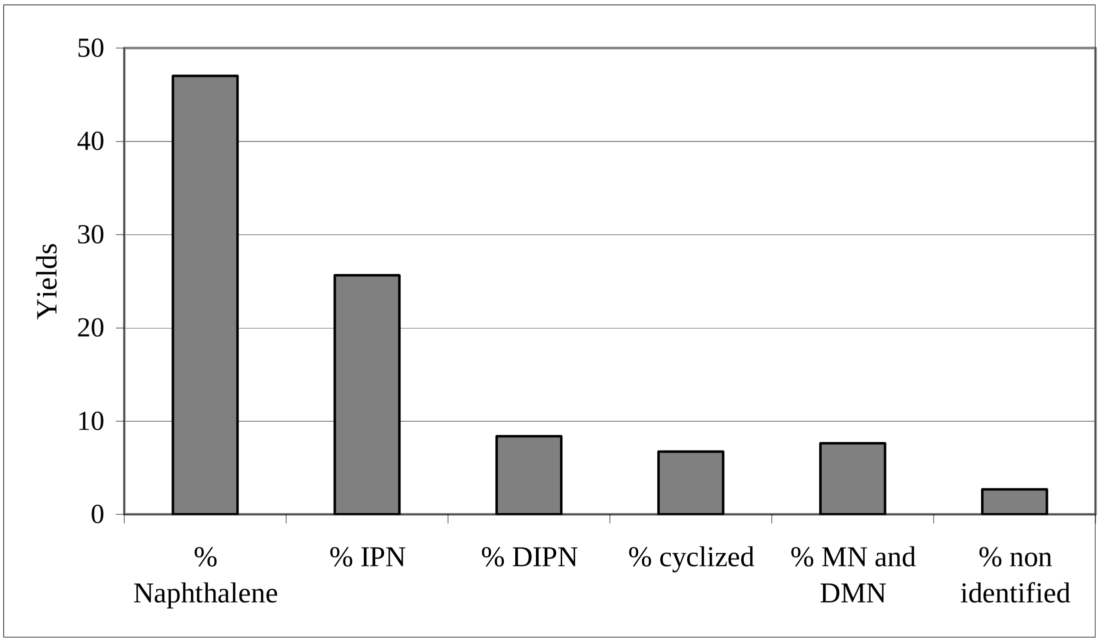

Figure 2.10: Product distribution of the alkylation of naphthalene with 2-propanol over $AlCl_3$ after 5 h.

First of all, the mass balance based on naphthalene could only be closed below 20% as numerous products could not be characterised. Assuming that the response factor is identical for all compounds in the reaction mixture, conversion can be approximated around 65% but unknown products then account for about 20% of the mixture. Isopropylation becomes only slightly predominant over reagent degradation and dialkylation is very limited. A typical chromatogram of the reaction products for this reaction over $AlCl_3$ and the widely described shape-selective H-Mordenite is presented, in Figures 2.11 and 2.12 respectively. It more clearly points out that aluminium trichloride, besides being environmentally unfriendly, is also a very poor catalyst for this reaction, as it catalyses a lot of side-reactions. Degradation of 2-propanol is important as shown by the high peak density at low retention times and the amount of methylated and dimethylated naphthalenes (MN and DMN).

Additionally, running the reaction only twice resulted in an important corrosion of the equipment and most of the consumable parts had to be changed before starting to investigate other catalysts.

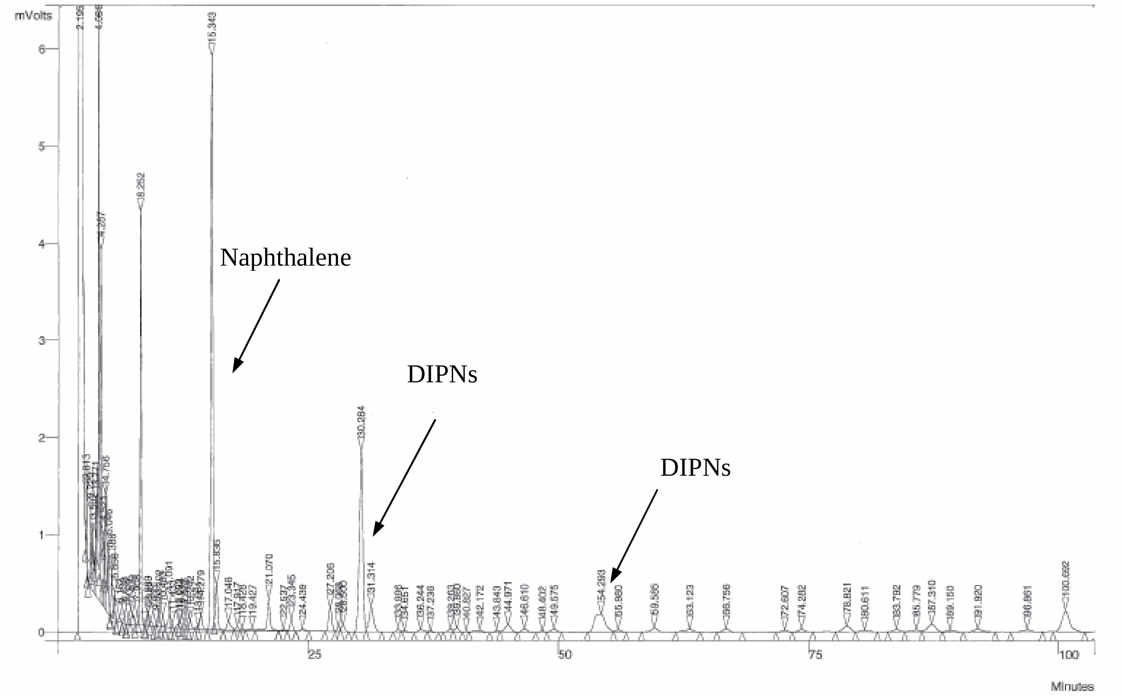

Figure 2.11: Chromatogram for the alkylation of naphthalene with 2-propanol over $AlCl_3$ after 5 h.

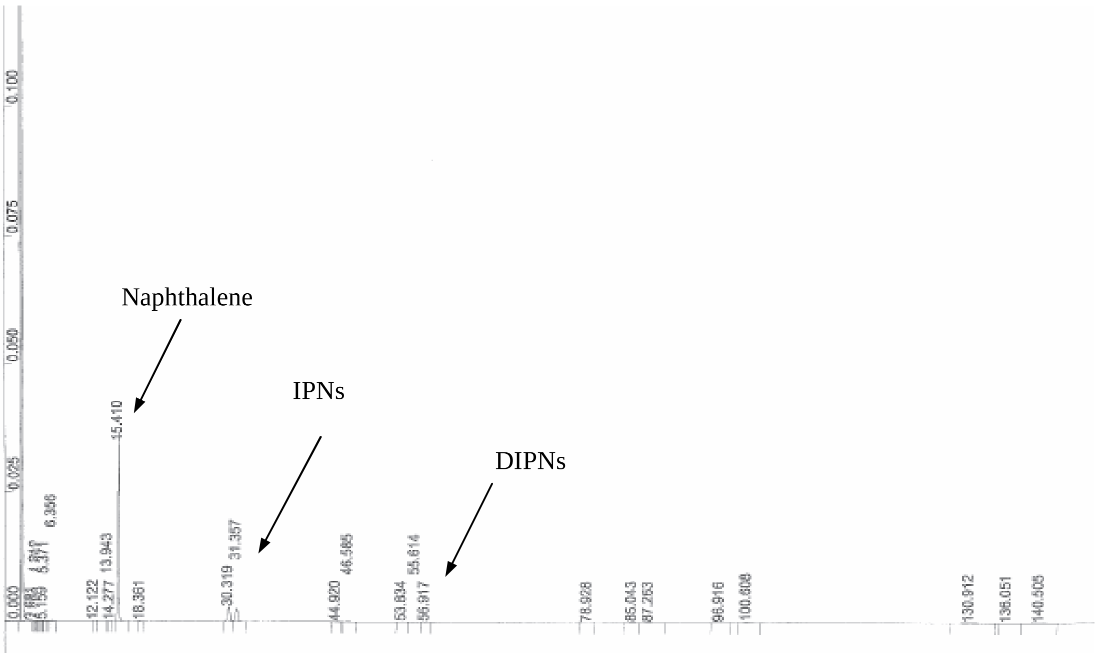

Figure 2.12: Chromatogram for the alkylation of naphthalene with 2-propanol over H-Mordenite after 20 h.

These results clearly confirm that zeolitic catalysts should be used as an alternative for $AlCl_3$, both because of their probable increase in selectivity towards isopropylation and their better fit to sustainability.

2.5. Modelling

2.5.1. Molecular modelling approach

All quantum chemical calculations were carried out using the Spartan ’06 molecular modelling suite of programs [11]. First, the most stable DIPN conformers were determined using molecular mechanics (MMFF), next the resulting structures were fully geometry-optimised at the B3LYP/6-31 G^* level, using the semi-empirical PM3 data as input. A frequency calculation was performed to allow thermodynamic corrections.

Finally, single point calculations on the B3LYP/6-311++G(2df,2p) level were performed on the B3LYP/6-31G* structure. Structures of the different conformers are presented in the Appendix.

2.5.2. Thermodynamic isomer distribution of DIPNs

Determination of the distribution of the DIPN isomers at thermodynamic equilibrium is important as it allows a better understanding of the reaction itself.

For these reasons, several groups have studied it, either computationally or experimentally. Tasi *et al.* [12] did, but never considered the thermodynamic partition of DIPN isomers as an explanation for the catalytic behaviour. Table 2.1 gives an overview of the results obtained at different calculation levels or with H-USY used as a catalyst at 200°C. Thermodynamic distributions of the isomeric DIPNS were calculated using the standard method given by Equation 2.2.

Compound	**Calculated[a] with MP2**	**Calculated[b] with B3PW91**	**Obtained[b] over H-USY**
1,2-DIPN	0.00	0.00	0.00
1,3-DIPN	2.10	5.11	3.78
1,4-DIPN	0.00	0.47	0.05
1,5-DIPN	0.00	0.43	0.08
1,6-DIPN	1.10	5.02	7.59
1,7-DIPN	1.70	2.51	4.92
1,8-DIPN	0.00	0.00	0.00
2,3-DIPN	0.10	1.45	0.40
2,6-DIPN	48.70	42.03	40.34
2,7-DIPN	46.00	42.98	42.90

[a]: Reference [12]; [b]: Reference [13];

Table 2.1: Experimental and calculated distributions of all DIPN isomers.

$$Distribution = \frac{e^{-\sum_{i=1}^{n}\frac{E_{Isom}}{RT}}}{\sum_{i=1}^{n} e^{\frac{\sum_{i=1}^{n} E_{Isom}}{RT}}} x100 \qquad (2.2)$$

As can be seen, calculations and experiments are in a relatively good agreement and the thermodynamic mixture contains between 80 and 95% of only 2 isomers, namely 2,6-DIPN and 2,7-DIPN. This result is very important, as only 2,6-DIPN can be used for the production of PolyEthylene Naphthalate (PEN) and that these 2 compounds are very similar in terms of physical properties, such as molecular dimensions and boiling point. There is therefore a real need for a selective catalysis or for a good purification technique.

2.5.3. Molecular dimensions

In order to consider shape-selectivity, it is essential to have a good estimate of the isomer molecular dimensions. Several approaches can be used and they all lead to slightly different results. Table 2.2 shows results available in the literature and the results belonging to this work.

Tasi *et al.* [12] used a parallelepiped to describe DIPNs. The c value is assumed to be the longest and is not given here as it has no influence on whether the isomer may fit or not in a zeolite channel. Discussion on how accurately the smallest surface was calculated was not provided in the article.

In this work, a direct measurement was performed in order to get rid of part of the unoccupied surface and to match as closely as possible the molecular size. This was made by first determining the plane showing the smallest section of the molecule and making sure no perspective distortion was involved by applying an orthogonal view. A reference distance in this plane was then computed and molecular dimensions were extrapolated. Further details about this procedure, as well as planes chosen to determine minimal values of molecular dimensions are presented in the Appendix.

Small differences have to be expected between literature results and this work as Tasi *et al.* used kinetic diameters corresponding with an electron density of 0.001 e/(au)^3 (charge contained in a cube having an edge length of 0.529167 Å) while in this work "normal" van der Waals diameters were used, corresponding with electron density of 0.002 e/(au)^3. Van der Waals surface generates slightly smaller molecules. Validation of the accuracy of the whole method was performed by comparing the pore size of Faujasite from the IZA website [14] (7.4 Å) with the one obtained by correcting the computed value (7.35 Å). These results can be found in a more detailed presentation in the Appendix. In all cases, this approach is still an approximation, based on the most stable conformer. Molecules are not fixed objects and some small rotation may provide smaller molecular dimensions as presented in the Appendix.

Compound	**a[12]**	**b[12]**	**a (direct)**	**b (direct)**
1,2-DIPN	6,95	8,72	6.69	9.00
1,3-DIPN	6,89	9,96	6.55	9.80
1,4-DIPN	6,22	9,46	6.58	9.17
1,5-DIPN	6,45	8,78	6.08	8.76
1,6-DIPN	6,81	8,10	6.65*	8.65*
1,7-DIPN	6,87	8,96	6.55	9.34
1,8-DIPN	6,59	9,99	6.59	9.70
2,3-DIPN	6,76	9,86	6.70	9.53
2,6-DIPN	6,61	6,61	6.56	7.27
2,7-DIPN	6,62	7,26	6.54	7.17

*: it is impossible to see both shortest distances on one single graph, so 2 graphs were used.

Table 2.2: Kinetic diameters in Ångstroms from literature [12] and calculated.

In order to ease comparison, a and b values (as defined for example in Figure 2.13) from both parallelepipedic approaches are plotted in Figure 2.14.

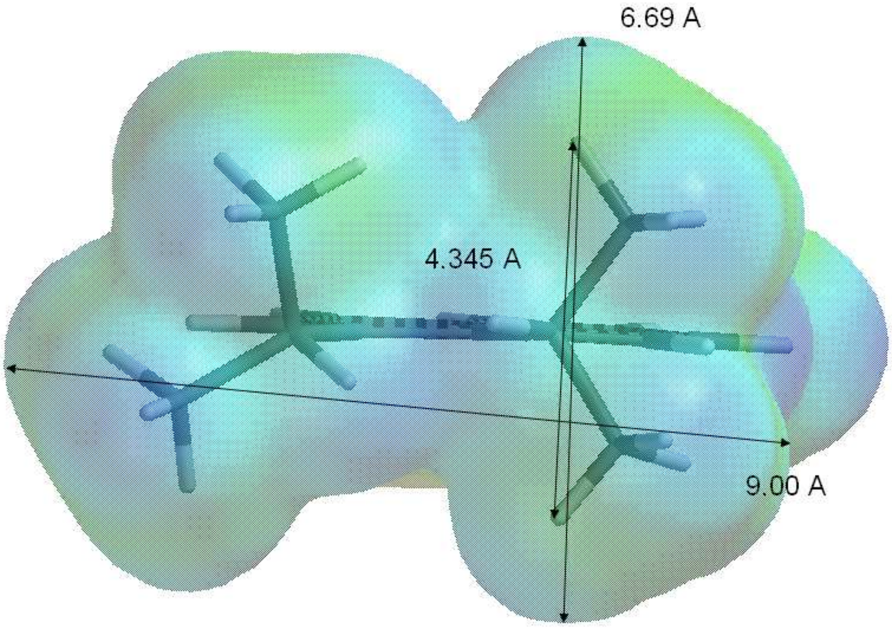

Figure 2.13: Representation of a (short axis) and b (long axis) for 1,2-DIPN.

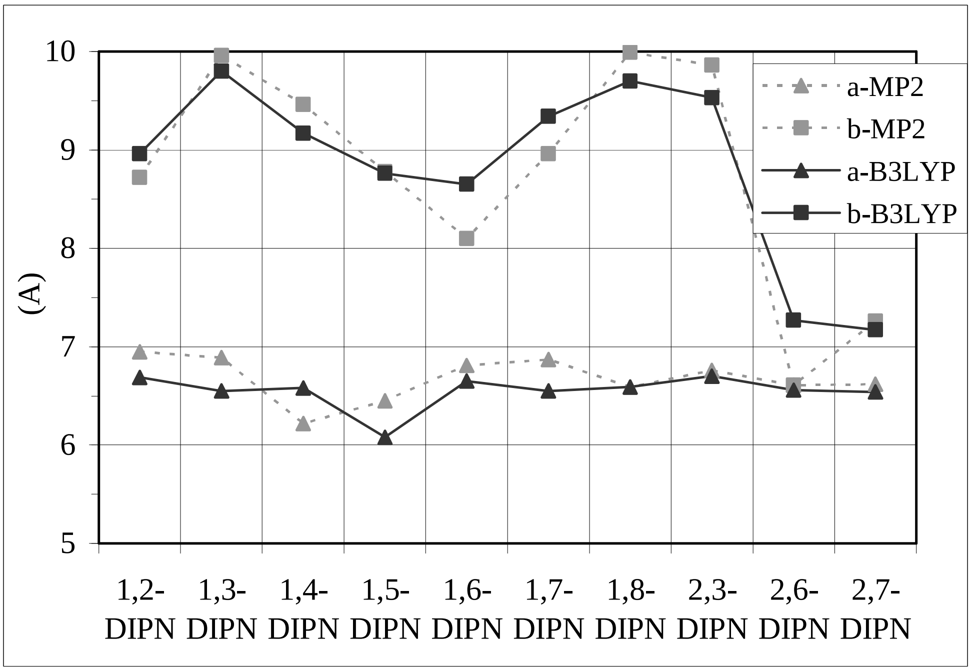

Figure 2.14: a and b values for both parallelepipedic approaches.

MP2 refers to [12] and B3LYP to this work

What first appears from Table 2.2 is that results are generally speaking in good agreement with the kinetic diameters reported by Tasi *et al.* An interesting difference appears with respect to 2,6- and 2,7-DIPN. It was not possible to measure a size difference in good agreement with the reported work. If similar values are obtained for the length of the isopropyl group, the second diameter b, corresponding to the distance between *para* hydrogens including van der Waals radii in one of the aromatic ring, does not seem to be 0.5Å bigger for 2,7-DIPN, as can be seen in Figure 2.15.

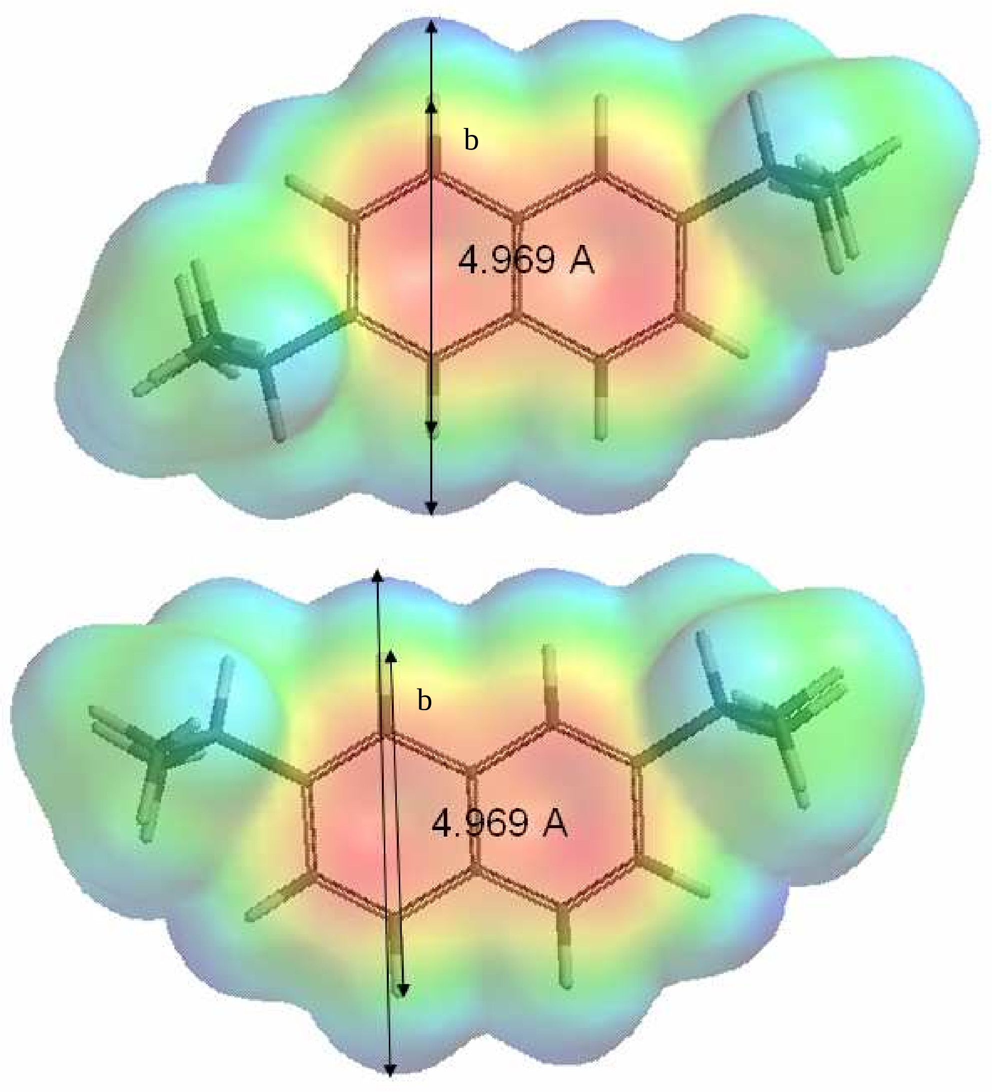

Figure 2.15: Representation of 2,6-DIPN and 2,7-DIPN at the same scale.

2.5.4. Zeolite characteristics

The International Zeolite Association's website [14] provides access to framework characteristics of all the described zeolites. Data for those studied in this thesis are displayed in Table 2.3. Parameters a, b and c represent the length of the axes of the crystal unit cell and the major and minor axis refer to the dimensions of the pore seen as an ellipse.

	Faujasite	**Mordenite**	**Beta**	**MFI**
a	24,345	18,256	12,632	20,09
b	24,345	20,534	12,632	19,738
c	24,345	7,542	26,186	13,142
major axis largest window	7,4	7,0	7,3	5,6
minor axis largest window	7,4	6,5	6,6	5,3

Table 2.3: Framework characteristics of some zeolites in Ångstroms.

Faujasite is a generic family containing the USY zeolites used in this work and MFI framework relates among others to ZSM-5 type of zeolites. The MFI unit cell is presented in Figure 2.16 and pores of all commercial zeolites used in this work are presented in Figures 2.17, 2.18, 2.19 and 2.20.

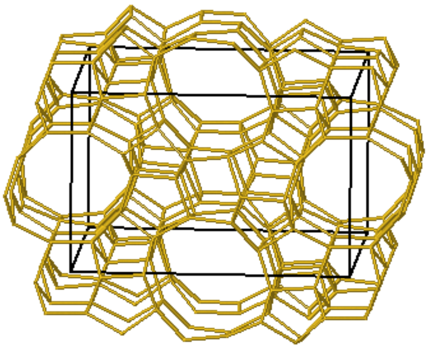

Figure 2.16: unit cell for an MFI-type zeolite.

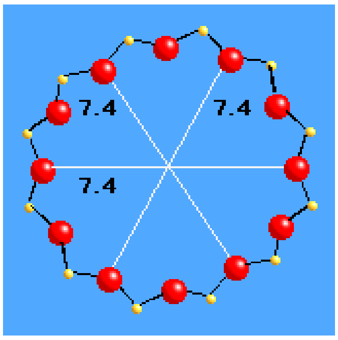

Figure 2.17: Faujasite viewed along [111]

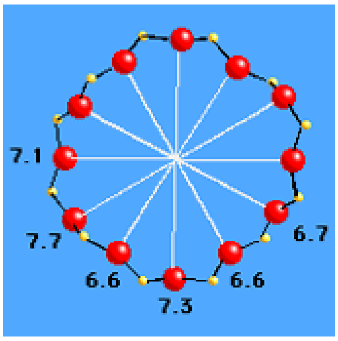

Figure 2.18: Beta zeolite viewed along [100]

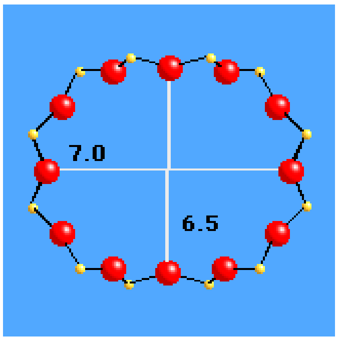

Figure 2.19: Mordenite viewed along [001]

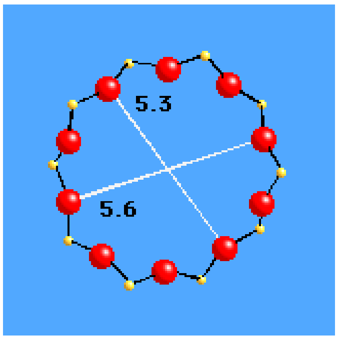

Figure 2.20: MFI zeolite viewed along [010]

Considering the dimensions presented in paragraph 2.5.3, 2,6-DIPN and 2,7-DIPN might very well enter Faujasite and Beta zeolite pores. Pore dimensions of Mordenite (6.5x7.0) are very close to the molecular dimensions of these 2 isomers (~6.5x 7.3 and ~6.5x7.2 respectively) justifying the abundant claims for shape-selectivity in the literature. However it does not appear straightforward, as the isomers are slightly bigger than the pore dimensions and not the opposite, suggesting that shape-selective catalysis will be very slow if possible. Catalysis in MFI pores seems completely impossible.

2.5.5. Shape-selectivity

Comparison between values presented in Tables 2.2 and 2.3 should lead to the conclusion that MFI zeolites do not offer a pore opening big enough to allow even the smallest DIPN (namely 2,6-DIPN) to reach the active sites within the pore. If data from Tasi *et al.* are considered to be correct, then 2,6-DIPN only should fit in the pores of Mordenite and 2,6-DIPN and 2,7-DIPN in those of zeolite Beta. If the results obtained in this thesis are believed to be more relevant, 2,6-DIPN and 2,7-DIPN should reach the active sites only with Faujasite and Beta zeolites but no DIPN should fit into Mordenite or MFI zeolites.

Shape-selectivity is very frequently proposed as an explanation of (experimentally observed) DIPN isomer distribution when Mordenite is used as a catalyst. This seems to be in possible agreement with the data presented by Tasi *et al.* but not with the molecular dimensions determined in this thesis. While the authors report 2,6-DIPN being half an Ångstrom smaller than 2,7-DIPN, it was found in this work that 2,7-DIPN was slightly smaller. This statement raises questions about the abundant shape-selective claims in the literature.

Shape-selectivity can occur at three different levels: at the feedstock level, at the transition state level and at the product level.

Shape-selectivity at the feedstock level is observed when discrimination is made based on the substrate dimensions. This happens very frequently with enzymes. Shape-selectivity at the product level occurs when a product is formed but cannot exit the active site. This is for example the case of toluene disproportionation and is likely to be the case in diisopropylation of naphthalene. Both these concepts are quite understandable and regularly used to explain (un)expected selectivity. Transition state shape-selectivity couples the structure of the transition state of the reacting substrate with the structure of the catalyst. Although at first sight pretty well imaginable, it should be stated that among the different types of shape-selectivity that have been proposed, transition state shape-selectivity is quite a fuzzy concept for two reasons: 1) transition states structures cannot be adequately observed but are usually the result of a type of quantum chemical calculation with all its inherent uncertainties, 2) it is known from the same quantum chemical calculations that transition state structures are usually located on a rather flat part of the potential energy surface diagram, which makes it even harder to couple the structural features of the reacting substrate and catalyst.

In order to get a better understanding of what is allowing or forbidding shape-selectivity, it may be interesting to consider reactions where the scientific community agrees on its influence. A very good example is the now industrially applied disproportionation of toluene over ZSM-5 zeolites to increase the *p*-xylene selectivity up to 80% when the thermodynamic distribution allows only around 20% [15].

It seems well agreed in the literature that molecular dimensions are 5.8 Å for the *para*-isomer and 6.8 Å for the *ortho*- and *meta*-isomers when the pore size of the ZSM-5 zeolite is 5.6 x 5.3 Å. Minachev *et al.* [16] explain that the selectivity is related to the ability for the molecule to fit within the zeolite channels as well as possible in terms of either size or shape. In the case of xylene disproportionation, *p*-xylene seems 0.2 Å too big but still can diffuse through ZSM-5 membranes when the two other isomers that are 1.2 Å too big, cannot. Because of the zeolite framework flexibility, pores can expand and therefore allow molecules that seem to be too big to fit in.

If it is assumed that, first, the same phenomena may apply for DIPNs, and second, that for DIPNs the isopropyl groups may get an orientation which is not necessarily the one from the conformer with the lowest heat of formation, (it might even enter the zeolite channel through a transition state), one should then realise that it may be very well possible to see several isomers diffuse through zeolites and not only 2,6-DIPN. This would be true for any approach presented in Table 2.2. Further explanation can be found in the Appendix.

This leads to the conclusion that even if reasonably possible, full shape-selectivity toward one and only one specific isomer should at least be questioned for DIPN formation over zeolites.

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3

Catalysis over classical commercial zeolites

Abstract

Selective diisopropylation of naphthalene to 2,6-diisopropylnaphthalene is a challenging goal in sustainable catalysis. Ultrastable Y and H-Mordenite zeolite are the best catalysts reported in the literature with respect to 2,6-diisopropylnaphthalene selectivity. It is generally accepted that in the case of H-Mordenite molecular shape-selectivity is responsible for the observed 2,6-diisopropylnaphthalene selectivity, while on Y zeolite the diisopropylnaphtalene selectivity reflects the internal thermodynamic equilibrium among positional isomers. Revisiting both the experimental and the computational work in this field now leads to the conclusion that, for both catalysts, thermodynamic control adequately explains the observed 2,6-diisopropylnaphthalene selectivity. Shape-selectivity of whatever kind can be ruled out in the case of H-Mordenite.

3.1. Introduction

Selective diisopropylation of naphthalene to 2,6-diisopropylnaphthalene (2,6-DIPN) is an important step towards an attractive and sustainable route to 2,6-naphthalene dicarboxylic acid. Inspection of the literature [1-18] showed that among the different zeolitic catalysts investigated, H-USY and H-Mordenite are the best with respect to selectivity, though they largely differ in activity.

Naphthalene alkylation is an intriguing reaction system. Naphthalene has two aromatics rings, strongly reducing directing electronic effects. The α position is considered to be kinetically favored, whereas the β position is thermodynamically favoured. As described in Chapter 2, the dialkylnaphthalenes are prone to many types of reactions such as isomerisation, transalkylation and dealkylation [2, 19-23]. Selectivity towards the industrially relevant 2,6-positions has to be maximised. To this aim, molecular shape-selectivity has been proposed to discriminate among the dialkylnaphthalene isomers based on their molecular dimensions.

So far, many research teams have focused on H-Mordenite, its dealuminated versions [1, 3, 10, 24-27], specimens with surface modifications [28-30], as well as on theoretical studies about the isomer formation [19, 23, 31-36]. On the other hand, studies using H-USY [2, 4-5, 8, 13, 37] showed even higher yields towards DIPNs in general and 2,6-DIPN specifically. To a lower extent, some work has been published with catalysis over other zeolites such as MCM-22 [38], Beta zeolite [39], and MCM-48 [40].

It was found intriguing that in the case of H-Mordenite shape-selectivity is used as the dominant explanation for the observed yield and selectivity, while in the case of H-USY thermodynamic control (relative stability of DIPNs isomers) seems to be the case. The latter was not clearly stated thus far. This prompted us to reinvestigate the two cases both experimentally and computationally.

3.2. Isopropylation of naphthalene and isomerisation of 2,6-DIPN

The consecutive reaction steps in the isopropylation of naphthalene are presented in Figure 3.1. Naphthalene with up to 4 isopropyl substituents could be detected in the reaction mixture depending on the reaction conditions. Some polyalkylated unsaturated products (further defined as "Unsaturates") with mass 252 described by Moreau *et al.* [5, 41] were observed as well.

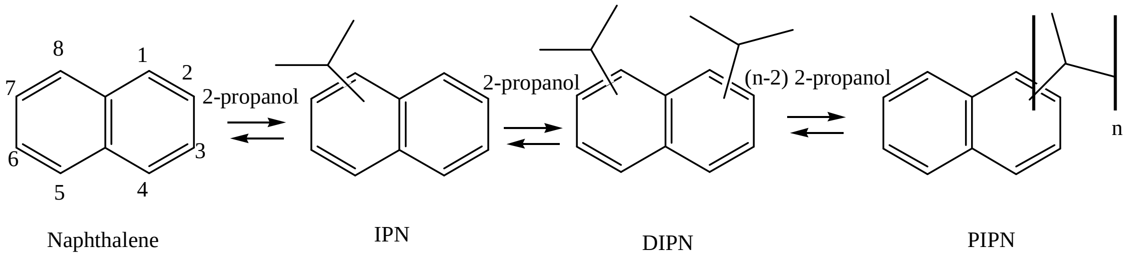

Figure 3.1: Consecutive reaction steps in catalytic naphthalene isopropylation.

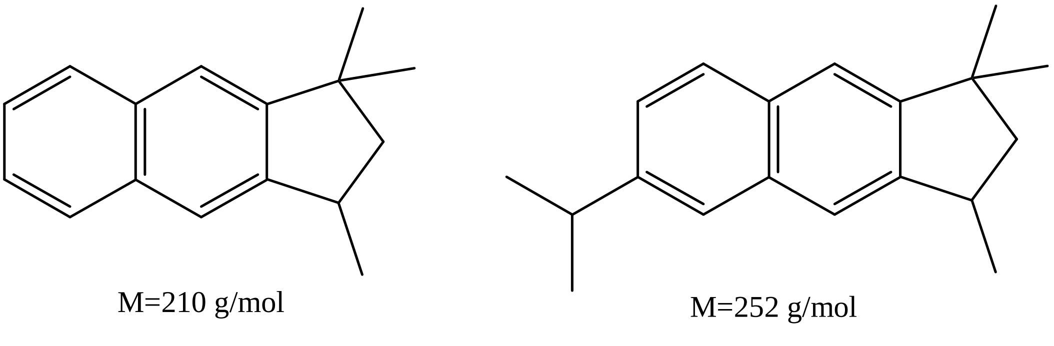

Figure 3.2: Unsaturates as described by Moreau [5, 41]

In close analogy to 2-butene [42], 2-propanol can be activated by an acidic zeolite to either the isopropyl cation or the isopropyl alkoxide after the removal of water. Reaction with naphthalene with release of a proton leads to an isopropylnaphthalene. Dealkylation can be considered as the reversed reaction. The isopropyl cation can release a proton, leading to propene formation. The reaction of the isopropyl species with propene is the first step of C_3-oligomerisation. Cracking of these propene oligomers may occur as well. Reaction products with methyl or ethyl substituents on the naphthalene rings were detected in the reaction products, as well as propene and C_5-alkenes. Evidence for the formation of these light compounds was obtained by bubbling nitrogen through the reaction mixture at 80ºC. The resulting flow was contacted with a solution of bromine in dichloromethane and the corresponding dibrominated species identified with GC-MS.

3.2.1 Isopropylation of naphthalene and isomerisation of 2,6-DIPN over H-USY

The product distribution and the isomer distribution within each family over H-USY, provided by PQ, are presented in Table 3.1. Si/Al ratio was 25.

Compound		Yield (%)		isomer distribution (%)
Naphthalene		9,0	9,0	
IPNs	1-IPN	37,5	2,5	6,6
	2-IPN		35,0	93,4
DIPNs	1,3-DIPN	38,4	2,1	5,5
	1,4-DIPN		0,3	0,7
	1,5-DIPN		0,8	2,0
	1,6-DIPN		2,0	5,2
	1,7-DIPN		1,9	4,9
	2,3-DIPN		1,3	3,5
	2,6-DIPN		13,9	36,3
	2,7-DIPN		16,2	42,2
PIPNs		5,0	5,0	
Unsaturates		4,3	4,3	
Others		5,8	5,8	

Table 3.1: Composition of the reaction products of the isopropylation of naphthalene over H-USY after 24 h.

After 24 h, H-USY realised an excellent 91.0% conversion of naphthalene combined with a rather high yield to DIPNs of 38.4%, and the intermediate IPNs of 37.5%. PIPNs, Unsaturates and Others account for 15% (Table 3.1). Figure 3.3 shows the evolution with time of the conversion and the yield of the different reaction products over H-USY.

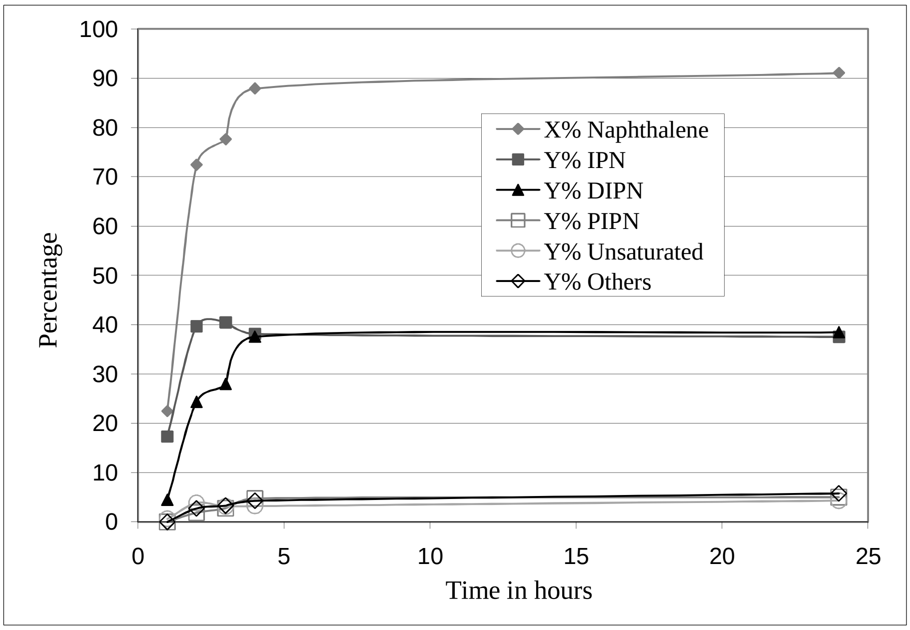

Figure 3.3: Naphthalene Conversion (X) and Yields (Y) of various products in the isopropylation of naphthalene over H-USY against reaction time

H-USY converted naphthalene up to 87% (Figure 3.3) within a period of 4 h. After short reaction times, the (molar) sum of the products and naphthalene was very close to 100%. Later on the molar sum of identified naphthalene-based reaction products slightly decreased due to the formation of some heavy side products. IPNs (mainly 2-IPN) were formed first and consecutively transformed into 2,6- and 2,7-DIPN. H-USY showed a gradual build-up of DIPNs in the first 4 hours, as can be seen in Figure 3.3. The apparently initially high relative selectivity towards 2,6- and 2,7-DIPN was due only to the very low conversion and the resulting very low amounts of 1,3- and 1,7-DIPN. In fact the selectivity for all DIPN-isomers remained rather constant within the whole period (Table 3.2).

Time (hours)	DIPN isomer distribution (%)							
	1,3	1,4	1,5	1,6	1,7	2,3	2,6	2,7
1	n.i.	n.d.	n.d.	n.d.	n.i.	n.d.	45,0	55,0
2	6,2	n.d.	n.i.	n.d.	5,3	n.i.	39,3	49,1
24	5,5	0,7	2,0	5,2	4,9	3,5	36,3	42,2

Table 3.2: DIPN distribution obtained in the isopropylation of naphthalene over H-USY in time. n.i: not integrated; n.d.: not detected

To improve our understanding of the catalytic chemistry of H-USY, isomerisation experiments starting from 2,6-DIPN were undertaken (Table 3.3 and Figure 3.4).

Compound		**Yield (%)**		**Isomer distribution (%)**
Naphthalene		9,1	9,1	
IPNs	1-IPN	38,9	2,3	5,9
	2-IPN		36,6	94,1
DIPNs	1,3-DIPN	37,3	2,1	5,7
	1,4-DIPN		0,3	0,8
	1,5-DIPN		0,7	2,0
	1,6-DIPN		1,2	3,2
	1,7-DIPN		1,8	4,8
	2,3-DIPN		1,8	4,7
	2,6-DIPN		19,1	51,2
	2,7-DIPN		10,6	28,3
PIPNs		4,4	4,4	
Unsaturates		4,2	4,2	
Others		6,1	6,1	

Table 3.3: Composition of the reaction product mixture in the isomerisation of 2,6-DIPN over H-USY after 24 h.

The conversion of 2,6-DIPN reached a maximum of ca. 85% after 4 h and decreased to ca. 81% after 24 h (Figure 3.3). The main products were 2-IPN and DIPN isomers with after 24 h yields of 38.9%, and 18.2%, respectively (Table 3.3). Within the product fraction of DIPNs, the formation of 2,7-DIPN with a yield of 10.6% was dominant (Table 3.3). The yield evolution (Figure 3.3) revealed that naphthalene and 2,7-DIPN were intermediate products in the reaction network. The naphthalene yield showed a minimum of 7.0% after 2 h; 2,7-DIPN a maximum of 21.7% after 3 h (Figure 3.4).

It is noteworthy to mention that the highest naphthalene yield (13.0%) is obtained after already 1 hour. This is a kinetic effect that can be explained by the fact that at 200°C dealkylation is already faster than alkylation, and that C_3 moieties can build up at the catalyst surface. The selectivity to α-substituted products was low (Table 3.3). Finally H-USY remained active over the whole period and in the end the DIPNs distribution obtained was similar to that obtained in naphthalene isopropylation experiments.

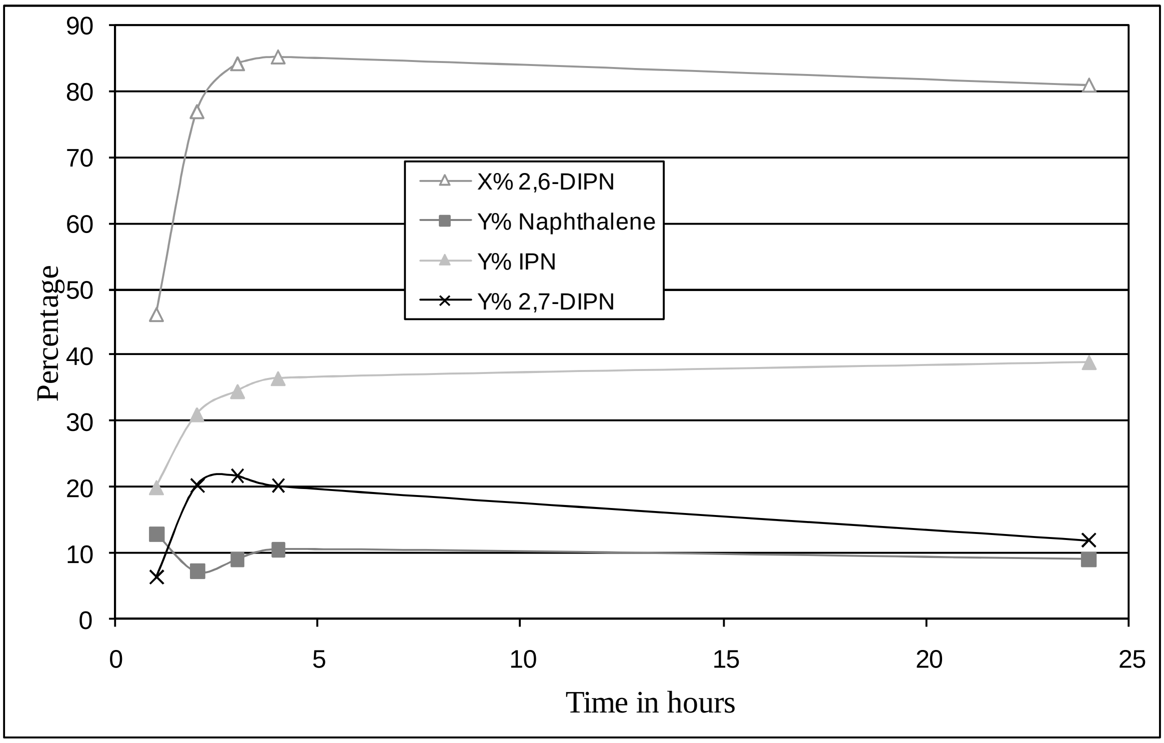

Figure 3.4: 2,6-DIPN conversion and yield of products in the isomerisation of 2,6-DIPN over H-USY against time.

3.2.2 Isopropylation of naphthalene and isomerisation of 2,6-DIPN over H-Mordenite

Compound		**Yield (%)**		**Isomer distribution (%)**
Naphthalene		79,2	79,2	
IPNs	1-IPN	17,2	8,1	47,3
	2-IPN		9,1	52,7
DIPNs	1,3-DIPN	1,1	0,2	16,8
	1,4-DIPN		0,0	0,0
	1,5-DIPN		0,0	0,0
	1,6-DIPN		0,1	7,8
	1,7-DIPN		0,2	19,2
	2,3-DIPN		0,0	0,0
	2,6-DIPN		0,3	30,0
	2,7-DIPN		0,4	34,0
PIPNs		0,4	0,4	
Unsaturates		1,9	1,9	
Others		0,2	0,2	

Table 3.4: Composition of the reaction product mixture in the isopropylation of naphthalene over H-Mordenite after 20 h.

In naphthalene isopropylation over H-Mordenite, the naphthalene conversion reached only ~ 20% after 20 h (Table 3.4). The main reaction products were 1- and 2-IPN with a total IPN yield of ~ 17%. The 1-IPN and 2-IPN isomers were present in an almost 1/1 ratio. The selectivity towards DIPNs was only 1.1% while PIPNs, Unsaturates and Others accounted for 2.5%. Within the DIPN-isomers, the relative yields of 2,6- and 2,7 DIPN were 30 and 34% respectively, while the 1,3- and 1,7-isomer represented ~ 17% and 19%, respectively. It should be noted that with such a low yield of DIPNs, the accuracy of the product analysis was somewhat lower than in the experiment with H-USY. The time evolution of conversion and yield (Figure 3.5) revealed the parallel formation of 1- and 2-IPN followed by the DIPNs and side products.

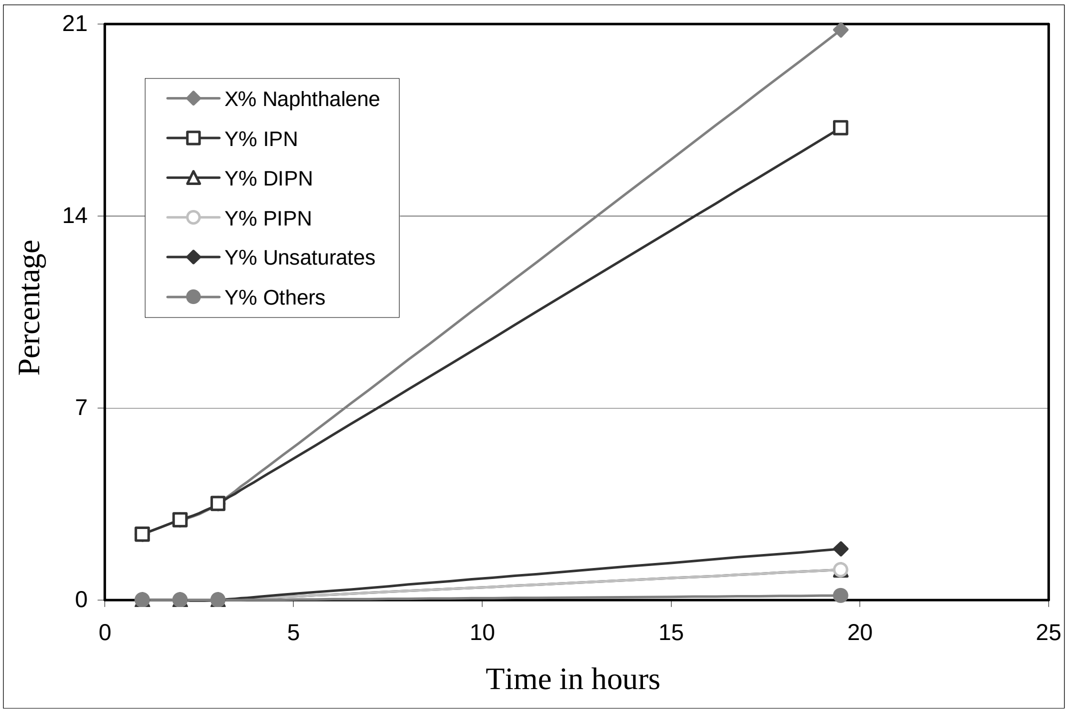

Figure 3.5: Naphthalene Conversion (X) and yields (Y) of various products in the isopropylation of naphthalene over H-Mordenite against time.

In the isomerisation of 2,6-DIPN over H-Mordenite, ~ 20% conversion was obtained after 20 h. The main reaction products were 2,7-DIPN, 2-IPN, PIPNs and naphthalene with yields of 10.2, 4.8, 1.3, and 2.0%, respectively. Other DIPN-isomers beside 2,7-DIPN did appear but in very low amounts. The 2-IPN/1-IPN ratio was close to 20. Analysis of the evolution of the yields (Figure 3.6) showed a regular build-up of most products, except for naphthalene which showed a maximum yield of 5% after 2 h and then gradually decreased to 2%.

At the same time the conversion of 2-6-DIPN showed a similar drop. This behavior and its possible explanation are very similar to what was observed over H-USY, except the fact that H-Mordenite is a slower catalyst. When dealing with very low conversions, the first data obtained after a short reaction time are frequently not accurate as they are subject to two kinds of errors: the stability of the reaction device and the accuracy of the area integration in the analysis. For this reason, the mixture composition after 1 h was not determined. However, the difference in naphthalene concentration between 2 and 4 h cannot be explained by these two reasons. A possible explanation for these unexpected behaviors is that dealkylation with a fresh Mordenite catalyst precedes isomerisation and realkylation. Inspection of the relative yields of 2- and 1-IPN (as shown in Table 3.6) and the other non-integrated DIPNs showed that dealkylation towards naphthalene in this case is the fastest process and that realkylation to various products became significant after 3 h only. It seems that first a reservoir of isopropyl moieties on the catalytic surface has to be built up.

Compound		**Yield (%)**		**Isomer distribution (%)**
Naphthalene		2,0	2,0	
IPNs	1-IPN	5,1	0,3	5,1
	2-IPN		4,8	94,9
DIPNs	1,3-DIPN	91,5	0,2	0,3
	1,4-DIPN		0,0	0,0
	1,5-DIPN		0,0	0,0
	1,6-DIPN		0,1	0,2
	1,7-DIPN		0,4	0,4
	2,3-DIPN		0,1	0,1
	2,6-DIPN		81,5	89,0
	2,7-DIPN		9,4	10,2
PIPNs		1,3	1,3	
Unsaturates		0,0	0,0	
Others		0,1	0,1	

Table 3.5: Reaction mixture composition in the isomerisation of 2,6-DIPN over H-Mor after 20 h.

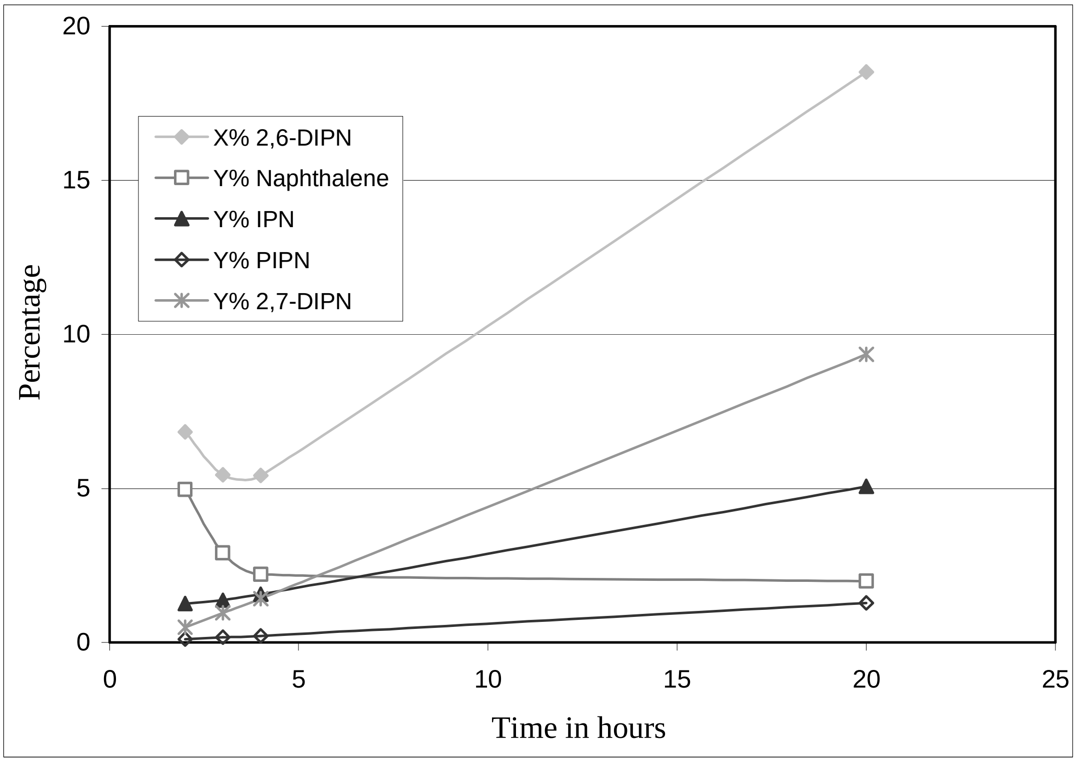

Figure 3.6: 2,6-DIPN conversion (X) and yields (Y) to various products in the isomerisation of 2,6-DIPN over H-Mor against time.

3.2.3 Isopropylation of naphthalene and isomerisation of 2,6-DIPN over H-Beta

The product distribution and the isomer distribution within each family over H-Beta, provided by PQ, are presented in Table 3.6 and the time dependence is presented in Figure 3.7 and Table 3.7. Si/Al ratio was 25.

After 23 h, the conversion is really bad (24%) and the selectivity towards desired products even worse (0.3%). Selectivity among the DIPNs is irrelevant regarding the very low amounts detected. In fact, all isomers were formed but only three were present in amounts above the detection limit for integration. The main products over H-Beta consist for about 50% of unsaturated products probably similar to those described by Moreau *et al.* [5, 41], though complete identification was not performed. A structural search with the

Beilstein software did not return any hit with these structures and they cannot be seen so far as potential valuable starting materials for any application.

Time dependence results show that H-Beta has a high activity during the first hours but that product decomposition or rearrangement occurs very rapidly.

Considering the pore size of Beta zeolites, these results are surprising as reaction products have dimensions close to the channels of the zeolite. However, Beta zeolites have a high acidity and this probably explain better the importance of the side-reactions.

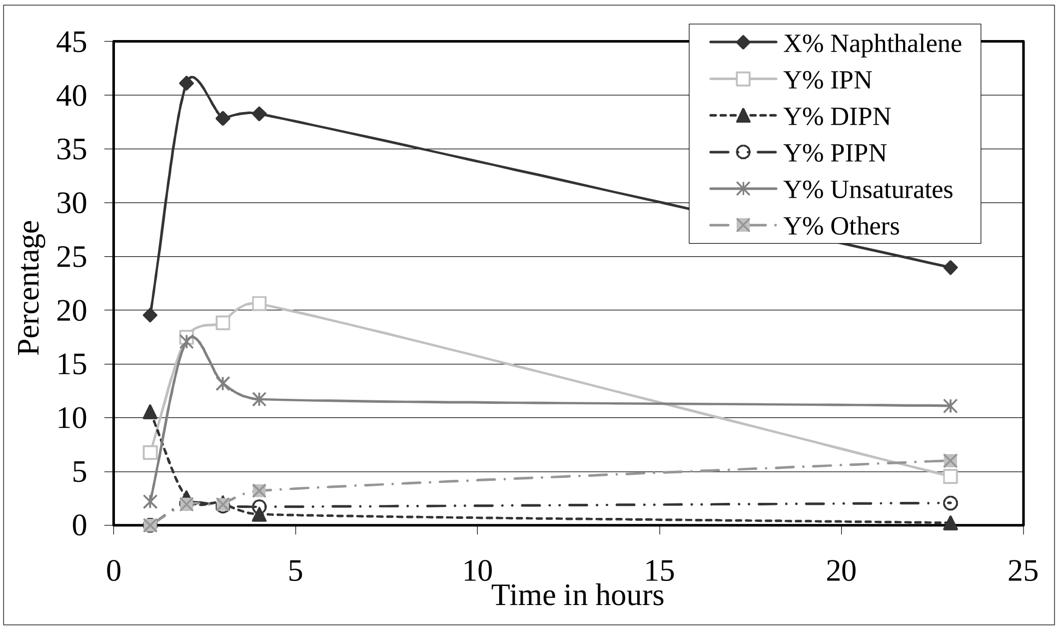

Figure 3.7: Naphthalene Conversion (X) and Yields (Y) to various product families in the isopropylation of naphthalene over H-Beta in time.

Compound		**Yield (%)**		**Isomer distribution (%)**
Naphthalene		76,0	76,0	
IPNs	1-IPN	4,5	1,1	25,3
	2-IPN		3,4	74,7
DIPNs	1,3-DIPN	0,3	n.i	0,0
	1,4-DIPN		n.i	0,0
	1,5-DIPN		0,1	39,4
	1,6-DIPN		n.i	0,0
	1,7-DIPN		n.i	0,0
	2,3-DIPN		n.i	0,0
	2,6-DIPN		0,1	33,3
	2,7-DIPN		0,1	33,3
PIPNs		2,1	2,1	
Unsaturates		11,1	11,1	
Others		6,0	6,0	

Table 3.6: Product distribution in the isopropylation of naphthalene over H-Beta after 23 h.
n.i.: not integrated.

As displayed in Table 3.7, isomerisation was not observed over H-Beta. After 24h, 2,6-DIPN is fully converted towards naphthalene or unsaturated products.

Dealkylation of 2,6-DIPN proceeds very fast first towards 2-IPN and subsequently towards naphthalene, as can be seen in Figure 3.8. Isomerisation occurs in the beginning of the run, but 2,7-DIPN reactivity being very similar to 2,6-DIPN's, it is dealkylated as well with time.

Compound		Yield (%)		Isomer distribution (%)
Naphthalene		75,9	75,9	
IPNs	1-IPN	3,7	0,8	22,1
	2-IPN		2,9	77,9
DIPNs	1,3-DIPN	0,5	0,2	33
	1,4-DIPN		0	0
	1,5-DIPN		0	0
	1,6-DIPN		0,1	18,8
	1,7-DIPN		0	0
	2,3-DIPN		0	0
	2,6-DIPN		0,1	16,8
	2,7-DIPN		0,1	28,7
PIPNs		2,2	2,2	
Unsaturates		10,9	10,9	
Others		6,8	6,8	

Table 3.7: Product distribution in the isomerisation of 2,6-DIPN over H-Beta after 24 h.

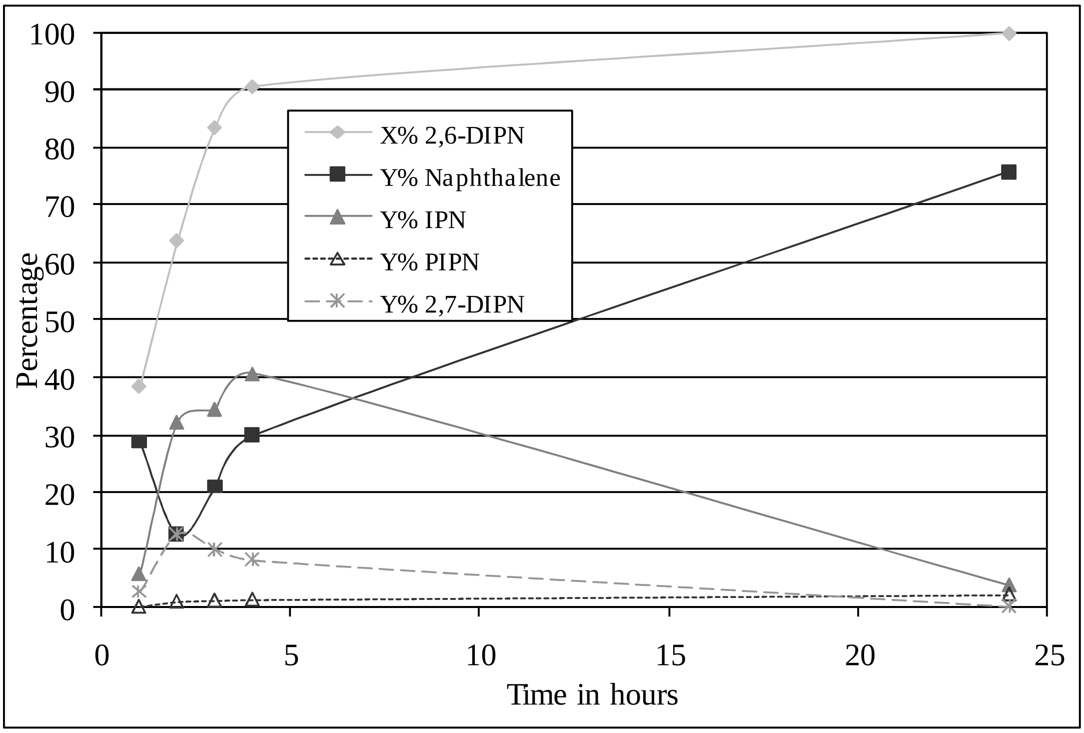

Figure 3.8: 2,6-DIPN conversion (X) and yields (Y) to various products in the isomerisation of 2,6-DIPN over H-Beta in time.

These results confirm those obtained in alkylation where DIPNs were formed shortly and then either dealkylated to naphthalene or transformed to yield unsaturated products. H-Beta behaves similarly to H-USY and H-Mordenite but much faster. Moreover its high acidity favours the formation of side-products. It is therefore clear that Beta zeolites are not suitable for this reaction.

3.2.4. Isopropylation of naphthalene and isomerisation of 2,6-DIPN over H-ZSM-5

The product distribution and the isomer distribution within each family over H-ZSM-5, provided by Süd-Chemie, are presented in Table 3.8 and the time dependence is proposed on Figure 3.9. Si/Al ratio was 50.

Catalysis over H-ZSM-5 proceeds very slowly and is not selective towards dialkylation. The final conversion is only 20%. About 70% of the reaction products consist of unsaturated products and hardly any DIPNs are detected after 23 h, therefore, similarly to H-Beta, relative selectivity among the DIPNs has no meaning. H-ZSM-5 appears to be the worst catalyst tested, not even reaching the level of aluminium trichloride. It must be stated still that considering the Si/Al ratio of 50, the acidity is lower than for the other catalysts tested and the activity should be lower as well. This should impact more the side-reactions than alkylation but also contributes to the bad evaluation of the catalyst.

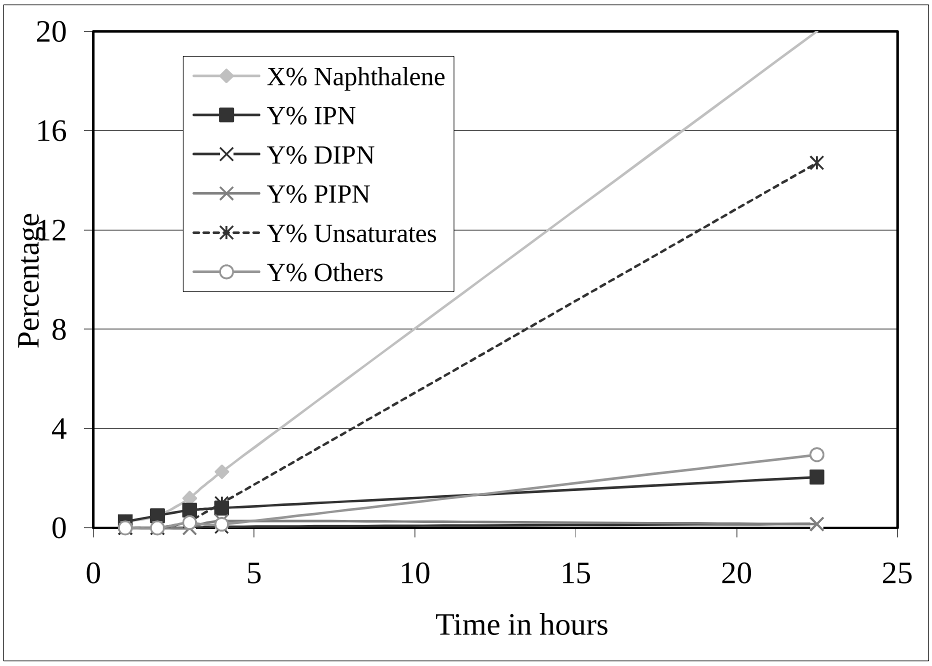

Figure 3.9: Naphthalene Conversion (X) and Yields (Y) to various product families in the isopropylation of naphthalene over H-ZSM-5 in time.

Compound		**Yield (%)**		**Isomer distribution (%)**
Naphthalene		80,0	80,0	
IPNs	1-IPN	2,0	0,2	11,5
	2-IPN		1,8	88,5
DIPNs	1,3-DIPN	0,2	n.i.	28,4
	1,4-DIPN		n.i.	0,0
	1,5-DIPN		n.i.	0,0
	1,6-DIPN		n.i.	0,0
	1,7-DIPN		0,1	48,6
	2,3-DIPN		n.i.	0,0
	2,6-DIPN		n.i.	6,3
	2,7-DIPN		n.i.	0,0
PIPNs		2,3	2,3	
Unsaturates		14,7	14,7	
Others		0,8	0,8	

Table 3.8: Product distribution in the isopropylation of naphthalene over H-ZSM-5 after 23 h. n.i.: not integrated.

Similarly to H-Beta, H-ZSM-5 does not catalyse isomerisation. The difference lays in the type of products formed, as can be seen in Table 3.9. Because of the very low conversion, no time dependence results are plot. Dealkylation occurs stepwise, first towards 2-IPN and then towards naphthalene.

H-ZSM-5 seems to catalyse only dealkylation and its lower acidity compared to H-Beta may explain the absence of unsaturated side-products.

Compound		**Yield (%)**		**Isomer distribution (%)**
Naphthalene		0,8	0,8	
IPNs	1-IPN	14,1	0,5	3,4
	2-IPN		13,6	96,6
DIPNs	1,3-DIPN	85,1	0,1	0,2
	1,4-DIPN		n.i.	0,0
	1,5-DIPN		n.i.	0,0
	1,6-DIPN		n.i.	0,0
	1,7-DIPN		0,2	0,2
	2,3-DIPN		n.i.	0,0
	2,6-DIPN		74,4	87,4
	2,7-DIPN		10,4	12,2
PIPNs		0,0	0,0	
Unsaturates		0,0	0,0	
Others		0,0	0,0	

Table 3.9: Product distribution in the isomerisation of 2,6-DIPN over H-ZSM-5 after 24 h.

To summarise, over the 4 catalysts applied, dealkylation is a general phenomenon. Pores of the MFI-type zeolite are probably too small to allow anything else than a slow outer surface catalysis. H-Beta despite its more appropriate pore dimensions is simply too acidic and therefore also catalyses side-reactions. The two best catalysts are thus H-USY and H-Mordenite, in very good agreement with the amount of articles dealing with them for this specific application.

3.3 Shape selectivity vs. thermodynamic control

H-USY and H-Mordenite are selective catalysts for the formation of 2,6-DIPN in the diisopropylation of naphthalene. Explanations in literature for the high selectivity of naphthalene alkylation towards 2,6-DIPN go in the direction of thermodynamic control for H-USY and shape-selectivity for H-Mordenite.

For H-USY, Brzozowski et al. [19] showed that the partition of DIPN-isomers observed experimentally agreed very well with the one obtained computationally assuming the internal thermodynamic equilibrium among the isomers, not only with respect to 2,6-DIPN (~ 40%) and to 2,7-DIPN (~ 40%), but also 1,3-DIPN (~ 4%), 1,6-DIPN (~ 7.5%) and 1,7-DIPN (~ 5%). A relative increase in the amount of 2,6-DIPN relative to 2,7-DIPN and the other DIPN isomers with increasing temperature is theoretically expected. In our isopropylation and isomerisation experiments with H-USY, a very similar repartition of DIPN-isomers was obtained. Calculations using both standard DFT (B3LYP/6-31G*) and single point (sp) B3LYP/6-311++G(2df,2p) on the B3LYP/6-31G* structures confirmed the findings of Brzozowski et al. [19]. Our calculations also pointed to an increase of the 2,6-DIPN/2,7-DIPN ratio with temperature, ranging from ~ 0.9 at 0K to ~ 2.9 at 623K. Thus, thermodynamic control explains the observed partition of DIPN-isomers, the resulting high selectivity to 2,6- and 2,7-DIPN and the effect of temperature quite satisfactorily. Computational and experimental data on the distribution of all DIPN isomers are summarised in Table 3.10.

Compound	**Calculated**		**Obtained**	**Calculated**		**Obtained**	
	with MP2[a]	with B3PW91[b]	over H-USY[b]	with B3LYP/6-31G*[c]	with sp B3LYP/6-311++G(2df,2p)[c]	over H-USY[c]	over H-MOR[c]
1,2-DIPN	0.00	0.00	0.00	0.00	0.00	n.d.	n.d.
1,3-DIPN	2.10	5.11	3.78	4.00	3.84	5.0	16.8
1,4-DIPN	0.00	0.47	0.05	0.07	0.07	0.7	n.d.
1,5-DIPN	0.00	0.43	0.08	0.07	0.06	2.0	n.d.
1,6-DIPN	1.10	5.02	7.59	4.49	4.14	5.2	7.8
1,7-DIPN	1.70	2.51	4.92	3.77	3.79	4.9	19.2
1,8-DIPN	0.00	0.00	0.00	0.00	0.00	n.d.	n.d.
2,3-DIPN	0.10	1.45	0.40	0.34	0.36	3.5	n.i
2,6-DIPN	48.70	42.03	40.34	40.46	40.86	36.2	30.0
2,7-DIPN	46.00	42.98	42.90	46.80	46.87	42.1	34.0

[a]: Reference [23]; [b]: Reference [19]; [c]: our results; n.d.: not detected; n.i.: not integrated

Table 3.10: Experimental and calculated repartition of DIPN isomers.

H-Mordenite has been used by several authors as catalyst for the diisopropylation of naphthalene [1-3, 5, 7, 9, 11, 23, 26, 33, 36, 41]. Moreau *et al.* [11] found that mordenite catalysts were less active than Y-zeolites in the liquid phase isopropylation using cyclohexane as a solvent. The most active Mordenite sample, with a Si/Al = 9, gave a conversion of 12% after 1 h and 60% after 24 h. For H-Mordenite with a Si/Al = 6.9 a conversion of 18% was obtained after 24 h at 200°C. The reaction products were composed of 81% of 2-IPN, 11% of dialkylnaphthalenes, and 8% of trialkylnaphthalenes. A later study [5] using a H-Mordenite with Si/Al = 10.8 yielded a conversion of 19% with reaction products composed of ~80% of IPNs, ~6% of DIPNs, 13% of so called cyclizates and 1.3% of other alkylnaphthalenes. Those authors explained the relative high selectivity to 2,6-and 2,7-DIPN as a result of transition state shape-selectivity.

On the other hand Song *et al.* [3, 33] put forward product shape-selectivity as the explanation for the relative high amount of 2,6-DIPN formed over Mordenite catalysts at 250°C. They reported a slightly smaller molecular diameter of 2,6-DIPN compared to

2,7-DIPN. However, the occurrence of transition state shape selectivity as proposed by Katayama *et al.* [7] and Moreau *et al.* [41] was not ruled out completely. Taking into account the higher reaction temperature of 250°C, the catalytic activity was rather low, and especially the activity for DIPNs formation. The highest yield of 2,6-DIPN was ~ 2.9% (X = 27.6%, S = 10.7%) with a 2,6-DIPN content of the DIPN-isomers of 67%. Whereas Moreau *et al.* [11] did not observe any 1-IPN, Song *et al.* [3] in their investigations did observe this reaction product, up to 30% of the total amount of IPNs formed. In a later study [26] Schmitz and Song showed the beneficial effect of a low conversion on the β-selectivity. In their catalytic study at a reaction temperature of 200°C the ratio of 2,6-DIPN/2,7-DIPN product formation was ~ 2.3. Furthermore, water in the feed seemed to lower coke formation. In a review [1] Song showed the effect of the reaction temperature. Increasing the temperature from 200°C to 275°C increased the 2,6-DIPN/2,7-DIPN ratio from ~ 2.1 to 2.6, slightly depending on the type of Mordenite catalyst.

Based on the outcome of high-level computational methods (MP2), Tasi *et al.* [23, 32] stated that 2,6-DIPN was the best fitting molecule in the H-Mordenite elliptical main channel, with 2,7-DIPN being only slightly less favorable. In agreement with Song *et al.* [33], Tasi *et al.* concluded that the selective formation of 2,6-DIPN over H-Mordenite was the result of product shape-selectivity. However, they did neither account for framework flexibility, as described by Jansen *et al.* [42-43], nor variations in H-Mordenite chemical composition when comparing data. Those authors also reported a computed internal thermodynamic equilibrium distribution of DIPN-isomers (Table 3.10). Their high level computational study also showed that the occurrence of (electronic) transition state shape-selectivity was very unlikely. Their calculations were in line with the results of both Brzozowski *et al.* [19] and us, with respect to the DIPN isomer distribution and the absence of (electronic) transition state shape-selectivity. The outcome of an investigation of 2,6-DIPN isomerisation over H-mordenite was in line with our results as far as the pattern of DIPN isomers formation is concerned. In that work no attention was paid to the formation of naphthalene and IPNs.

Cutrufello *et al.* [9] revealed the importance of coke formation on the performance of H-Mor in the isopropylation of naphthalene at 350°C. Conversions decreased from

30% to 20% in time for naphthalene, and from 80% to 60% for isopropanol. It was concluded that fast oligomerisation of C_3-species and cracking of oligomers caused almost immediate pore blocking, suggesting that the actual isopropylation occurred on or near the outer surface. Very interestingly it was reported that the ratio 2-IPN/1-IPN amounted to 4 and that the DIPN product mixture consisted of ~ 8 % of 1,3-DIPN, <5% of 1,7-DIPN, <5% of 1,6-DIPN, up to 60% of 2,6-DIPN and up to 30% of 2,7-DIPN. There was a marked influence of time-on-stream on the 2,6-DIPN/2,7-DIPN ratio, starting from ~ 1 after 50 min and reaching ~ 3 after 350 min on stream. Steric factors were thought to be responsible for the formation of the different DIPN-isomers.

Our experimental results with H-Mordenite (Table 3.10) are in line with the results of Song *et al.* [1, 3, 26], Tasi *et al.* [23] and Cutrufello *et al.* [9] but not with Moreau *et al.* [11]. Our computational results are in line with the results of Tasi *et al.* [23]. However, our interpreatation of the experimental data is in disagreement with the interpretation of the data by the above-mentioned authors, which is in favor of molecular shape-selectivity. Considering all the experimental data, there is little difference if any between the selectivity patterns obtained over H-Mordenite and H-USY. The relative contribution of outer surface or pore mouth catalysis on H-Mordenite will be large, as diffusion inside the pores, if possible at all, will be very slow. Pore blocking, due to C_3-oligomerisation and cracking, is very important in this catalysis. The difference in molecular size between 2,6- and 2,7-DIPN as reported by Tasi [32] is too small to explain the excess of 2,6- over 2,7-DIPN at high reaction temperatures and definitely cannot explain the reverse selectivity pattern at low temperatures. It can be also expected that the reported good fit of 2,6- and 2,7-DIPN in the main channel of Mordenite will cause very slow diffusion, thus also leading to pore mouth or external surface catalysis. The results of Cutrufello *et al.* [9] combined with the computational results point out to that the 2,6-DIPN/2,7-DIPN ratio of ~ 3 is in fairly good agreement with the trend of our calculations. Furthermore, the DIPN-distribution found by Cutrufello *et al.* at 350°C and by ourselves at 200°C show in fact slightly lower amounts of 2,6- and 2-7-DIPN and slightly higher amounts of the other DIPN-isomers than predicted by internal thermodynamic equilibrium. This can be expected from a rather slow catalyst, which is not fast enough to reach completely the thermodynamic distribution.

3.4. Conclusions

H-USY and H-Mordenite are selective catalysts for the isopropylation of naphthalene to 2,6-DIPN. High 2,6-DIPN yields can be obtained in the liquid phase with H-USY only. Investigation of naphthalene isopropylation and 2,6-DIPN isomerisation with H-USY and H-Mordenite revealed that under the investigated conditions the selectivity among DIPN isomers is under thermodynamic control. Shape-selectivity of whatever kind can be ruled out for both the USY and the Mordenite catalyst.

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4

Catalysis over BIPOMs

Abstract

Several BImodal POrous Materials (BIPOMs) are compared in the isopropylation of naphthalene with 2-propanol.

A series of BIPOMs, ranging in particle size, clearly showed that the best catalyst for isopropylation of naphthalene with 2-propanol is the nano zeogrid, and not the bulk zeolite. The added super-microporosity allows better access to the active sites of the catalyst and therefore considerably increases the reactivity while keeping a high selectivity. This may be seen as a proof of principle for the BIPOM approach.

4.1. Introduction

Sustainability is getting more and more importance in the development of new chemical processes. Such processes [1] should minimise energy and water consumptions and all waste streams. Furthermore they should use fast, selective and atom-efficient catalysts that can be easily removed and regenerated.

An excellent example of processes with a high potential for improvement is the alkylation of aromatics. Industrial R&D effort has already been invested to develop alternative solid-acid technologies free of drawbacks [2]. In the case of ethylbenzene and cumene several zeolite catalysts are successfully applied (H-ZSM-5, H-Y, H-Beta, MCM-22, H-Mordenite). When developing a new plant, the question is not whether a zeolite-catalyst process will be chosen but which one.

As described in Chapter 3, naphthalene alkylations are already reported on several zeolitic catalysts [3-13], but it is still impossible to get a specific compound with high yield, even though numerous reaction conditions [14] or alkylating agents [15, 16] have already been investigated. So far, many research teams have been focusing on H-Mordenite and the possibilities of dealumination [17-24] and surface modifications [25-27], or doing theoretical studies about isomer formation [28-33].

A new type of catalysts called BImodal POrous Materials (BIPOMs) has recently been proposed by the group of Profs. Jacobs and Martens in Leuven [34-38]. Building units for these new materials are nanoslabs of uniform size having a zeolite-type framework. At the second structural level, nanoslabs are linked through their corners, edges or faces following patterns imposed by interaction with organic molecules. After evacuation of the organic molecules, ultra-microporosity is obtained inside the nanoslabs, and a precise super-microporosity between the nanoslabs depending on the fixing pattern as presented in Figure 4.1. With this self-assembly system the generation of porous bodies is much better controlled as compared to the conventional zeolite crystallisation methods involving solubility driven-nucleation and crystal growth. Moreover, structure control at any level from the nanoscale to the macroscopic scale is possible. Their super-micropores should allow mass-transfer limitation free access of substrates to, and products from the catalytic sites. It is expected that they exceed the performance of classical zeolite catalysts.

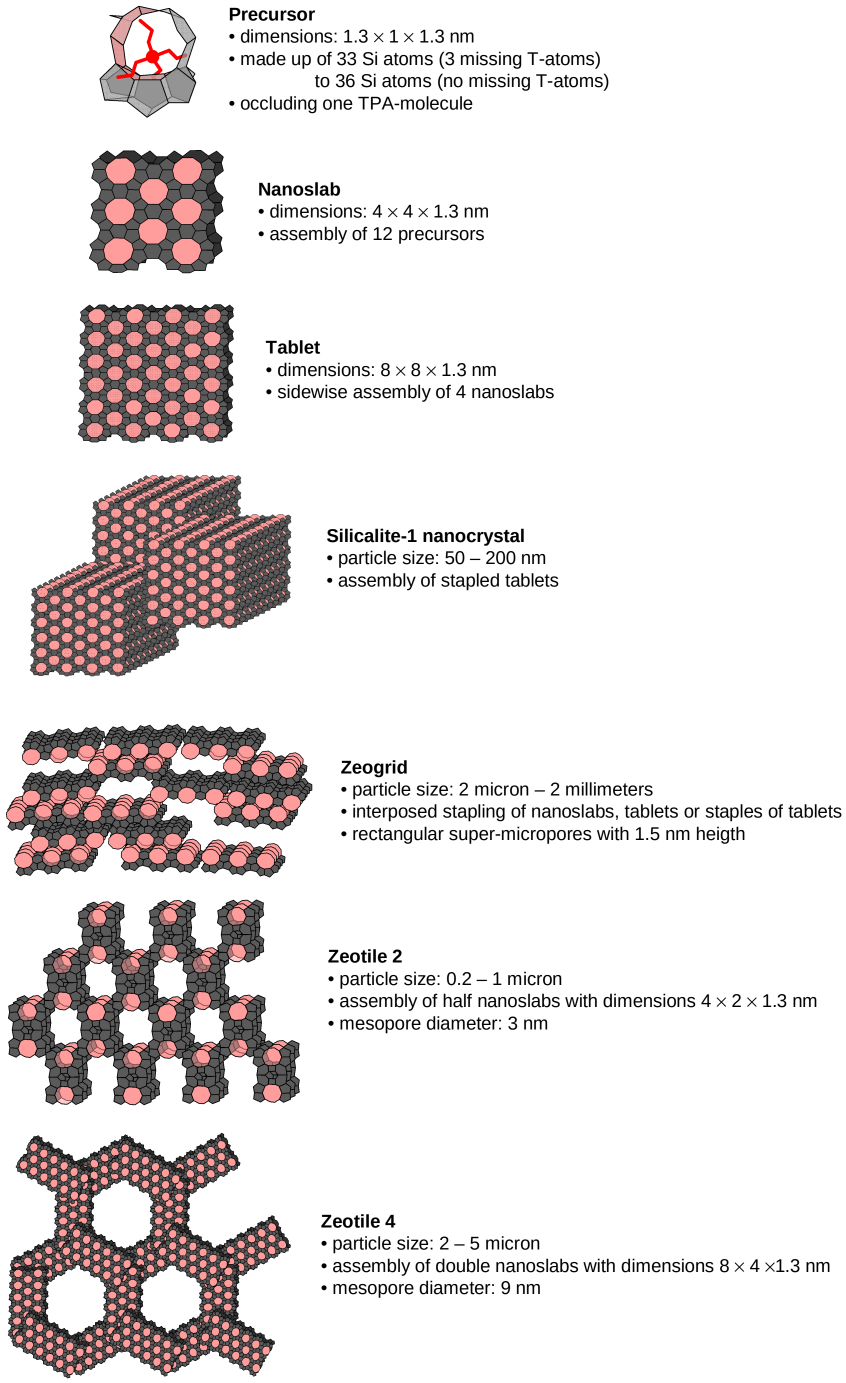

Figure 4.1: Overview of the first BIPOM samples

4.2 Synthesis and characterisation of BIPOM samples

4.2.1 Synthesis

Synthesis of Clear Solution Si/Al=50 [34-35]

0.0948 g Al (powder) was dissolved in 32.09 g of tetrapropylammonium hydroxide (TPAOH) under mild stirring at room temperature for 24 h. 36.57 g of tetraethyl orthosilicate (TEOS) were then added under vigorous stirring. After the mixture became clear, stirring was continued for another 10 minutes before adding 31.33 g of deionised water. The final mixture was stirred for another 24 h at room temperature.

The resulted solution is referred to as “clear solution Si/Al=50”, CS (50), and was used in the synthesis of all BIPOM materials.

Synthesis of Zeogrid Si/Al=50, coded ZG (50) [36-37]

20 ml of ethanol were mixed with 20 g of CS (50). To the resulted solution, 60 ml of a 10 wt % aqueous solution of cetyltrimethylammonium bromide (CTAB) were added dropwise under vigorous stirring. The resulted precipitate was aged under quiescent conditions for 24 h at room temperature. The precipitate was separated under vacuum filtration and washed with ethanol to remove the excess of CTAB. The powder was dried in an air oven at 60°C for 24 h and calcined at 400°C for 1 day in N_2 and 3 days in O_2.

Synthesis of Zeogrid 1d Si/Al=50, coded ZG1d (50) [38]

The synthesis procedure is similar to the one for ZG (50) with the exception that the clear solution used was heated for 24 h at 120°C prior to the addition of ethanol. The additional heating time allowed a partial crystallisation of zeolite precursors into crystals around 100 nm.

Synthesis of Colloidal ZSM-5 Si/Al=50, coded cZSM-5 [36-37]

100 g of CS (50) were loaded in a stainless steel autoclave and heated at 120°C for 3 days without stirring. After cooling to room temperature the mixture was transferred in polypropylene bottles. The resulting zeolite crystals were separated by centrifugation at 12.000 rpm for 15 min and washed with ethanol. The centrifugation step was repeated 3 times. The sample was dried in an air oven at 60°C for 24 h and calcined for 5 h at 550°C.

4.2.2 Characterization

SEM

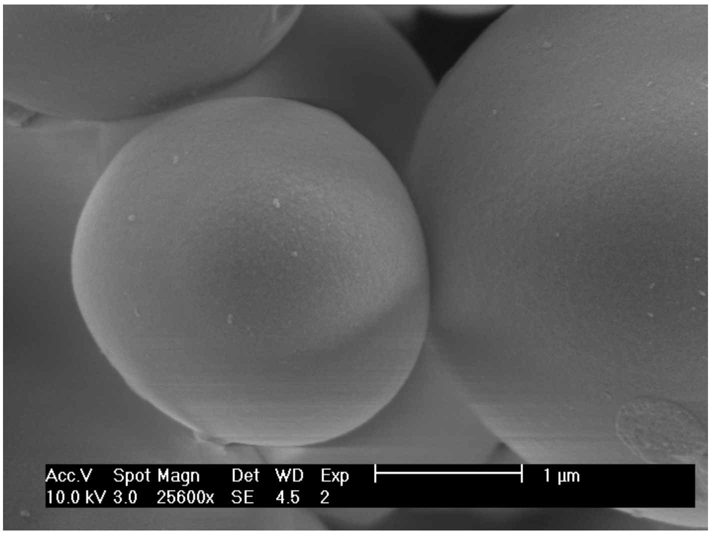

Figure 4.2: SEM picture of the ZG (50)

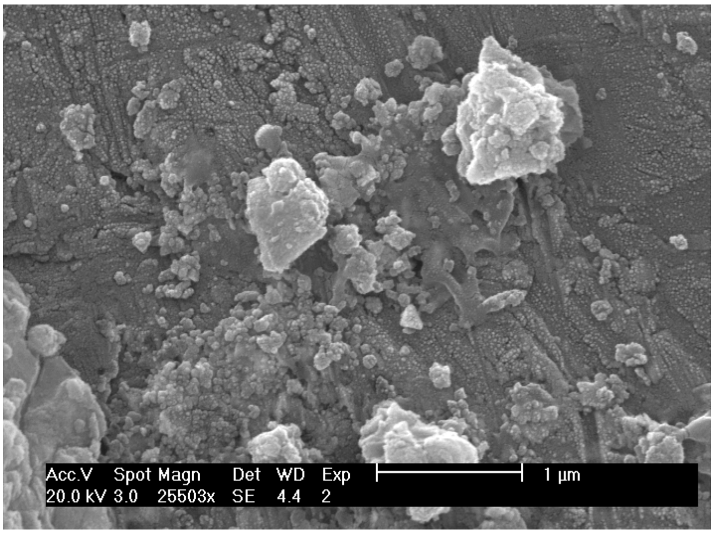

Figure 4.3: SEM picture of the ZG1d (50)

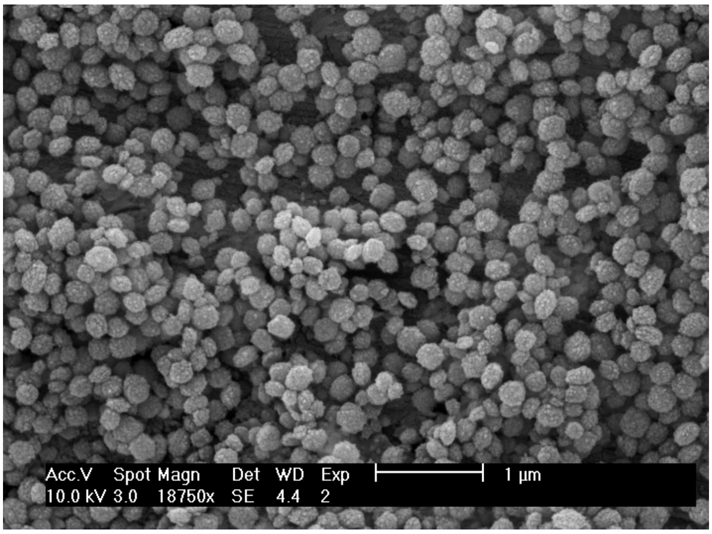

Figure 4.4: SEM picture of the cZSM-5 (50)

As can be seen in Figures 4.2, 4.3 and 4.4, SEM pictures show a different morphology for each of the BIPOM samples even though they were synthesised from the same zeolite precursor units. The ZG (50) sample consists of sphere like particles of 2-5 µm with a smooth surface. However, the preheated analogue of ZG, ZG1d (50), contains particles of around 1 µm with an irregular shape. The cZSM-5 (50) sample is formed of individual zeolite crystals of around 150-200 nm that present an irregular surface unlike normal zeolite crystals.

N_2 adsorption

Catalyst	**ZG**	**ZG (50)**	**ZG1d (50)**	**cZSM-5 (50)**	**ZSM-5 as-synthesised**
V_t (cm^3/g) [a]	0.63	0.82		0.13	
S_{ext} (m^2/g)[b]	20	20		236	
V_D (cm^3/g) [c]	0.51	0.67		0.23	
E (kJ/mol) [d]	3.6	3.2		6.1	
V_U (cm^3/g) [e]	0.05	0.04		0.14	
n [f]	2.3	2.0		-	
C_{BET} [g]	47	49		-	
S_S (m2/g) [h]	1292	1790		-	

[a] Total pore volume determined using the *t*-plot of Carruthers *et al.* at $0.6 < P/P^0 < 0.8$ [39].

[b] External surface area determined using the *t*-plot of Carruthers *et al.* at $0.6 < P/P^0 < 0.8$ [39].

[c] Micropore volume calculated with the Dubinin-Radushkevich method at $0.01 < P/P^0 < 0.1$ [40].

[d] Adsorption energy calculated with the Dubinin-Radushkevich method at $0.01 < P/P^0 < 0.1$ [40].

[e] Ultra-micropore volume determined using the *t*-plot of Carruthers *et al.* at $0.6 < P/P^0 < 0.8$ [39].

[f] Number of adsorbed nitrogen layers in super-micropores calculated according to a BET model with limited layer thickness at $0.001 < P/P^0 < 0.4$ [41].

[g] The BET constant for sorption in super-micropores calculated according to a BET model with limited layer thickness at $0.001 < P/P^0 < 0.4$ [41].

[h] Super-micropore specific surface area calculated according to a BET model with limited layer thickness at $0.001 < P/P^0 < 0.4$ [41].

Table 4.1: Analysis of nitrogen adsorption isotherms of the BIPOM samples [36]

Results presented in Table 4.1 originate from Aerts *et al.* with the following nomenclature correlations: ZG (50) corresponds to ZG 2.0 and the cZSM-5 is equivalent to the AS1 2.0 sample. No data were obtained for the ZG1d (50) sample but its properties are expected to lie in between those of the ZG (50) and the cZSM-5 as it has a crystal size close to cZSM-5 with extra super-micropores.

Among the 3 BIPOM samples the ZG (50) sample shows the highest BET surface area and total pore volume. The ZG1d (50) sample has a slightly lower surface and pore volume due to the partial aggregation of the zeolite precursors during the extra heating time of the clear solution. The cZSM-5 sample presents typical textural properties for a small crystal ZSM-5.

XRD

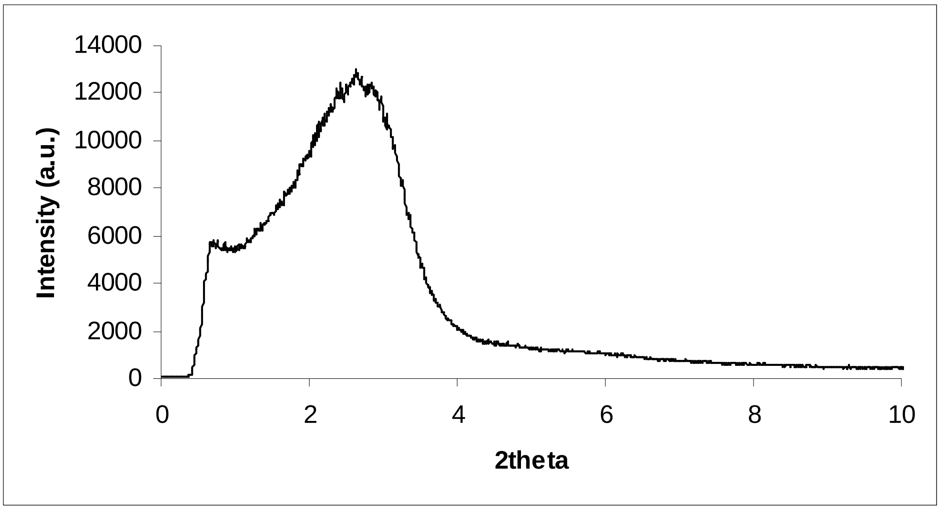

Figure 4.5a: XRD pattern for the ZG (50) sample at low angle.

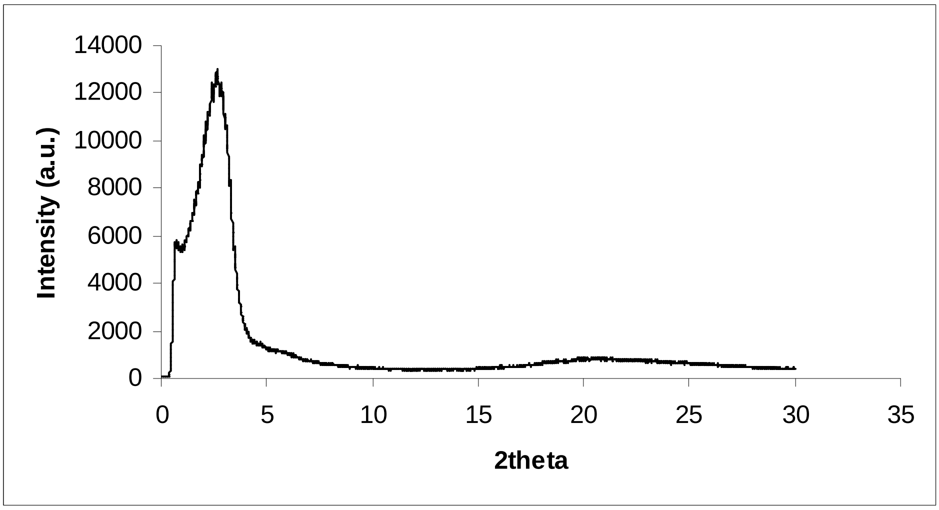

Figure 4.5b: XRD pattern for the ZG (50) sample at high angle.

X-Ray Diffraction (XRD) patterns of the ZG (50) sample (presented in Figures 4.5a and b) show only a broad peak at around 2.6 2theta, which is representative for a layered structure with a d value of 3.4 nm. Analysis at higher 2theta angles shows that no diffraction peaks are present.

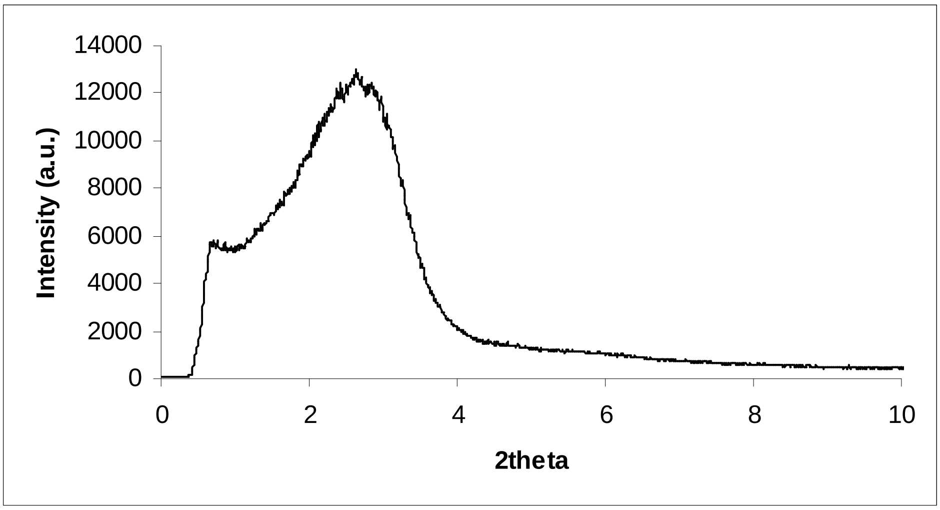

Figure 4.6a: XRD pattern for the ZG1d (50) sample at low angle.

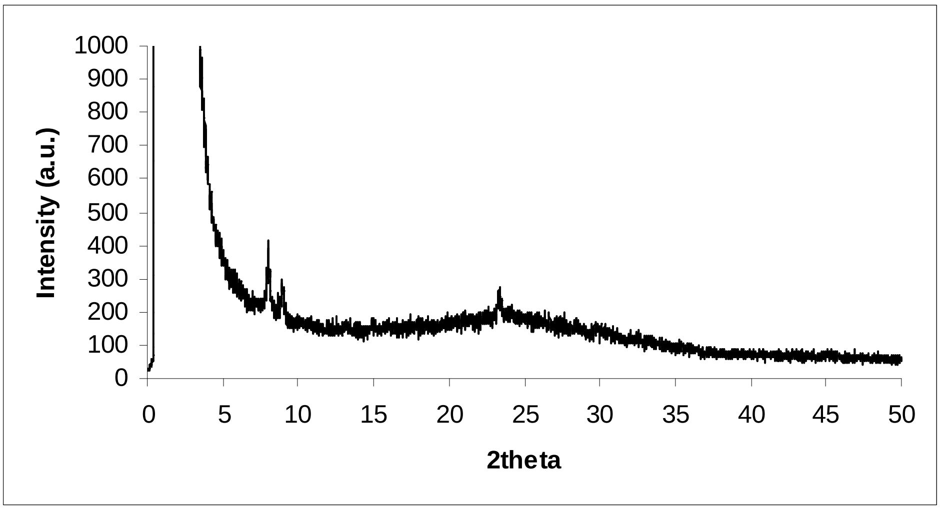

Figure 4.6b: XRD pattern for the ZG1d (50) sample at high angle.

The ZG1d (50) sample also presents a broad diffraction peak at low 2theta values, as can be seen in Figures 4.6a and b. However, the maximum is at 2 2theta, which corresponds to a d value of 4.4 nm. The increase in the d value can be explained by the presence of larger zeolite crystals in the ZG1d (50) sample than in the ZG (50). This assumption is also supported by the high angle XRD analysis of the ZG1d (50) sample.

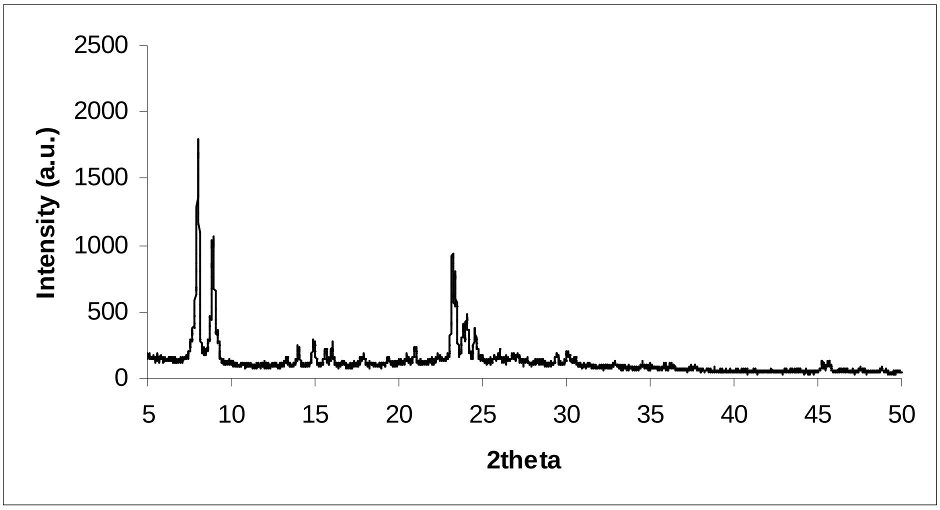

Figure 4.7: XRD pattern for the cZSM-5 (50) sample at high angle.

Diffraction lines specific to MFI structure are identified 8.03, 8.95 and 23.22 2theta. The cZSM-5 (50) shows a typical XRD pattern for MFI zeolites with no additional peaks at lower angles, as presented in Figure 4.7.

4.3. Alkylation and isomerisation

4.3.1 Activity and selectivity of BIPOMs in alkylation reactions

Results for alkylation of naphthalene with 2-propanol after 24 h are presented in Figure 4.8. BET areas were not considered as an interesting parameter as the product distribution does not vary linearly with it.

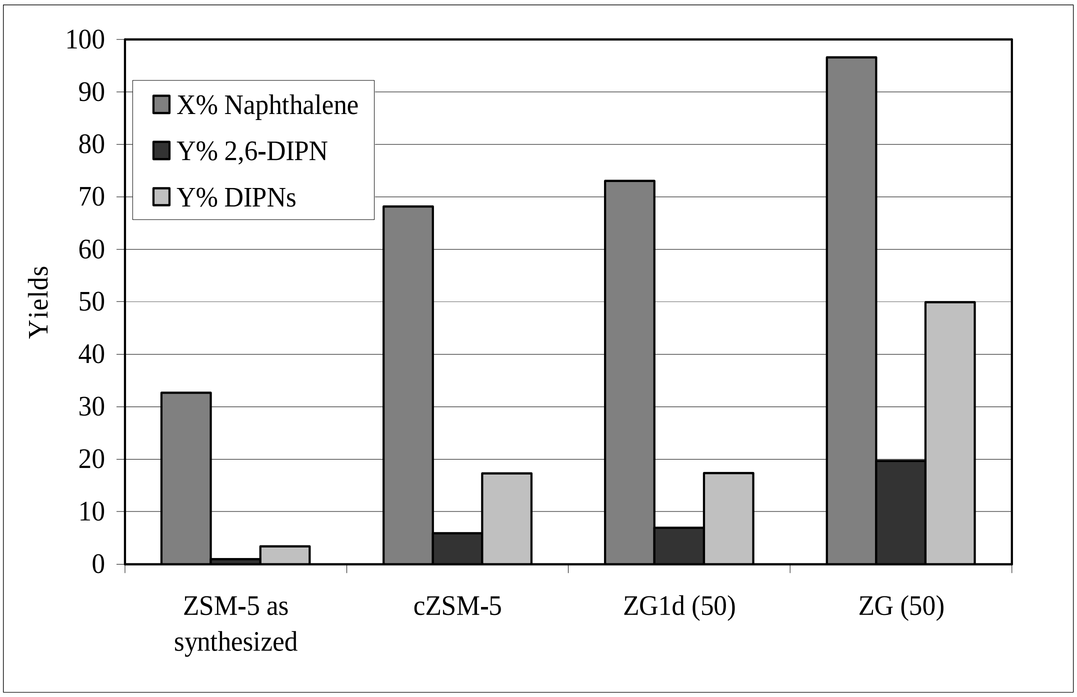

Figure 4.8: Naphthalene Conversion (X) and Yields (Y) of various products in the isopropylation of naphthalene over the four catalyst samples of Table 4.1.

Conversion and selectivity towards DIPNs in general, and 2,6-DIPN in particular were increased when the amount of super-micropores was increased, as can be seen by comparing the ZSM-5 as-synthesized with the ZG1d (50), and the cZSM-5 with the ZG (50). Smaller building units in the final catalytic particle also contribute to an important increase in conversion and selectivity, as seen when comparing ZSM-5 as-synthesized with colloidal ZSM-5 or ZG1d (50) with ZG (50). Conversion is nearly complete over ZG (50) when the reference ZSM-5 catalyst yields to a conversion of only 32% and interestingly the extra conversion yields extra DIPNs in general (50%) and 2,6-DIPN (20%) particularly. The similar performances of ZG1d (50) and cZSM-5 might relate to their principal crystal size of 100 nm and 150 nm respectively.

The Zeogrid catalysts therefore clearly outperformed their classical parent ones.

4.3.2 Activity and selectivity of BIPOMs in 2,6-DIPN isomerisation reactions

Results obtained for the catalysts screened under standard conditions are presented in Figure 4.9.

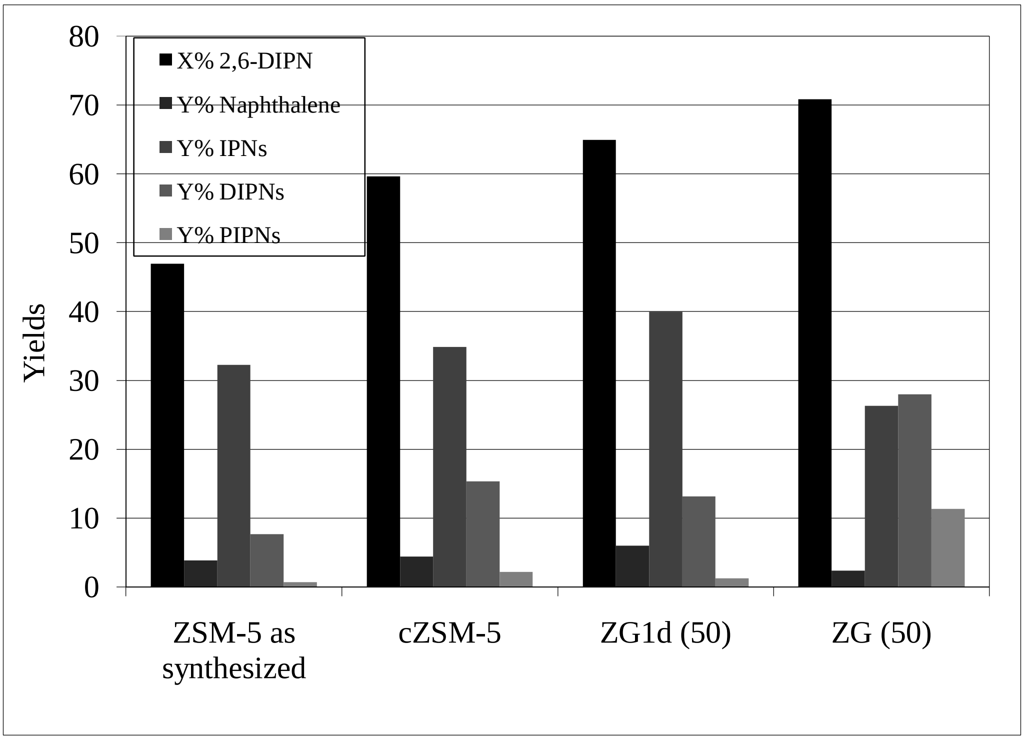

Figure 4.9: 2,6-DIPN Conversion (X) and Yields (Y) of various products in the isomerisation of 2,6-DIPN over the four catalyst samples of Table 4.1.

In isomerisation as well, an increase in the number of super-micropores, as well as a smaller building unit, enable a better product distribution. 2,6-DIPN becomes more prone to isomerisation and transalkylation than to dealkylation. The as-synthesised ZSM-5 mainly produces IPNs (30% yield) while the ZG (50) generates similar amounts of IPNs and DIPNs (around 25%). This makes this type of catalysts more interesting to apply in a process as the recycled feed will be more interesting. It is likely to believe that other isomers may just follow the same trend and therefore yield extra 2,6-DIPN. Concerning the importance of isomerisation and therefore the yield to DIPNs, the catalysts show the same order as in alkylation with the very best yield and conversion to DIPNs for the ZG (50)

4.4. Comparison with H-USY

Since the ZG (50) is to be considered as the current best available BIPOM catalyst for this reaction, a comparison with the best commercial type of catalyst, namely H-USY as stated in Chapter 3, is proposed. Comparison was made at 200°C with all variables identical besides the catalyst and is presented in Figure 4.10.

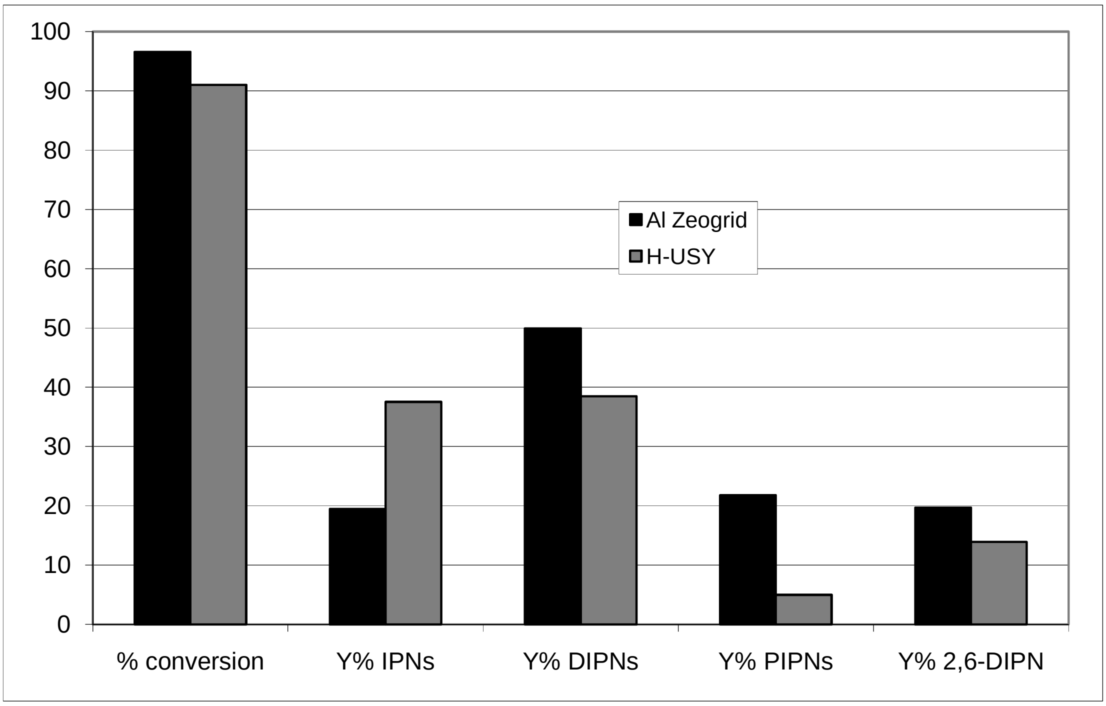

Figure 4.10: Product distribution over ZG (50) and H-USY in the isopropylation of naphthalene at 200°C after 24 h.

It can be concluded that under these test conditions both catalysts behave in a relatively similar way, the ZG (50) yielding even slightly more DIPNs in general and 2,6-DIPN in particular. The main difference lays in the side-product distribution as it appears that the extra porosity of the Zeogrid allows over-alkylation more than H-USY. Still, for both catalysts, IPNs and PIPNs account together for about 40% of the mixture.

Table 4.2 displays the DIPN isomer distribution at 200°C for H-USY and the ZG (50).

	H-USY	**ZG (50)**
1,3-DIPN	3,8	8,9
1,7-DIPN	4,9	6,4
2,3-DIPN	0,4	0,8
2,6-DIPN	40,3	38,4
2,7-DIPN	42,9	38,1
1,6-DIPN	7,6	7,1
1,5-DIPN	0,1	0,4
1,4-DIPN	0,1	n.d.

Table 4.2: Experimental isomer distribution over H-USY and the ZG (50).
n.d.: not detected.

Considering the results presented in Table 4.2, it can be said that the partition over H-USY and over the ZG (50) is very similar. However, the equilibrium is not fully reached over the ZG (50) at 200°C. Catalysis over the ZG (50) is nearly controlled by thermodynamics at 200°C.

4.5. Conclusions

Super-microporous aluminium Zeogrids and particularly those obtained from small building nanoblocks are clearly among the best zeolitic catalysts for the isopropylation of naphthalene to 2,6-DIPN with respect to rate and selectivity. They clearly outperform catalysts with a bulk MFI structure and extensively reported catalysts like Mordenites and are already allowing similar yields than the best commercial catalyst.

These findings open a new window to the development of a sustainable process for the production of 2,6-DIPN, inspired by the actual Kureha process [42]. The separation of 2,6-DIPN from the reaction mixture now becomes a crucial issue. By using the ZG (50) or H-USY as a catalyst in a reaction operating under thermodynamic control, PIPNs, isomeric DIPNs, and IPNs can possibly be recycled to the reactor to yield additional 2,6-DIPN. The ZG (50) catalyst performance can theoretically still be optimised as this is a first generation of catalysts and that they were not designed specifically for this reaction.

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5

Aiming for an industrial process: a temperature study

Abstract

Under standard conditions H-USY and the BIPOM catalyst ZG (50) are the best available catalysts for the diisopropylation of naphthalene. The product distribution follows thermodynamic distribution in both cases. A temperature study to the catalytic performance of H-USY and ZG (50) for this reaction was performed to optimise yield and selectivity.

It was found that H-USY had an optimum yield of 17% to 2,6-DIPN at 150°C, while ZG (50) showed a maximum yield of 20% to 2,6-DIPN at 225°C. Also the yield to 2,7-DIPN, a difficult to remove isomer, is favoured over ZG (50). Furthermore the larger operating window and higher process temperature allow a better selectivity control and heat recovery. Thus, ZG (50) is now the best available catalyst for selective diisopropylation of naphthalene.

5.1. Introduction

With shape-selectivity having no influence on the reaction outcome, as described in Chapter 3, high conversion has to be aimed as it will maximise the yield towards 2,6-DIPN. Among the commercially available zeolites, H-USY was found to be from far the best catalyst in terms of conversion and selectivity. Chapter 4 showed that some first generation BIPOM catalysts, such as ZG (50) obtained from small nanoblocks, can match these performances under the test conditions.

When aiming for a sustainable industrial application, one should take into account parameters that differ from those generally applied at the lab scale. Being able to run a process at a higher temperature will have a significant positive impact both on the production cost and the energy consumption. H-USY as best commercial catalyst and the ZG (50) as potential new alternative were therefore studied under several reaction temperature, for both alkylation of naphthalene and isomerisation of 2,6-DIPN. It is noteworthy to say that despite numerous publications discussing the ideal catalyst for diisopropylation of naphthalene, reaction temperature has not been addressed by any research group.

5.2. H-USY

Conversion and yields obtained for alkylation over H-USY are presented at various temperature on Figures 5.1 and 5.2, following the standard procedure described in Chapter 2. If the reaction is run at 25°C, no conversion occurs.

For all the temperatures studied, conversion of naphthalene over H-USY remains above 90%. At low temperature, kinetic products are formed. This is showed by the excess of 1-IPN over 2-IPN at 80 and 100°C and by the important amount of over-alkylated species. Between 100 and 150°C, thermodynamic control starts to take over and the reaction outcome changes. Dealkylation starts to be important and over-alkylated species yield extra DIPNs and IPNs. 2-IPN becomes largely dominant over 1-IPN and the total amount of 2,6-DIPN and 2,7-DIPN, the most thermodynamically stable isomers, increases significantly. The highest conversion is reached at 100°C and the highest yield towards 2,6-DIPN at 150°C, albeit 2,7-DIPN is still in slight access over 2,6-DIPN.

It clearly appears that at low temperatures, alkylation and isomerisation are favoured as can be seen by the decrease of the IPNs yield at 100°C compensated by the increase in DIPNs and PIPNs. When the temperature is further increased, dealkylation starts to be the fastest reaction involved and the yield to PIPNs considerably decreases. The same pattern probably concerns DIPNs but their loss towards IPNs, and particularly 2-IPN, is compensated by their production from PIPNs.

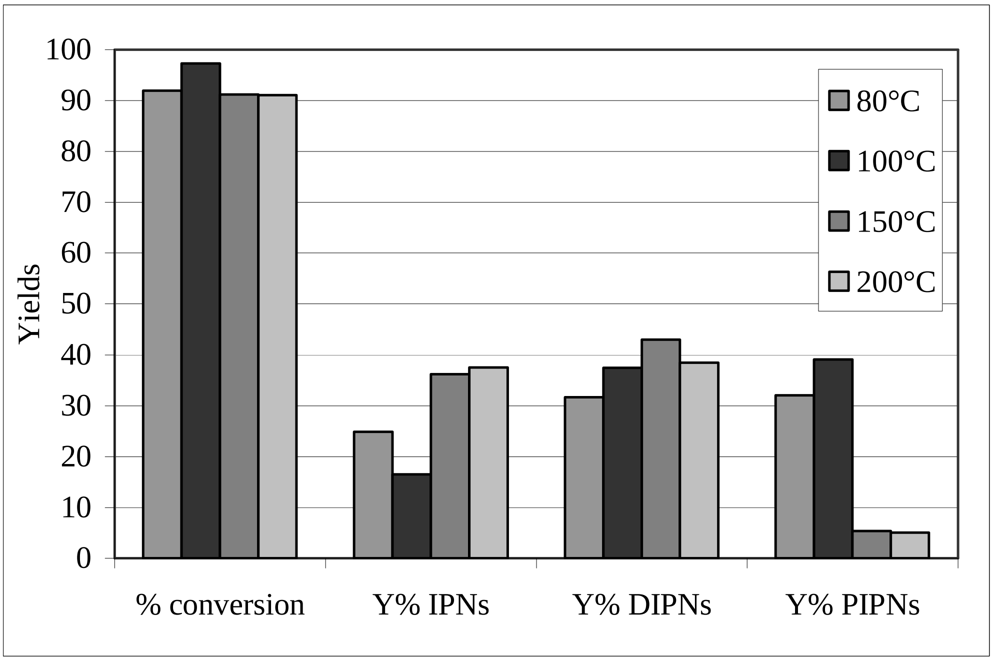


Figure 5.1: Yields towards specific families as a function of temperature in the isopropylation of naphthalene over H-USY.

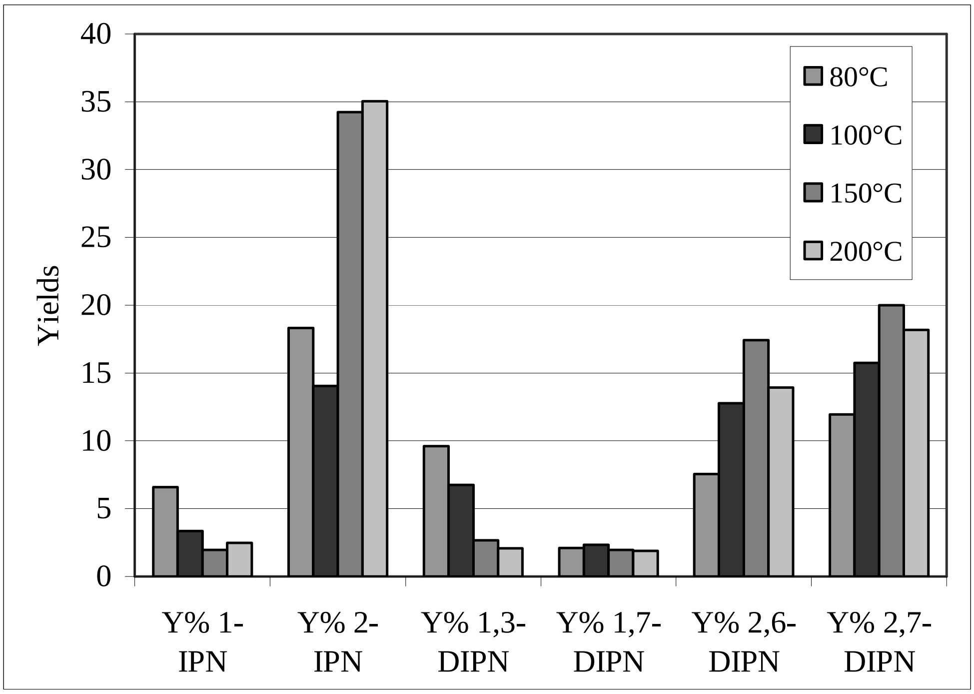


Figure 5.2: Specific yields as a function of temperature in the isopropylation of naphthalene over H-USY.

The conclusions obtained for alkylation are confirmed by the results of 2,6-DIPN isomerisation, as presented in Figure 5.3. At 100°C, conversion is still limited and products mainly belong to isomerisation or transalkylation. Temperature increase favours dealkylation first to IPNs and ultimately to naphthalene. Above 150°C dealkylation completely drive the reaction outcome and isomerisation becomes a side-reaction. For all temperatures tested, over-alkylation stays at a low level.

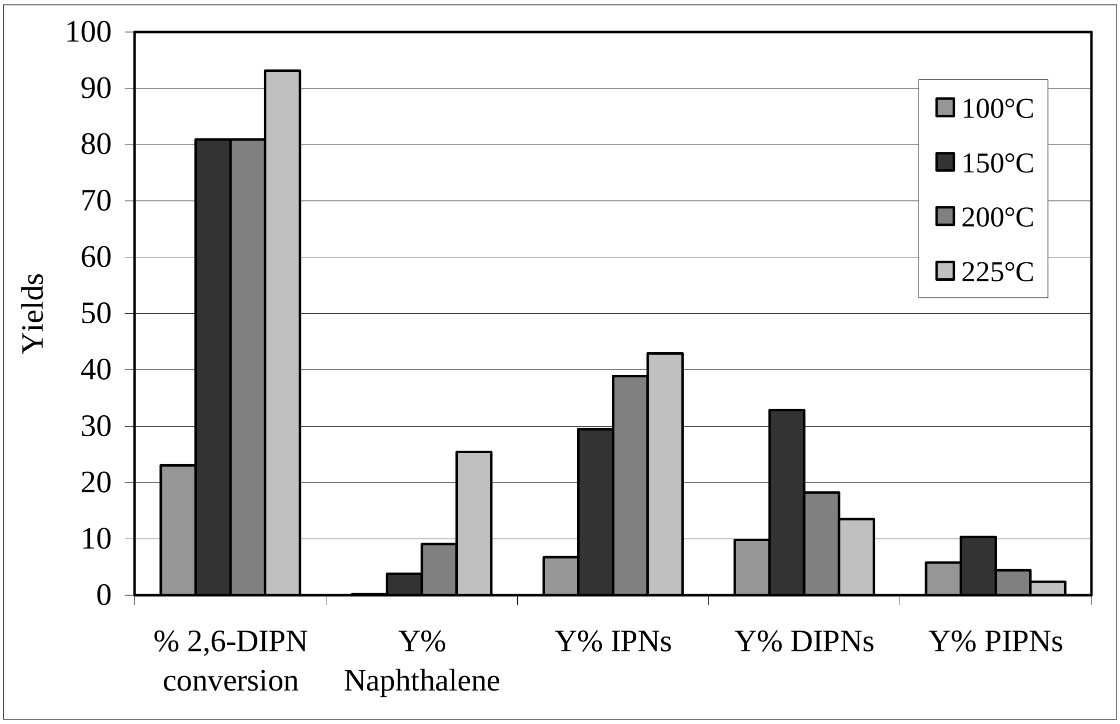


Figure 5.3: Yields towards specific families as a function of temperature in the isomerisation of 2,6-DIPN over H-USY.

5.3. Al Zeogrid ZG (50)

Since the ZG (50) from small nanoslabs is to be considered as our current best available BIPOM catalyst, a temperature study at otherwise standard conditions has been done with this catalyst to get a deeper insight in its performance (Figures 5.4 and 5.5). The highest naphthalene conversion (96.6%) and the highest yield to DIPNs (49.9%) are observed at 200°C, while the highest yield to 2,6-DIPN is observed at 225°C. Conversion at low temperatures is very low compared to H-USY and favours kinetic products as can be seen by comparing the yields towards 1-IPN and 2-IPN. Between 150°C and 200°C, the ZG (50) behaves in a similar way than H-USY and no longer follows a kinetic regime, as indicated by the important increase in the yields of 2-IPN, 2,6-DIPN and 2,7-DIPN. The BIPOM catalyst yields a maximum selectivity to 2,6-DIPN of 20% at 225°C, equalling the amount of 2,7-DIPN. At higher temperatures, dealkylation starts to play an important role over the ZG (50) as well and the apparent conversion therefore drops below 90%. This decreases the amount of over-alkylated species but also the DIPNs yield.

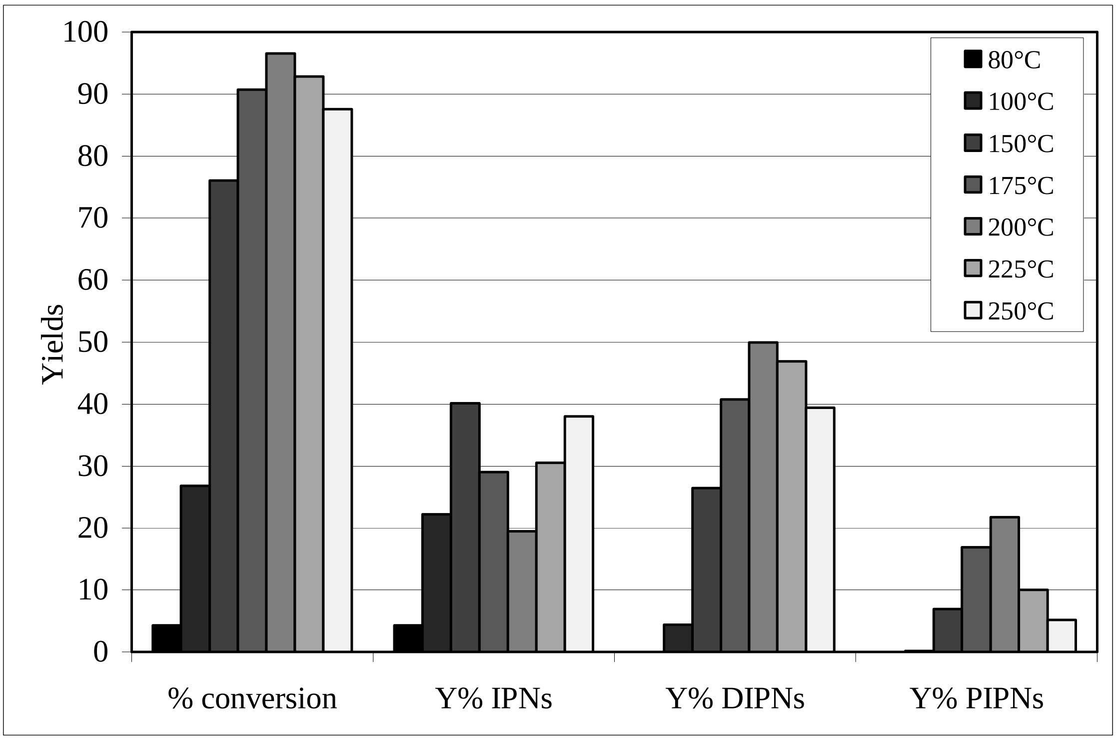


Figure 5.4: Yields towards specific families as a function of temperature in the isopropylation of naphthalene over the ZG (50).

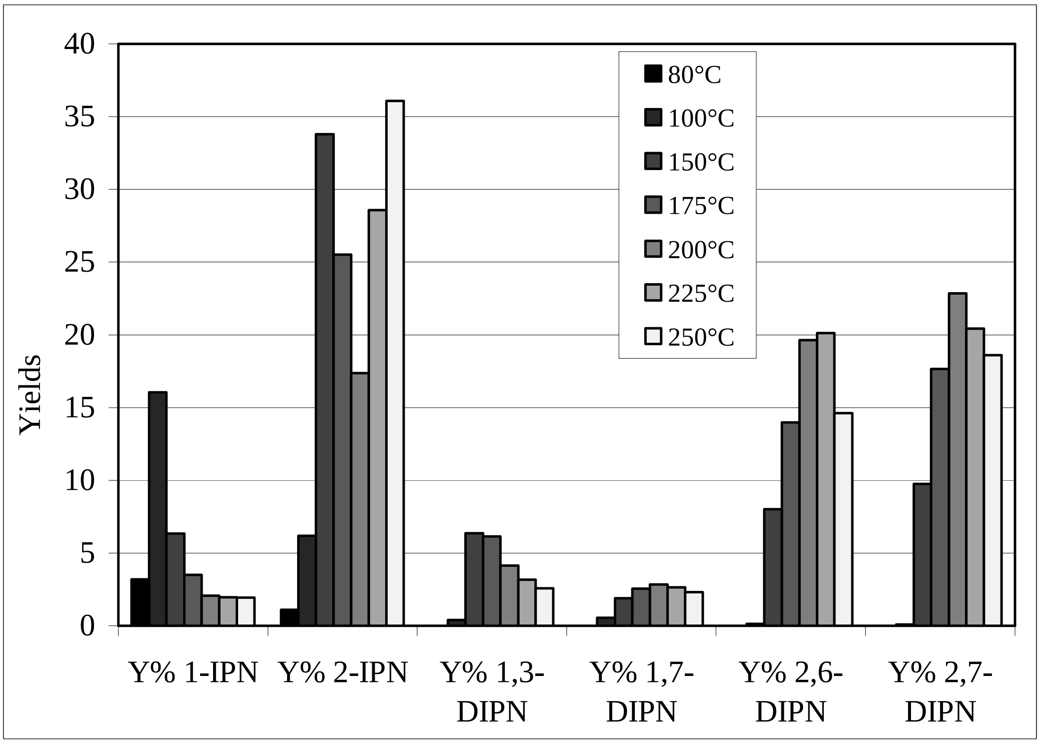


Figure 5.5: Specific yield as a function of temperature in the isopropylation of naphthalene over the ZG (50).

Results obtained in isomerisation are presented in Figure 5.6. They show a similar trend to the one obtained in alkylation. At temperatures below 150°C, conversion is close to 0. It increases then continuously with temperature and dealkylation is, similarly to H-USY, the main reaction taking place. Isomerisation is however present at a high level at high temperatures and is clearly more important than in the case of H-USY. Over-alkylation is as well more significant over the ZG (50).

The best yield towards 2,6-DIPN is reached over the ZG (50) at 225°C. The best yield (at 150°C) over H-USY is clearly outperformed (20% against 17%).

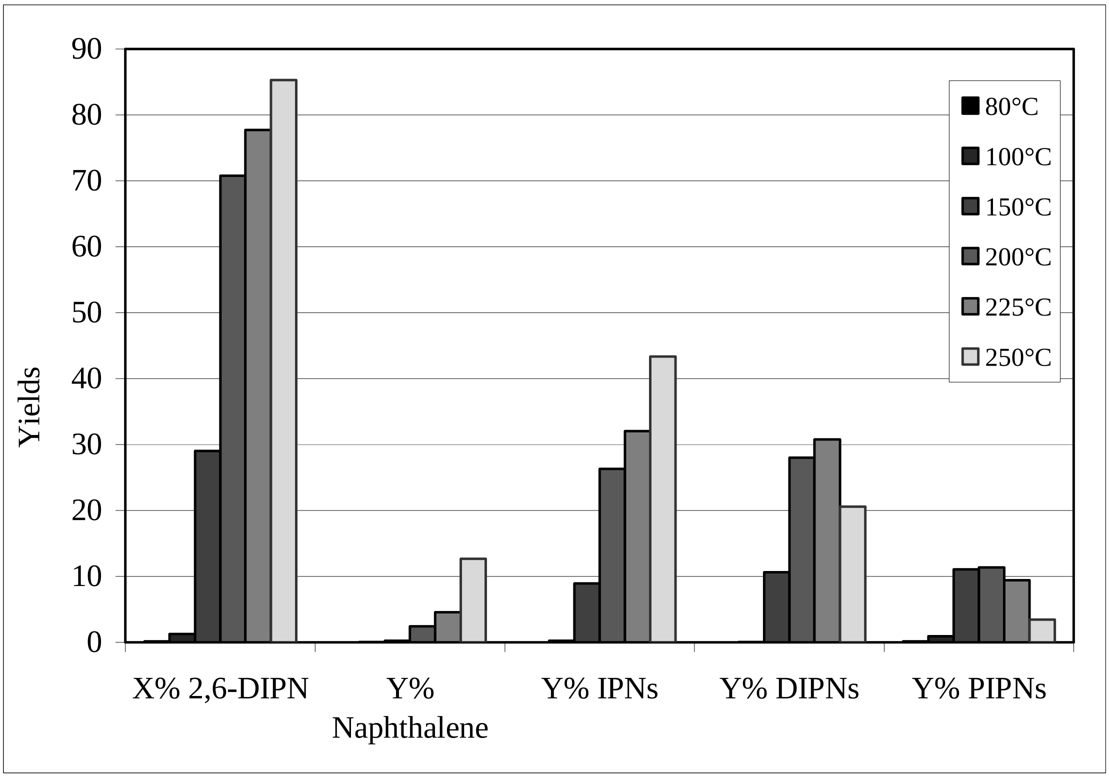


Figure 5.6: Yields towards specific families as a function of temperature in the isomerisation of 2,6-DIPN over the ZG (50).

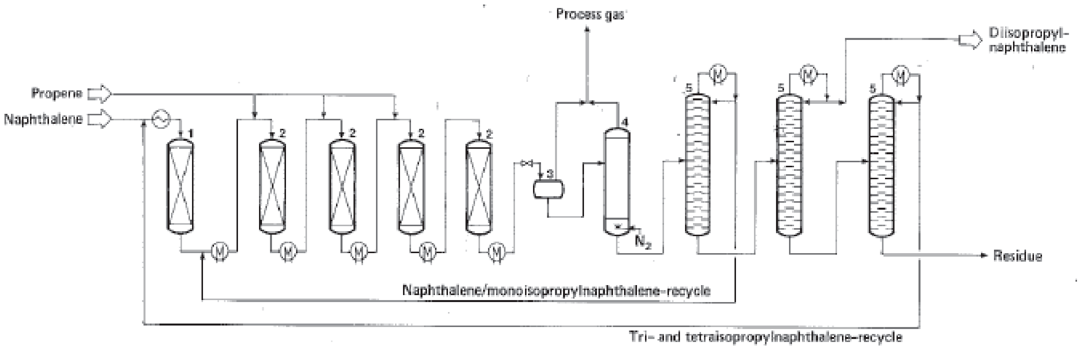
5.4 Discussion

Very interestingly, the ZG (50) shows a more extended temperature profile with a more subtle product partition than H-USY and therefore should allow more flexibility when applied in a process. Furthermore, the important amount of heat can be re-used within separations.

Due to the complexity of the reaction system involved, it seems difficult to derive kinetic data. It however clearly appears that at a given temperature (between 100 and 150°C for H-USY and around 200°C for the ZG (50)) dealkylation becomes the dominant reaction. This allows to state that the activation energies for both alkylation and isomerisation are similar and clearly lower than the activation energy needed for isomerisation.

Though these results clearly indicate that H-USY is more active than the ZG (50) at low temperature, the relevant temperature window for the ZG (50) is larger and this may allow a better selectivity control. The ZG (50) profits from the higher temperature in two ways: firstly, at higher temperature the relative amount of 2,6-DIPN within the DIPN-family increases, and secondly heat recovery is much simpler at higher temperature. Moreover isomerisation is still present at an important level at high temperatures, suggesting that more flexibility could be obtained and the recycled streams might be more balanced. Though not directly displayed in the corresponding figures, the ZG (50) produces slightly less Unsaturates and Others (5.4% vs. 6.5%). This is important for a full process as these side-products have to be purged along with some PIPNs (see Chapter 7).

These results allow as well understanding better the Kureha process [1] presented in Figure 5.7.



1 Transalkylation reactor; **2** Propylation reactor; **3** Pressure let-down vessel; **4** Strip column; **5** Vacuum-distillation columns

Figure 5.7: Flow diagram of the Kureha process

The reaction occurs at 200°C over an aluminosilicate catalyst. Their distillations and recycling suggest that the process generates IPNs and PIPNs as well. The first reactor allows over-alkylated species to react with naphthalene at a probably slightly higher temperature to undergo dealkylation, eventually followed by alkylation of naphthalene. Propene is fed in the following reactors to reach the stoichiometric composition of the feed.

5.5. Recyclability

In order to check as completely as possible whether both catalysts can be recycled without any activity loss, relative GC areas for each product family can be better considered than molar amounts, as it allows checking on the whole chromatogram and not only on the interesting parts. The behaviour of H-USY in the alkylation of naphthalene at 120°C is presented in Figure 5.8 and the behaviour of the ZG (50) in the alkylation of naphthalene at 150°C is presented in Figure 5.9.

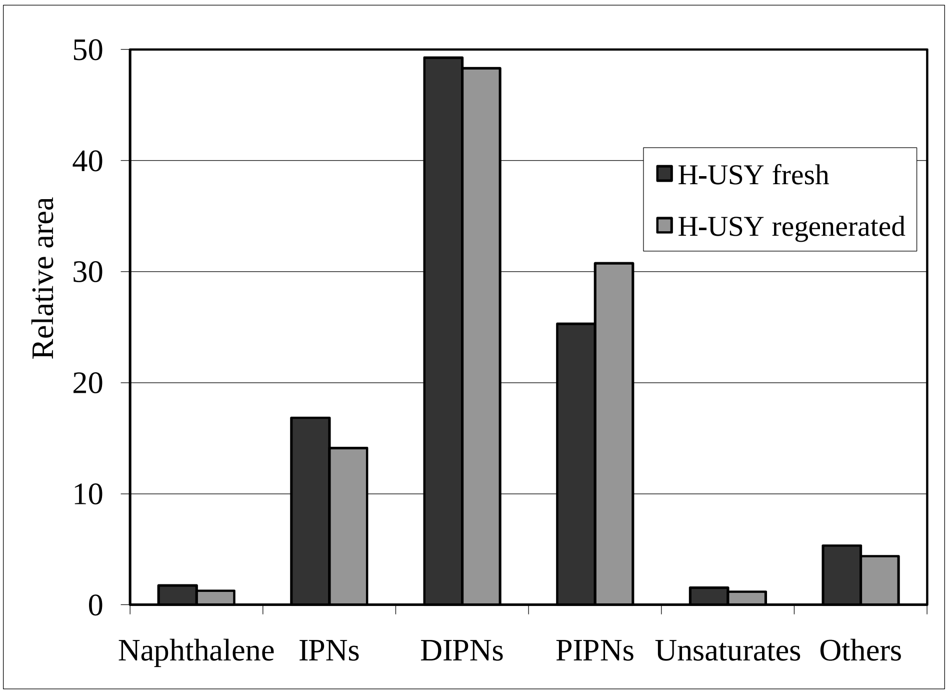


Figure 5.8: Relative areas for product family in the alkylation of naphthalene at 120°C over H-USY.

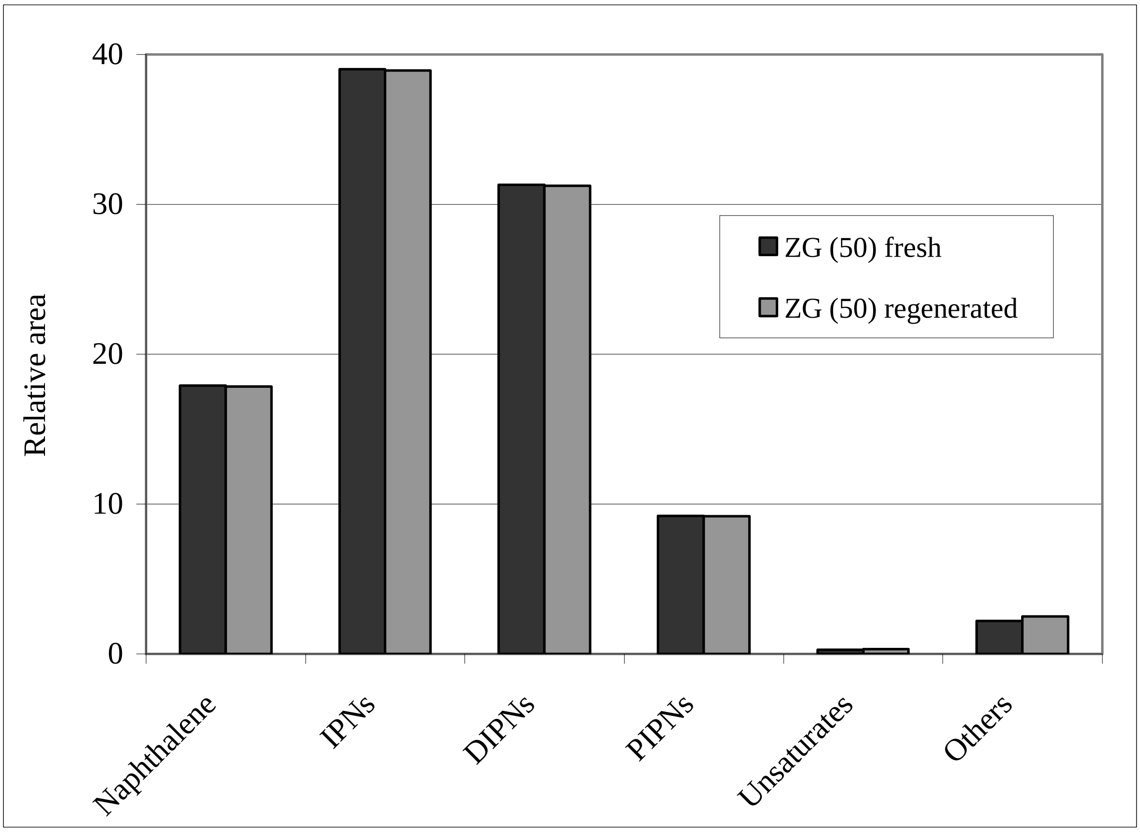


Figure 5.9: Relative areas for product family in the alkylation of naphthalene at 150°C over the ZG (50).

It is clearly shown that both catalysts, as expected, present a very stable behaviour after re-calcination. Variations are within few per cents for H-USY and can be partially explained by analytical reasons and the identification of heavy side-products, while both plots for the ZG (50) are nearly identical.

5.6. Conclusions

Aluminium zeogrids and particularly the ZG (50) should be considered as the best zeolitic catalyst to date for the isopropylation of naphthalene to 2,6-DIPN with respect to rate and selectivity. Besides this, results from the temperature studies with the ZG (50) seem to indicate that a larger temperature window at a higher temperature is available.

The present findings open a new window to the development of a sustainable process for the production of 2,6-DIPN, inspired by the actual Kureha process [1]. The separation of 2,6-DIPN from the reaction mixture now becomes an important issue. Using the ZG (50) as a catalyst in a reaction operating under thermodynamic control, PIPNs, isomeric DIPNs, and IPNs can possibly be recycled to the reactor to yield 2,6-DIPN. The Zeogrid catalyst performance can still be optimised as this is still a first generation.

Reference

[1] H.-G. Franck, J.W. Stadelhofer, Industrial Aromatic Chemistry, 1st Edition, Springer-Verlag, Berlin, **1987**, 329.

6

An exploration on separating diisopropylnaphthalene isomers

Abstract

The selective formation of 2,6-diisopropylnaphthalene (2,6-DIPN) does not seem to be possible, as shape-selectivity is not present for this system. There is therefore a real need for a good purification in order to meet the polymer industry needs. Two widely used separation techniques, namely distillation and crystallisation, are applied on the DIPN mixture in order to obtain a high 2,6-DIPN purity. Distillation under reduced pressure turns out to be ineffective, most likely due to complex azeotropic interactions. Crystallisation followed by methanol recrystallisation, however, allows isolation of 2,6-DIPN with a purity up to 95%, the main impurity being 1,5-DIPN. Crystallisation is therefore the most promising option with respect to both purity and energy consumption. This brings new possibilities for the industrial production of 2,6-DIPN.

6.1. Introduction

The previous chapters established that until now it is nearly impossible to achieve together high conversion and high selectivity towards 2,6-diisopropylnaphthalene (2,6-DIPN) by isopropylation of naphthalene at a reasonably low temperature. Thermodynamics will favour a mixture of β–β and α–β isomers with 2,6-DIPN contents about 40% maximum and 2,7-DIPN as main impurity in equal or slightly higher amounts at 200-225°C.

In order to meet the needs of the polymer industry, a very pure 2,6-naphthalene dicarboxylic acid is needed and this implies to be able to produce 2,6-dialkylnaphthalene in a very pure way. As the synthesis itself does not provide the expected requirements when dealing with 2-propanol, an additional purification step is mandatory. Separating isomers is difficult and even more if one has to deal with position isomers but several possibilities do exist for that purpose. To achieve this goal one has to play with physical properties of the compounds such as size, temperatures of phase transition or density. Selective adsorption will not be considered in this chapter as it is based on kinetic size of the molecules. Differences on this factor are too small to allow discrimination between 2,6-DIPN and especially 2,7-DIPN, one of the main impurities, as described in Chapter 3 on shape-selectivity. The main two options left are distillation and crystallization where the separation is based on differences in liquid-vapour data and melting points respectively.

Considering the selectivity obtained in the isopropylation of naphthalene, it is very likely that separation of the isomers will be a very important part in terms of energy consumption for the derived process for the production of 2,6-DIPN. Distillation requires a relatively cheap investment in terms of equipment but has a high energy consumption, while investment costs are usually important for crystallisation but the energy needed to operate the equipment is low.

Very recently a DIPN isomer mixture has become commercially available from Fisher Scientific. No information is provided on how it is produced, but the DIPN distribution is not the one of the thermodynamic equilibrium (as described in Chapter 2 page 43), which may suggest an alkylation at low temperature with a system operating under kinetic conditions over catalysts similar to H-USY or the ZG (50), as described in Chapter 5. Even if the composition is therefore quite different in terms of ratio, this mixture is still interesting as it contains all the main isomers present when alkylation occurs around 200°C. The main advantage lays in the fact that the first separation of DIPNs from the rest of the reaction mixture has already been done by rectification and that quantities that can be used exceed largely the outcome of a lab batch reaction.

A chromatogram of this mixture is presented in Figure 6.1 and its isomer distribution is presented in Table 6.1.

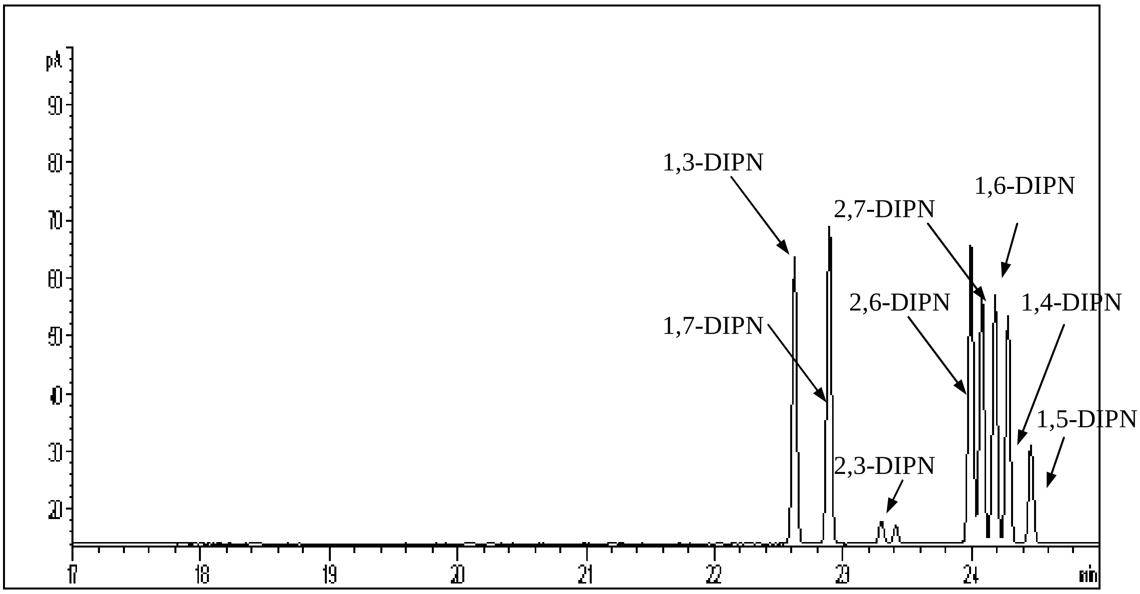


Figure 6.1: GC chromatogram of the commercial isomer mixture.

Compound	Percentage
1,3-DIPN	15.87
1,7-DIPN	17.87
2,3-DIPN	1.40
2,6-DIPN	17.59
2,7-DIPN	14.44
1,6-DIPN	14.29
1,4-DIPN	12.86
1,5-DIPN	5.68

Table 6.1: Isomer distribution in the commercial mixture, based on GC analysis.

6.2. Distillation

Boiling points of the 8 main DIPN isomers are available in the literature [1] and are presented in Table 6.2.

Compound	Boiling point
1,3-DIPN	309
1,7-DIPN	309
1,5-DIPN	311
1,4-DIPN	315
2,7-DIPN	317
1,6-DIPN	318
2,3-DIPN	318
2,6-DIPN	319

Table 6.2: Boiling points of the most abundant DIPNs in °C at atmospheric pressure.

Regarding the low difference between them, separation through distillation seems to be difficult. Good results in isomer separation are however achieved in Gas Chromatography, suggesting that it may still be relevant. Moreover, chromatograms display different groups of isomers and even if a full separation of the 10 isomers seems ambitious, it sounds reasonable to aim for at least several fractions considerably enriched in one or several isomers.

As thermal cracking of hydrocarbons becomes serious at about 300°C, vacuum distillation was applied. The main drawback of that approach lays in the fact that temperature differences between isomers are reduced along boiling points, which makes the separation even harder. To compensate for that effect a 50 cm long Vigreux column with a high amount of theoretical trays was chosen. Even after several attempts, it turned out impossible to purify any isomer or even to generate a substantial enrichment of one fraction, as can be seen in Figure 6.2.

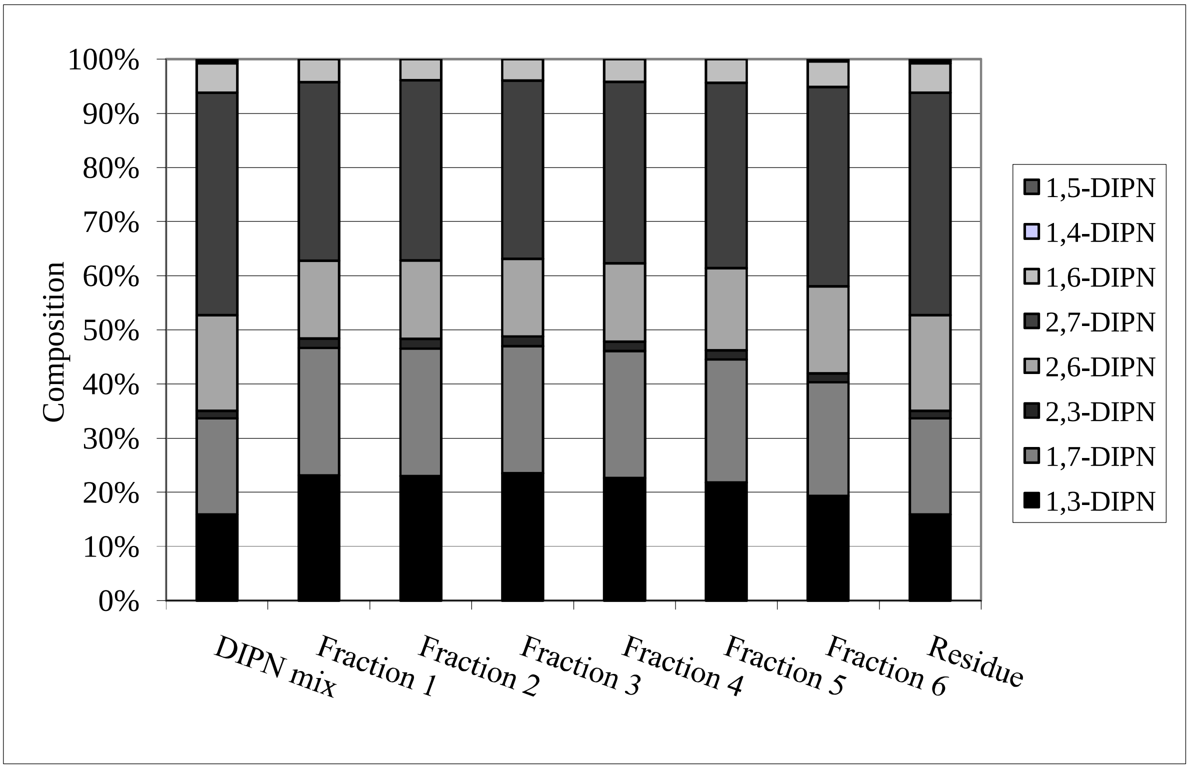


Figure 6.2: Composition of the different distillation fractions.

No isomer purification or substantial enrichment could be obtained in any fraction. Even though separation was achieved with GC, the properties of the columns are probably more important than the boiling point of each isomer and therefore the separation is far less effective in distillation. Moreover, the presence of several azeotropes may be a good explanation for the difficulty of this separation. This might be supported by an American patent [2]. According to it, dimethylnaphthalenes form binary eutectic and are very difficult to separate by distillation as well, but no clear mention of azeotropes is made.

These results lead to the conclusion that on a lab scale, at temperatures deliberately kept below 250°C, distillation is not an option to separate DIPNs.

It is still noteworthy to see that Brzozowski *et al.* analytically described DIPNs after purifying them partially through distillation at normal pressure [3] and that a patent on a process for production of 2,6-DIPN describes reduced pressure distillation to remove some of the DIPN from the mixture [1]. However, even if it appears that the technique exposed in the patent can remove efficiently 1,3- and 1,7-DIPN, the mass balance is not given and it is therefore impossible to know how much of the mixture had to be distilled before reaching that enrichment.

As the general idea of this thesis is about sustainability, waste reduction, and energy cost reduction, this option was simply not considered as applicable.

6.3. Crystallisation

Interestingly, differences in melting points are much more striking than differences between boiling points, even if this physical property is less described in the literature [3-5], as presented in Table 6.3.

Compound	Melting point
1,3-DIPN	46.2
1,4-DIPN	Liquid.
1,5-DIPN	104.6-105.6
1,6-DIPN	N.A.
1,7-DIPN	N.A.
1,8-DIPN	42.5-43.5
2,3-DIPN	N.A.
2,6-DIPN	68.5
2,7-DIPN	-3.0

Table 6.3: Melting points of the most abundant DIPNs in °C at atmospheric pressure.

6.3.1. Introduction on crystallisation

Tian *et al.* [4] published very recently a very interesting study on purification of 2,6-DIPN out of the 2,6-DIPN / 2,7-DIPN binary mixture by static melt crystallisation. Their most interesting finding is that separation is possible up to 97.9% pure 2,6-DIPN. Better purification is not possible due to the formation of an eutectic, as presented in Figure 6.3. This result is among the best results obtained in terms of 2,6/2,7 ratio, but is still not good enough for the polymer industry where very high purity is needed.

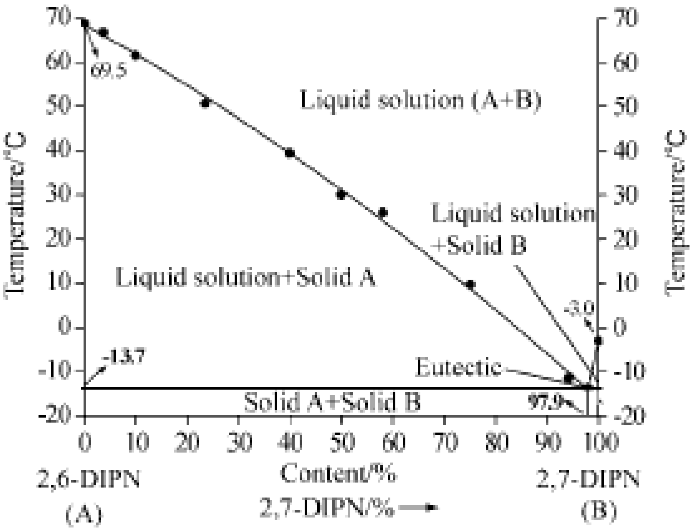


Figure 6.3: Phase diagram of the binary mixture as given in [4]

6.3.2. Binary mixture crystallisation

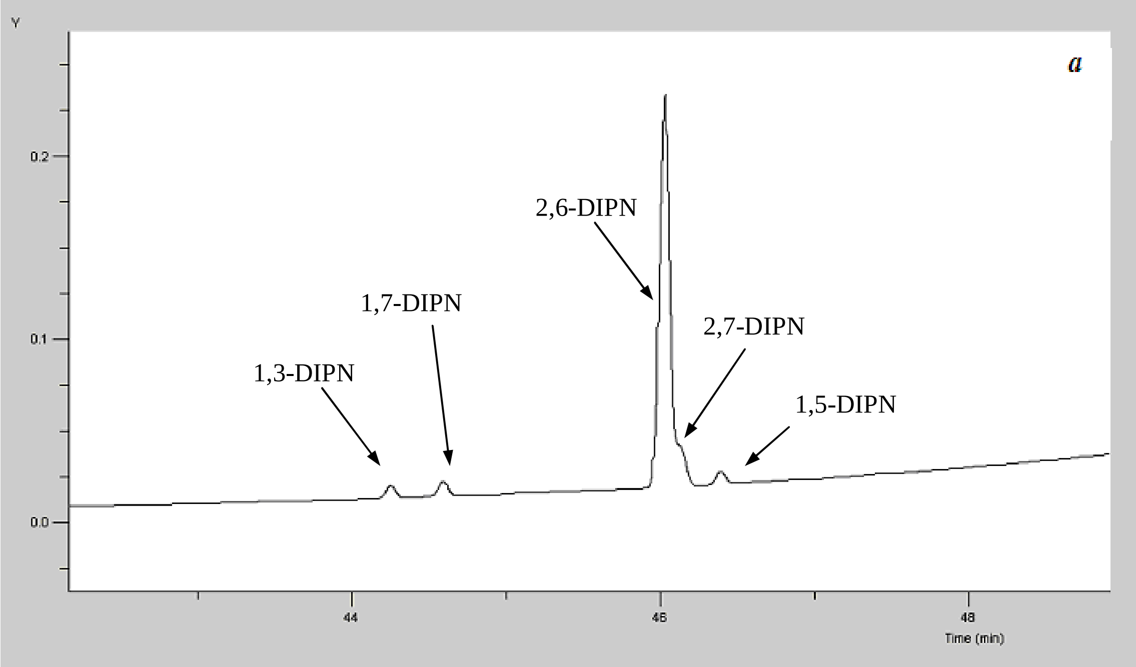
In order to confirm these results, a 1:1 mixture of both isomers was crystallised by placing it in a freezer at -21°C overnight. A rough estimation by Gas Chromatography showed a purity above 88% in terms of 2,6-DIPN. When the obtained crystals were washed with cyclohexane, purity above 96% was achieved.

These experiments clearly show that results are in line with those described in the literature [4] in a more sophisticated way. Crystallization might be a good technique for DIPNs separation. No extra effort was put into optimising this crystallisation as the real goal is to purify 2,6-DIPN from a reaction mixture where other isomers are present rather than optimising the yield of crystallisation of the binary mixture.

6.3.3. Isomer mixture crystallisation

When cooling the commercial isomer mixture (Figure 6.1) for several days at -21°C, it is possible to crystallise 2,6-DIPN with up to 70% purity. As can be seen in

Figure 6.4 (a), crystals obtained through direct crystallisation mainly contain 2,6-DIPN, and about 5% of 1,3-DIPN, 5% of 1,7-DIPN, 12% of 2,7-DIPN and 8 % of 1,5-DIPN. If methanol recrystallisation is then applied on these crystals, an even better purity can be achieved as can be seen in Figure 6.4 (b). Very interestingly the main impurity is then 1,5-DIPN, and not 2,7-DIPN, which might be present in trace amounts only. 2,6-DIPN purity can be raised up to 95% after recrystallisation.



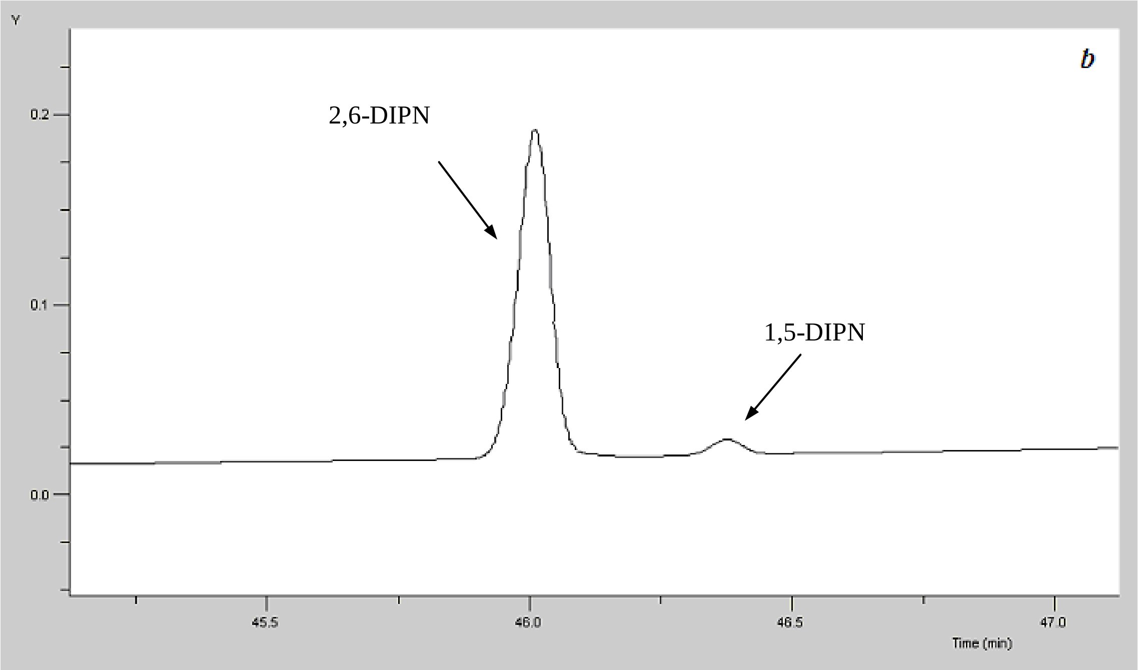
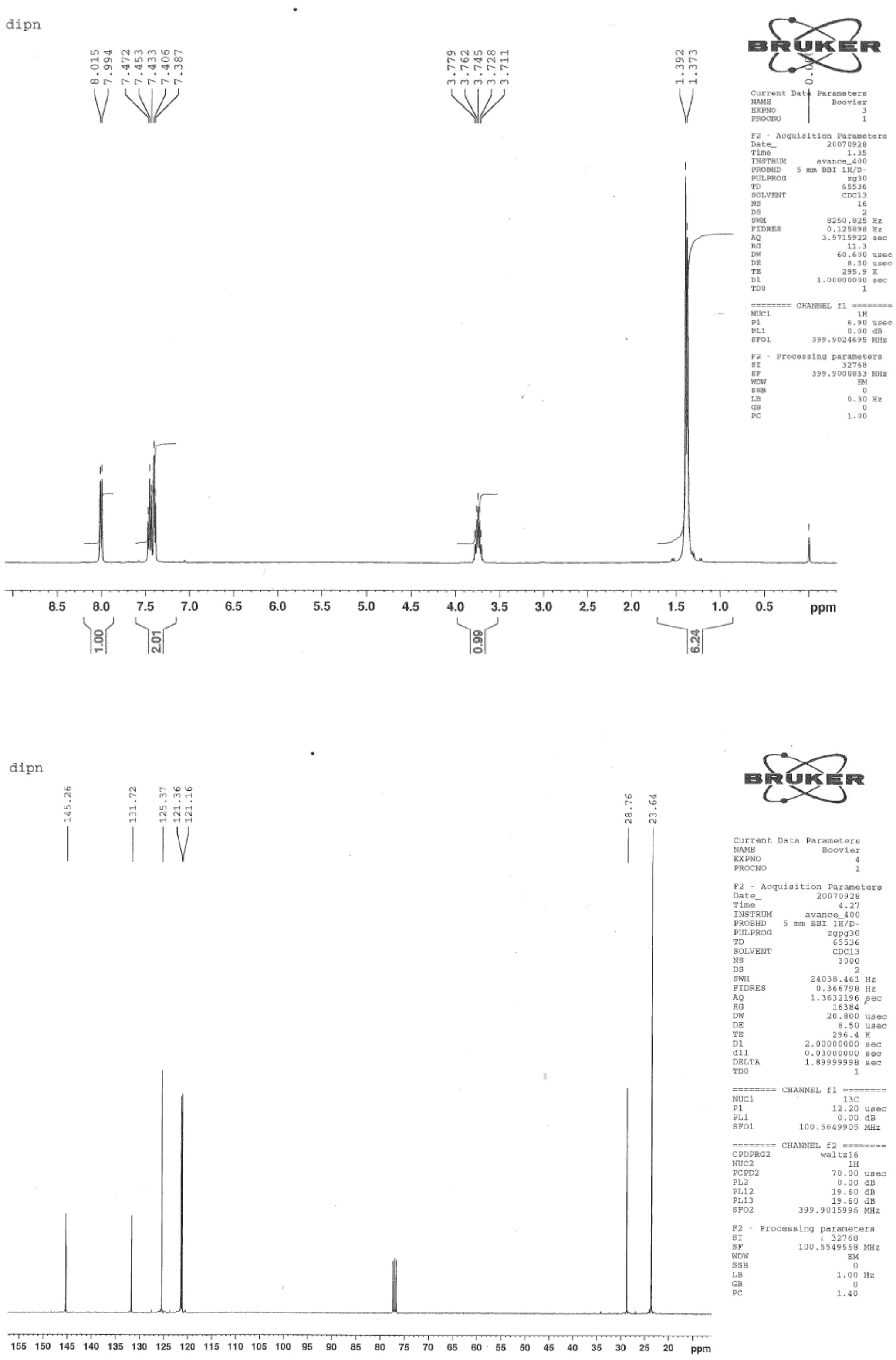


Figure 6.5: Crystals obtained from the isomer mixture (a) and after methanol recrystallisation (b)

Separation of 2,6-DIPN from 2,7-DIPN is difficult in general. Direct crystallisation of a DIPN mixture followed by methanol recrystallisation seems to be a very good solution for the production of 2,6-DIPN with high purity. The main impurity being a less abundant and less similar isomer and not 2,7-DIPN anymore, it can be hoped that purity close to 100% can be achieved. As reported in Chapter 2, 2,6-DIPN and 1,5-DIPN have much more differences in terms of kinetic diameters than 2,6-DIPN and 2,7-DIPN. It seems therefore possible to achieve a better purity by applying specific shape-selective adsorption on zeolites to further purify the isomer mixture in order to match standards for the polymer industry.

In an explorative experiment, it was possible to crystallise the high melting isomer 1,5-DIPN out of the mother liquor, as characterised by ^{1}H-NMR and ^{13}C-NMR (Figure 6.5), indicating that very pure 2,6-DIPN could be obtained after the whole crystallisation process. These spectra are in agreement with the chemical shifts reported by Brzozowski *et al.* [3]



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FIDRES            0.125898 Hz
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TE                   295.9 K
D1              1.00000000 sec
TD0                      1

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P1                    6.90 usec
PL1                   0.00 dB
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Figure 6.5: ^{1}H-NMR and ^{13}C-NMR of 1,5-DIPN obtained by crystallisation

Moreover, 2,6-DIPN purity might be increased even more by applying a different temperature (where 1,5-DIPN may not crystallise) or by adding a final separation over zeolitic membranes with a very precise pore size.

6.4. Conclusions

Distillation of the DIPN mixture does not seem to be interesting under reduced pressure and at relatively low temperatures. Crystallisation on the other hand seems to be very promising. Direct crystallisation from the isomer mixture yields 70% pure 2,6-DIPN and if followed by a methanol recrystallisation, up to 95%.

As a prelude to Chapter 7, these findings open a new road towards 2,6-DIPN production in a fully continuous process. Considering both the results presented in Chapter 3 and this chapter, it seems that production could be maximised by tuning the process conditions to work under the most favourable thermodynamic equilibrium with recycle of the light and heavy fractions and to perform purification by crystallisation followed by methanol recrystallisation. Besides these purely chemical aspects, it is also very interesting to obtain better results with crystallisation, as the energy consumption to operate it will be much lower than what would have been needed for distillation. This further improves the sustainability of the process, as high energy consumption is linked to unsustainable processes.

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7

The development of a sustainable process to dimethyl naphthalene-2,6-dicarboxylate.

Abstract

An industrial process for the production of dimethyl naphthalene-2,6-dicarboxylate over the ZG (50) as Best Available Technique (BAT) is presented and compared with the Amoco process using *ortho*-xylene as feedstock. Block diagram as well as stream flows related to a 45 000 tons per year scale, as a presumed base case, are given. Finally a cost study is presented for different production capacities and yields. Despite a small improvement in terms of sustainability, economic perspectives are not ideal with the yields obtained so far.

7.1. Introduction

PolyEthylene Naphthalate (PEN) is a relatively new polyester from 2,6-dimethylnaphthalene dicarboxylate (NDC) and ethylene glycol. It has the potential to fill the gap between PolyEthylene Terephtalate (PET) and higher performance materials such as polyphenylenesulfides and polyimides. This market potential results from PEN's superior mechanical, thermal and chemical resistance and barrier properties relative to PET. PEN has current application in magnetic recording tapes and in electronic and specialty films. Other potential applications include use in industrial fibres and in packaging resins for flexible and rigid containers.

The major factor hindering the large-scale PEN market potential is the cost of the polymer. The only current PEN application with a market price is film. PEN film is currently sold for about $20/lb compared to $1.35-3.25/lb for PET film. PEN's high cost comes from the high cost of its precursor, NDC, which was sold for $5.50/lb (equivalent to $12.10/kg) in 1993. It is anticipated that a selling price of 5.5 €/kg would allow industrial production of PEN now.

Several routes towards NDC have been investigated, such as acetylation of 2-methylnaphthalene followed by oxidation and esterification and naphthalene isopropylation followed as well by oxidation and esterification. Direct oxidation and esterification of 2,6-dimethylnaphthalene has also been developed.

This chapter will focus only on the route developed within this thesis, isopropylation of naphthalene towards 2,6-DIPN, followed by oxidation and esterification. The existing Kureha process for a DIPN mixture [1] and the SRI cost estimate for the Amoco process for NDC from *ortho*-xylene [2] were used as bases for this work.

7.2. Technical review

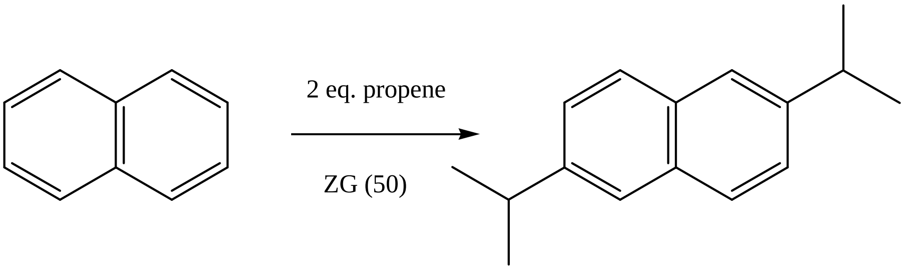
The importance of monomer purity for PEN application has several aspects. First, monofunctional impurities should be avoided as they would limit chain growth in polymerisation. Second, other monomers than the 2,6-isomer would modify the polymer orientation and therefore its physical properties. Small impurities may also have an impact on the ease of the process, the colour, the thermal and photochemical stability of the polymer and its long-term durability. Therefore the monomer purity aimed is greater than 99.5wt%. Moreover monofunctional impurity contents should be lower than 0.1% in order to allow chain lengths above 1000 units.

Similarly to the history of PET synthesis, PEN is produced through NDC because it is still difficult to produce it directly from 2,6-naphthalenedicarboxylic acid (NDA) in a high purity at reasonable prices.

A potential NDC production based on the results of this thesis and the SRI report [2] for the process developed by Amoco could be described in 8 steps, namely diisopropylation, distillation, crystallisation, recrystallisation, oxidation, purification, esterification and purification. Another alternative to produce NDA would be to apply a process similar to toluene oxidation towards benzoic acid. This would avoid the need of acetic acid as a solvent. The process would then be diisopropylation, distillation, crystallisation, recrystallisation, oxidation, crystallisation, esterification and purification.
This would allow sticking as much as possible to an existing technology and will allow keeping process cost realistic.

Diisopropylation

Results from this thesis (Chapters 3 and 4) showed that at 150°C about 17% of 2,6-DIPN could be formed over H-USY zeolites and about 20% over the ZG (50) at 225°C. Furthermore, for both catalysts, mono- and over-alkylated products can be recycled to undergo disproportionation, while the other DIPN isomers can undergo isomerisation. The amount of valuable products than could be recycled goes up to 75% for both catalysts, corresponding to a yield loss of 5% and 20% of desired product.



Distillation

Distillation allows recycling naphthalene and IPNs as light fraction. The heavy fraction contains PIPNs along with impurities such as unsaturated products and probably binaphthalenics. Even if over these two catalysts PIPNs are dominating, no information on their ease of recovery is available. The process applied by Kureha [1] combines 3 distillations in order to also recycle PIPNs. In order to recover as much side-products as possible the last distillation cannot be removed. However distillation at high temperature generates heavy side-products. In this study they have been considered to be mostly unsaturated products described by Moreau [3-4]. Their formation requires some PIPNs to lose an isopropyl group and this has been accounted by the generation of DIPNs in the last heavy product distillation tower to keep the mass balance consistent.

Crystallisation

Crystallisation from the commercial mixture allows enriching the isomer mixture from 16% (close to the experimental amount even if the distribution is more kinetic than thermodynamic) to 70%, as described in Chapter 6. It is still important to note that crystallisation studies were only performed at one temperature and that there is room for improvement.

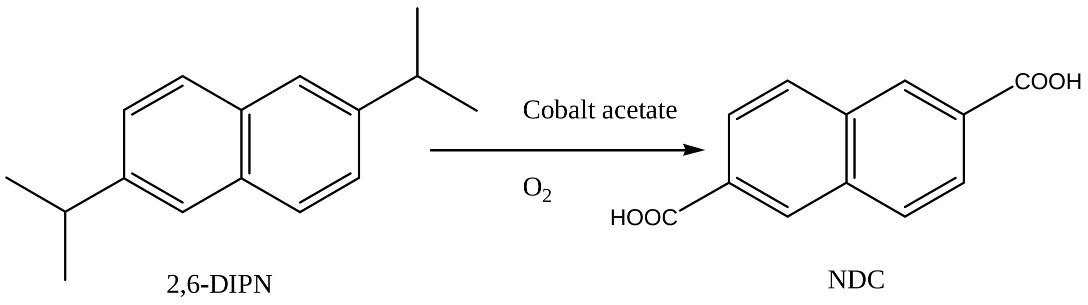
Recrystallisation

Recrystallisation with methanol allows further enriching the isomer mixture from 70% 2,6-DIPN to 95%, as described in Chapter 6. The impurities left are 5% of 1,5-DIPN and trace amounts of 2,7-DIPN. Even if not described in detail in this thesis, crystallisation of very pure 1,5-DIPN from this mixture was achieved suggesting that crystallisation could theoretically yield practically pure 2,6-DIPN. No further purification is then needed. Alternatively, further separation may be achieved by specific adsorption or separation by size exclusion on a zeolite. Dealuminated Mordenite may be a good candidate for this separation

Oxidation

In order to prepare polymer grade NDC, the 2,6-DIPN feed should be at least 99 wt % pure. Oxidation can be derived from the Amoco Mid-Century process originally developed for the oxidation of *p*-xylene to terephthalic acid. The reaction occurs in the liquid phase with acetic acid as solvent over a catalyst containing cobalt, manganese and bromine. Manganese and bromine allow oxidising the deactivated second methyl group. Temperature varies between 193°C and 213°C. The use of acetic acid is related to the solubility of terephthalic acid and allows heat removal through reflux.

As solubility issues seem not to apply to the 2,6-DIPN/NDA system and as the second isopropyl group is on a different aromatic ring, oxidation inspired by the DSM toluene oxidation process [5] seems more interesting. There, the reaction occurs in the liquid phase without solvent over a simple cobalt catalyst. Temperature has to be kept around 150°C to allow high selectivity. The only drawback of this option is that the boiling point of the reaction mixture is too high to allow heat removal by reflux, as in the classical toluene oxidation. Adding an active cooling coil in the reactor can circumvent this. Still the advantage of saving an expensive acetic acid recovery system is maintained and bromine can be avoided as no electronic deactivation is foreseen because of the 2 aromatic rings, therefore preserving a more sustainable process. The reaction is driven towards the maximum solubility of NDA to ease crystallisation in the next step.

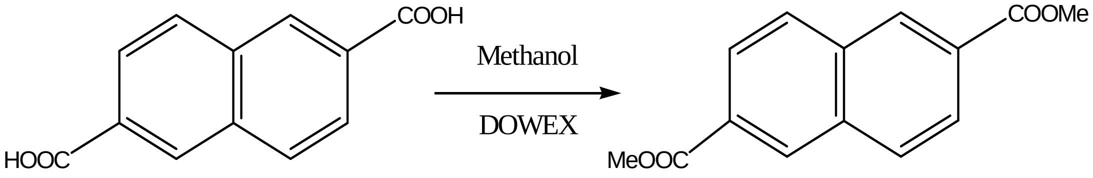


Purification

NDA is separated from the acetic mother liquor by mean of centrifugation or filtration when the Amoco process is applied. If the process for toluene oxidation is applied, crystallisation of NDA from the NDA/2,6-DIPN mixture can be performed.

Esterification

So far, polymerisation from NDA is not possible and an esterification is needed as good solubility and proper mixing are not achieved with the acid. This results in shorter chain lengths which is clearly seen as a disadvantage by the polymer industry. Esterification from NDA to NDC is described in an Amoco patent. It occurs with addition of methanol with sulphuric acid as catalyst at 120°C. Methanol is used in excess as it is also the reaction solvent. Distillation of the methanol/water system allows to exceed equilibrium conversion and to achieve a 100% yield. It seems more interesting to perform it over a DOWEX resin (polystyrene sulfonic acid).



Purification

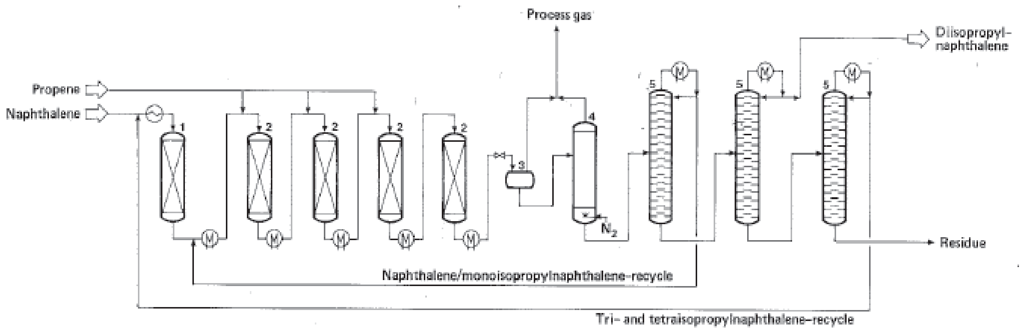
Crude NDC is recovered by centrifugation and may be purified further by recrystallisation in methanol followed by fractional distillation. The methanol is separated from water by distillation and recycled to the esterification reactor.

7.3. Process description

A process for making NDC from naphthalene and isopropanol can be described by combining results presented in this thesis and adapting the toluene oxidation process and the Amoco esterification process. The base case chosen for the economic analysis is 100 million lb/yr (45 000 t/yr) of crude NDA which roughly corresponds to an NDC plant capacity of 96 million lb/yr (43 000 t/yr). The very reason for this choice is that it allows using figures from the SRI report directly, whereas 10 kt/y is desirable for a new product and 100 kt/y for a mature one.

A block process flow diagram of a possible 45 kt/y process is shown in Figure 7.1 and corresponding stream flows are presented in Table 7.1.

Production of the 2,6-DIPN is proposed according to the Kureha process [1] presented in Figure 7.2.



1 Transalkylation reactor; 2 Propylation reactor; 3 Pressure let-down vessel; 4 Strip column; 5 Vacuum-distillation columns

Figure 7.2: Flow diagram of the Kureha process

Isopropylation takes place over ZG (50) in a trickle-bed flow reactor in order to tune propylene feed. This should allow reducing C_3 oligomerisation and therefore improve the C_3 balance to 90% instead of 70%.

There are however two main differences with the isopropylation presented in this thesis.

- First, propene and water will be used instead of isopropanol in order to reduce feedstock costs. Chemically speaking, isopropanol is transformed into propene or an isopropyl cation so no differences in reactivity should be expected. This furthermore allows controlling the amount of water added. Schmitz and Song [6] showed that addition of water was improving the β selectivity. This factor was not investigated in this thesis as the amount of water was related to the amount of isopropanol but as discussed in Chapter 3, evidences that the reaction occurs through propene as an intermediate are present and moreover the use of propene as feedstock has been largely described by other groups.
- Second, the Kureha process is designed to yield a DIPN mixture for solvating dyes in carbonless copy paper. To obtain a liquid mixture several isomers need to be present. A process towards 2,6-DIPN does not need such a variety of DIPNs present.

Oxidation follows the toluene oxidation process. While in the original process, toluene is distillated and recycled to remove the large reaction heat, the process proposed in Figure 7.1 needs an additional cooling source.

The final part of the process consists of the Amoco process designed for this reaction. Catalysis is however proposed over a DOWEX resin (polystyrene sulfonic acid) rather than with sulfuric acid in order to avoid its neutralisation and replacement, therefore consisting of a first important improvement with respect to sustainability.

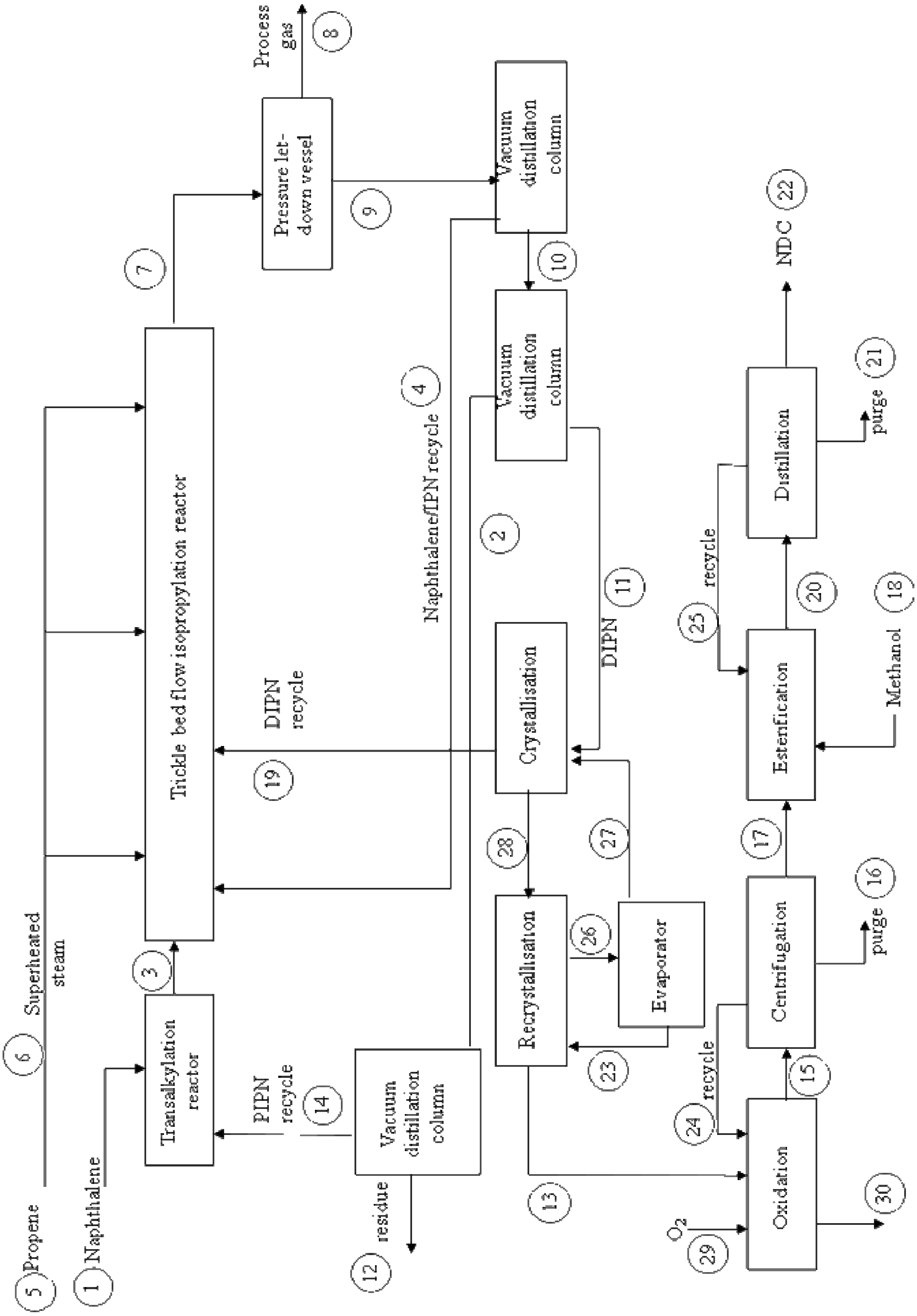


Figure 7.1: Block process flow diagram

Products	**Stream flows kmol/h**									
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
naphthalene	32,4	-	11,7	8,7	-	-	8,7	-	8,7	-
PIPN	-	12,2	-	-	-	-	12,2	-	12,2	12,2
others	-	6,6	-	-	-	-	6,6	-	6,6	6,6
IPN	-	-	31,7	37,2	-	-	37,2	-	37,2	-
DIPN*	-	-	-	-	-	-	32,6	-	32,6	32,6
2,6-DIPN	-	-	-	-	-	-	24,5	-	24,5	24,5
propene	-	-	-	-	101,9	-	21,4	21,4	-	-
water	-	-	-	-	-	101,9	101,9	101,9	-	-
methanol	-	-	-	-	-	-	-	-	-	-
NDA	-	-	-	-	-	-	-	-	-	-
NDC	-	-	-	-	-	-	-	-	-	-
O2	-	-	-	-	-	-	-	-	-	-
CO2	-	-	-	-	-	-	-	-	-	-
N2	-	-	-	-	-	-	-	-	-	-

Products	**Stream flows kmol/h**									
	11	**19**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**20**
naphthalene	-	-	-	-	-	-	-	-	-	-
PIPN	-	-	-	-	9,7	-	-	-	-	-
others	-	-	7,9	-	-	1,5	1,5	-	-	-
IPN	-	-	-	-	-	-	-	-	-	-
DIPN*	32,6	32,6	-	-	1,2	-	-	-	-	-
2,6-DIPN	24,5	-	-	24,5	-	17,2	-	-	-	-
propene	-	-	-	-	-	-	-	-	-	-
water	-	-	-	-	-	-	-	-	-	46,1
methanol	-	-	-	-	-	-	-	-	46,1	-
NDA	-	-	-	-	-	23,0	-	23,0	-	-
NDC	-	-	-	-	-	-	-	-	-	23,0
O2	-	-	-	-	-	-	-	-	-	-
CO2	-	-	-	-	-	-	-	-	-	-
N2	-	-	-	-	-	-	-	-	-	-

Products	**Stream flows kmol/h**									
	21	**22**	**23**	**24**	**25**	**26**	**27**	**28**	**29**	**30**
naphthalene	-	-	-	-	-	-	-	-	-	-
PIPN	-	-	-	-	-	-	-	-	-	-
others	-	-	-	-	-	-	-	-	-	-
IPN	-	-	-	-	-	-	-	-	-	-
DIPN*	-	-	-	-	-	10,5	-	10,5	-	-
2,6-DIPN	-	-	-	17,2	-	-	24,5	24,5	-	-
propene	-	-	-	-	-	-	-	-	-	-
water	46,1	-	-	-	-	-	-	-	-	147,0
methanol	-	-	245,0	-	245,0	245,0	-	-	-	-
NDA	-	-	-	-	-	-	-	-	-	-
NDC	-	23,0	-	-	-	-	-	-	-	-
O2	-	-	-	-	-	-	-	-	231,6	11,0
CO2	-	-	-	-	-	-	-	-	-	98,0
N2	-	-	-	-	-	-	-	-	926,3	926,3

DIPN*: all DIPNs except 2,6-DIPN

Table 7.1: Stream flows as displayed in Figure 7.1

Composition in stream 7 reflects experimental data obtained in the isopropylation of naphthalene over the ZG (50) at 225°C, as described in Chapter 5. Crystallisation and recrystallisation are represented in agreement with the data presented in Chapter 6.

Side-products obtained in the alkylation of naphthalene are estimated to be similar to products described by Moreau *et al.* [3-4] and are formally seen as tetraisopropylnaphthalenes. Side-products in the oxidation are postulated to be obtained by ring opening and to be position isomers of NDA and are therefore contributed with the same molecular weight than NDA.

Oxidation is meant to be achieved with air as a source of oxygen. While this is completely free, it requires an off gas treatment and a bigger volume.

The overall yield is ~ 70% based on naphthalene and propene and ~ 100% based on methanol. If the reaction is run at conditions allowing minimising the formation of PIPNs, high yield about 90% with respect to naphthalene and propene can be expected. If the purification of PIPNs from heavy side-products appears to be harder than expected, overall yield can be estimated to be as low as 60%. These three cases are therefore described later in the cost study.

The overall 30 % yield loss to carbon leads to the production of approximately 2 tons CO_2 per ton NDC and the energy recovery corresponding to that. For the Amoco process, this is 3 tons CO_2 per ton NDC. Both processes do not generate any serious amounts of other waste.

7.4. Product cost estimate

As the aim is here to obtain a rough estimate on the economic interest of such a process, production costs are presented in a slightly simpler way than in the original SRI document.

It is approximated that fixed costs including manpower, energy, maintenance, taxes, account for 20% of the investment over the capacity.

Addition of fixed costs and variable costs obtained through the feedstock need provide the “out of pocket” price.

Results obtained in the base case (70% yield based on naphthalene and propene) for three different capacities are presented in Table 7.2.

Feedstock price was determined from ISIS Chemical Business contract prices. Methanol was estimated at 295 €/t, propene at 927 €/t and refined naphthalene at 700 €/t (price in 2006). One should however keep in mind that prices are highly flexible as raw materials, energy cost and conversion rate between Euro and Dollar are fluctuating a lot as well.

The process proposed here has one operating unit less than the process developed by Amoco and comparison in terms of investment is therefore quite plausible. Apart from that, avoiding acetic acid and sulfuric acid in the oxidation and esterification may allow to using SS 304 instead of the more expensive 316 SS and further reduce the investment cost.

Economics for the whole process over exploitation time are displayed in Figures 7.2, 7.3 and 7.4 for yields based on naphthalene and propene at 60%, 70% and 90% respectively. In each case, the 3 capacities tested are displayed. Economics for the Amoco process is presented in Table 7.3 with updated feedstock prices.

Capacity (kt/y)		**10**	**45**	**100**
Investment (M€)		**71**	**191**	**324**
Variable cost:				
Naphthalene (€/t) Yield (%)	700 70	1000	1000	1000
Propene (€/t) Yield (%)	927 70	2649	2649	2649
Methanol (€/t) Yield (%)	295 100	590	590	590
Fixed cost 20% of Investment/capacity (€/t)		1418	850	648
Out of pocket price (€/t)		**5656**	**5089**	**4887**

Table 7.2: Production cost for the base case for different production capacities.

Capacity (kt/y)		**10**	**43**	**100**
Investment (M€)		**77**	**203**	**354**
Variable cost:				
o-xylene (€/t) Yield (%)	840 55	1527	1527	1527
butadiene (€/t) Yield (%)	1100 55	2000	2000	2000
Methanol (€/t) Yield (%)	295 100	590	590	590
Fixed cost 20% of Investment/capacity (€/t)		1547	944	707
Out of pocket price (€/t)		**5664**	**5061**	**4824**

Table 7.3: Production cost for the Amoco process for different production capacities.

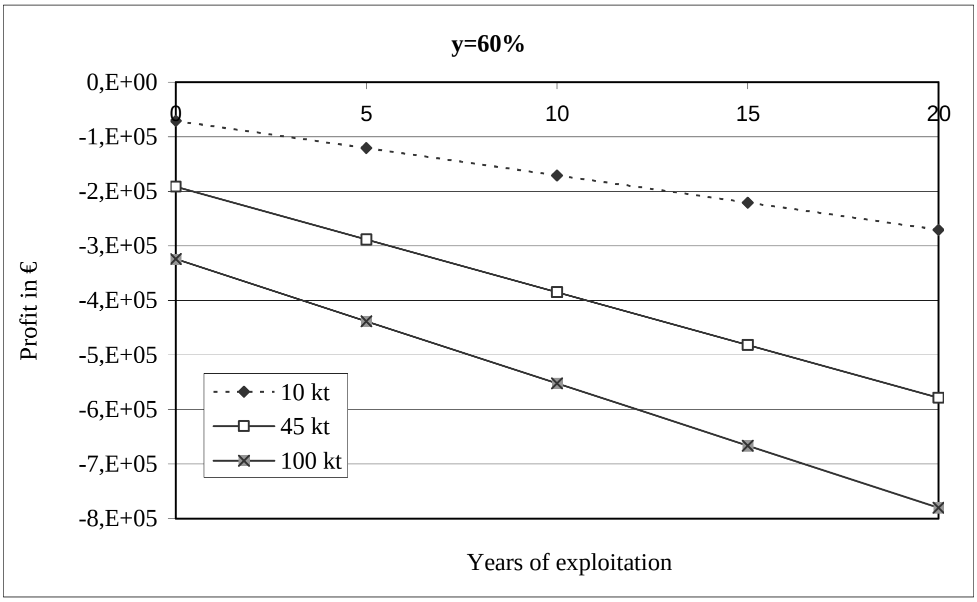


Figure 7.2: Profit over exploitation time with 60% yield for naphthalene and propene for a given capacity.

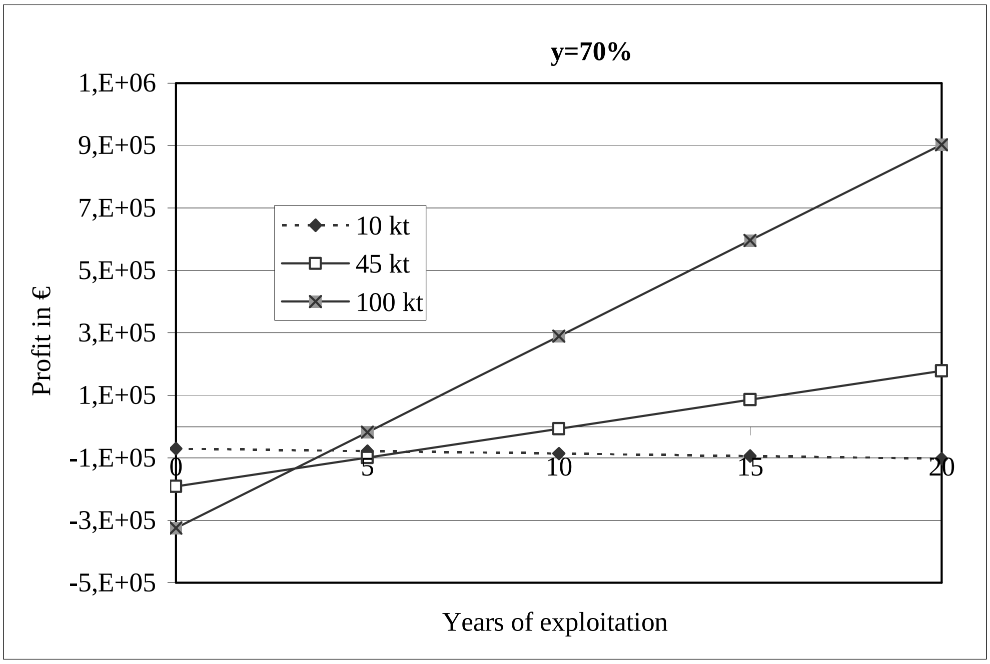


Figure 7.3: Profit over exploitation time with 70% yield for naphthalene and propene for a given capacity.

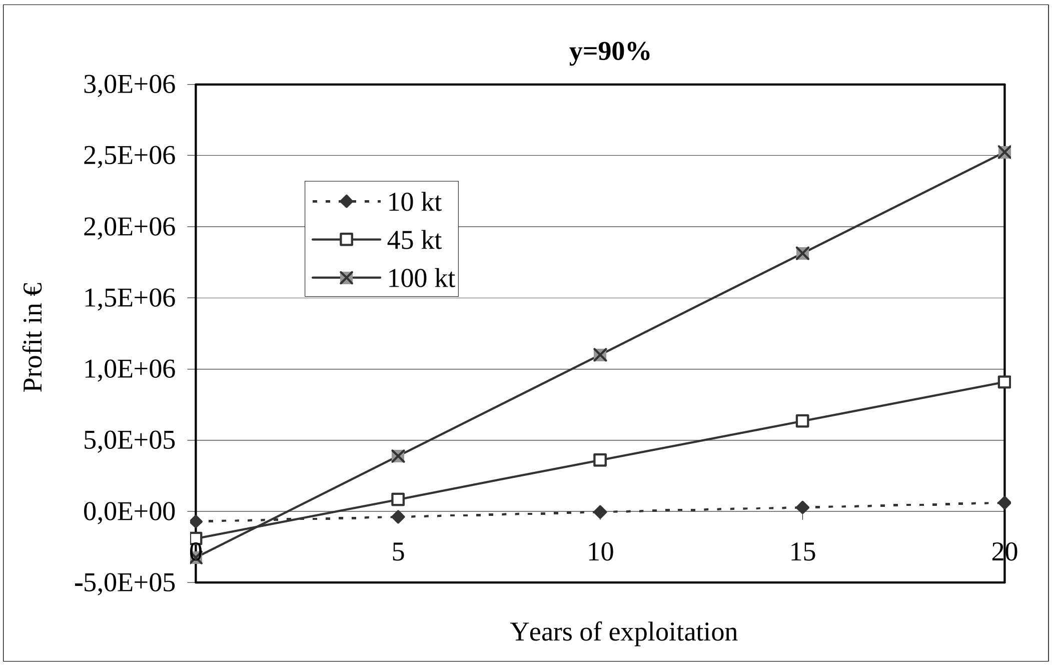


Figure 7.4: Profit over exploitation time with 90% yield for naphthalene and propene for a given capacity.

Figures 7.2, 7.3 and 7.4 show interesting results. Profits in euros were determined by using Equation 7.1.

$$\text{Profit}=\left(5500\text{ - out of pocket price}\right)\text{x year-investment} \qquad (7.1)$$

Though it would be desirable to introduce a new plant with the smallest capacity possible, it turns out that it is neither possible for the process presented here nor for the Amoco process: the out of pocket price in both cases is slightly above the desired selling price of 5.5 €/kg. On the other hand, the profitability increase above 45 kt/y, the base case, is rather small. Both processes on all scales behave very similarly. At the lowest yield of 60 %, the process presented here is never attractive. As presented in Figure 7.5, in the base case, the profitability, though positive, is still not sufficient at 4.1%. At high yields, the profitability reaches 12% approaching the minimum Return On Investment

(ROI). Furthermore it is clear that moving to 100 kt/y is not particularly attractive because of the minor increase of 2% only of the ROI.

As propene cost represents about half of the production cost, one should aim to reach the 90% conversion for naphthalene and propene. If this does not seem to be a problem regarding to naphthalene, it clearly stresses the fact that propene feed has to be optimised as much as possible in order to avoid C_3 oligomerisation. Though not realised experimentally in this thesis, this seems quite realistic, as the Kureha process already distributes the propene feed over several reactors.

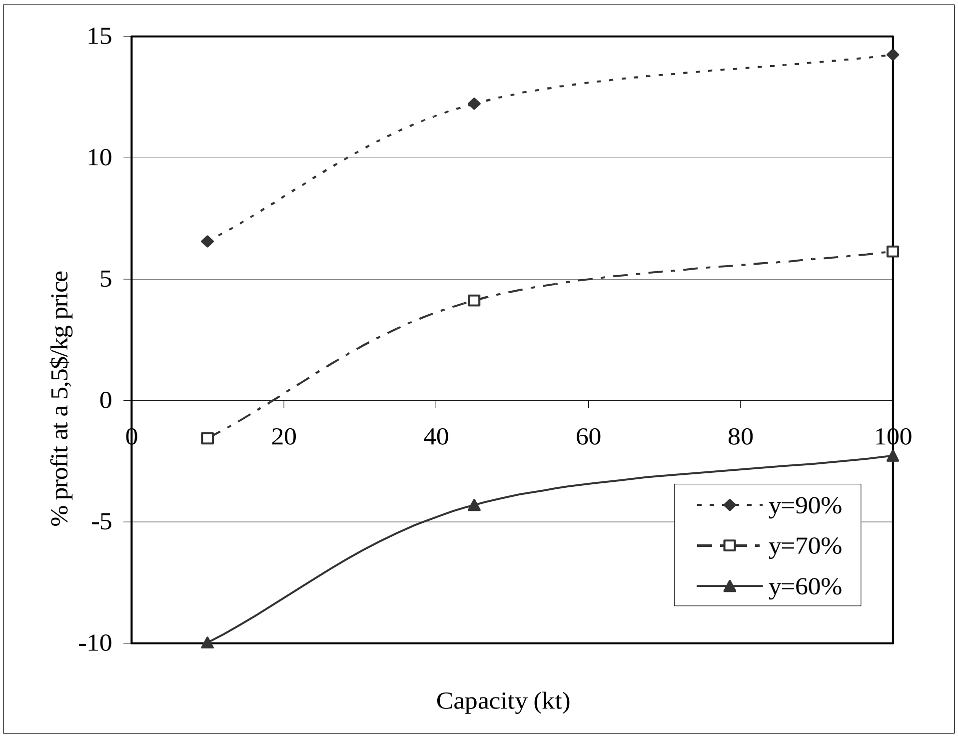


Figure 7.5: Profit percentage generated for a sell price of 5.5 €/kg as a function of production capacity.

Calculations in this work are based on the results obtained over the ZG (50), but transposition to a process using H-USY is possible. However, in the case of H-USY, the slightly lower selectivity towards 2,6-DIPN (3%) and the higher amount of undesired side-products (1%) may induce a higher investment cost of approximately 4%. The level of accuracy of this type of estimate is, anyway, not better than +/- 25% so no attempt has been undertaken to take it into it account. At the present level of accuracy, the ZG (50) and H-USY should be considered as BAT at the research scale.

Though plausible, the 90% yield maximum discussed before still equals only the best yield of 70% for the Amoco process. If yield of 90% can be obtained with a shape-selective catalyst, the investment left for the DIPN part of the process is 40%, resulting in overall investment amount of 60% for the whole process. In this case the Amoco process is completely outperformed. However, the profitability is increased to 15% only, which is still borderline with respect to economic feasibility.

7.5. Conclusions

The process proposed here has one operating unit less than the process developed by Amoco and comparison in terms of investment is therefore reliable. 15 years ago Amoco was targeting a selling price of 2 €/kg. However the costs of this process are now dominated by feedstock costs due to the tremendous increase in oil price over the last 15 years. In order to compete with PET production costs, a selling price about 5.5 €/kg should be aimed. The base case presented here allows about 4% profit, which is clearly not interesting. However, higher yields in principle can be achieved, mainly by feeding propene more properly. As indicated before, even the highest yield possible combined with a shape-selective catalyst (leading to the lowest investment cost) does not generate a clear economically attractive process, though in the latter case the Amoco process is clearly outperformed. The loss of 4 carbons out of 6 in the oxidation step is simply too much.

This process is, however, slightly more sustainable than the route from *ortho*-xylene. Yields are higher and a smaller number of different chemicals are needed.

7.6. Outlook

As it turns out that the higher yield and selectivity of the naphthalene/propene process is negatively compensated by the higher price of the propene and the low atom-efficiency, a possible way forward might be to use methanol as this feedstock has a much lower price and a much higher atom-efficiency. The challenge for catalysis is here to develop a really shape-selective catalyst as thermodynamics do not favour the formation of the 2,6-dimethylnaphthalene. Ethanol might be an alternative as the atom-efficiency is lower but both the thermodynamic preference for the formation of the 2,6-diethylnaphthalene and the selectivity in the oxidation towards NDA will be higher than with methanol.

The DIPN part of these processes only can approach the cost of the Kureha process and is expected to be more expensive. Their recycle amount is lower as the full DIPN mixture is sold while here only 2,6-DIPN is looked after. The only possibility to match this would be to (shape) selectively form 2,6-DIPN and no other DIPNs.

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Appendix: Molecular modelling

Chapter 2 presents in Table 2.2 values obtained for the molecular dimensions of the DIPN isomers. They were determined by working on the most stable conformer.

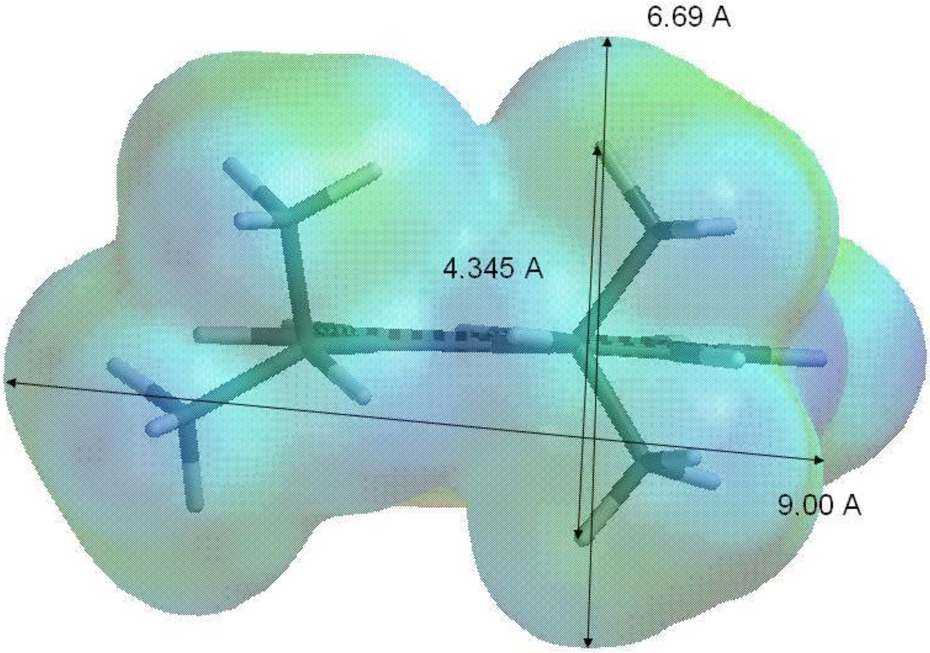
For each isomer, the two smallest dimensions were determined visually. The molecule was turned in order to have these 2 dimensions in the plane of the screen. Representation was made orthogonally in order to avoid projection errors. For each molecule, a computed distance was determined within the plane of the screen.

After printing, distances were measured and expressed back in Ångstroms by using the computed reference.

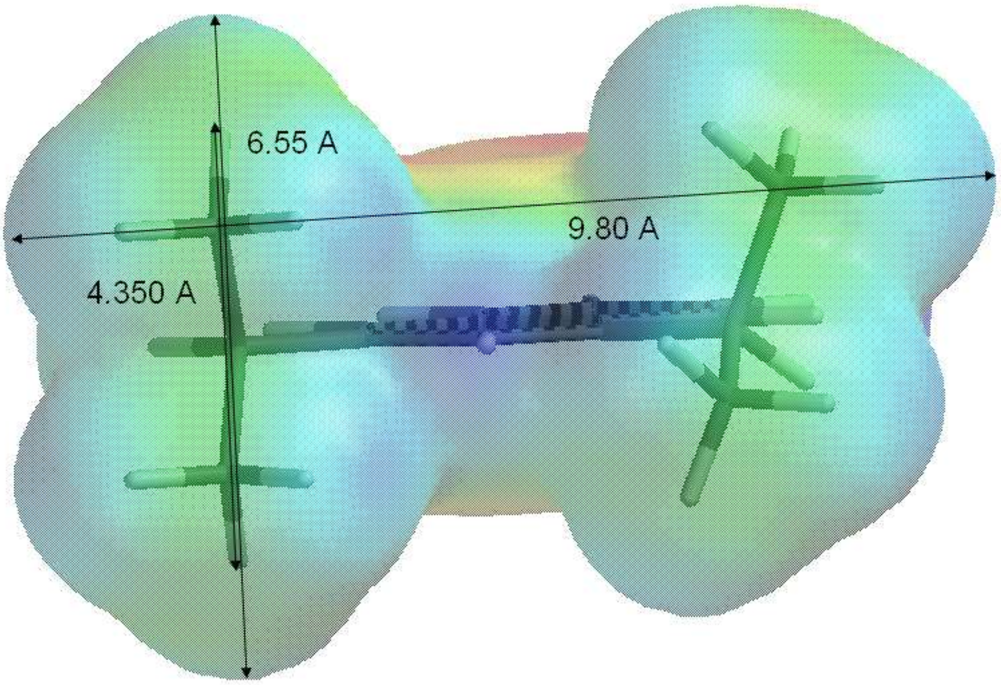
Planes for the smallest dimensions and the measured values are presented below.

In the only case of 1,6-DIPN, it was not possible to see both distances on one graph and therefore distances were determined thanks to 2 plots.

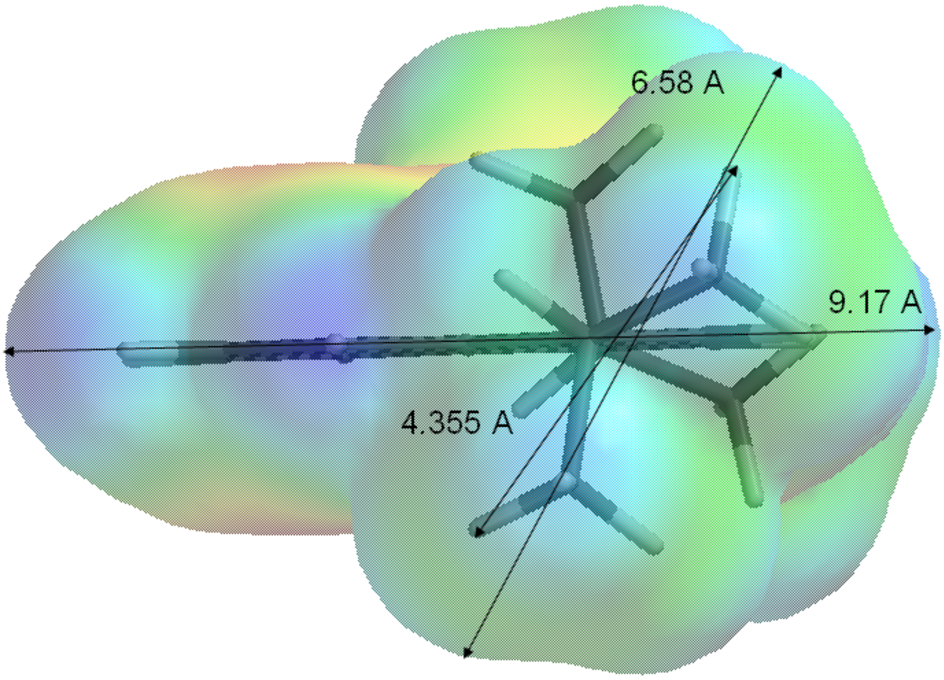
1,2-DIPN:



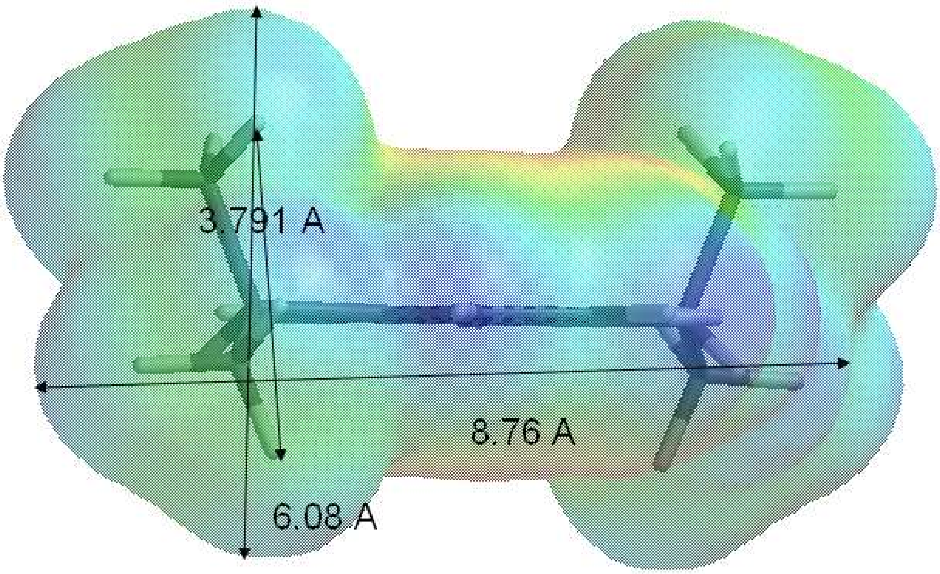
1,3-DIPN:



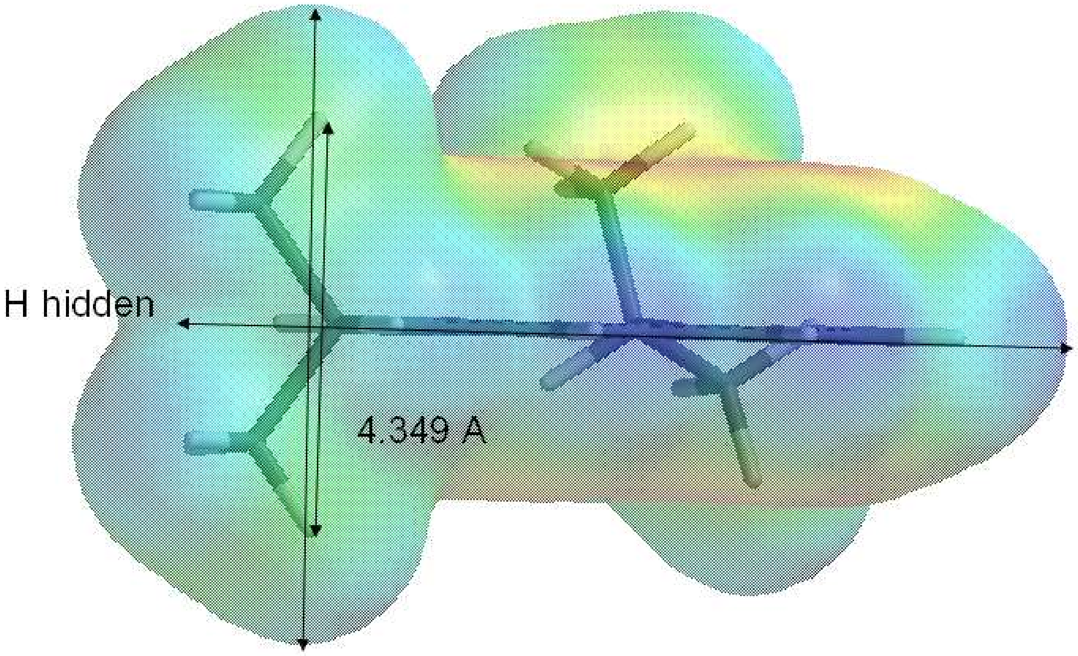
1,4-DIPN:

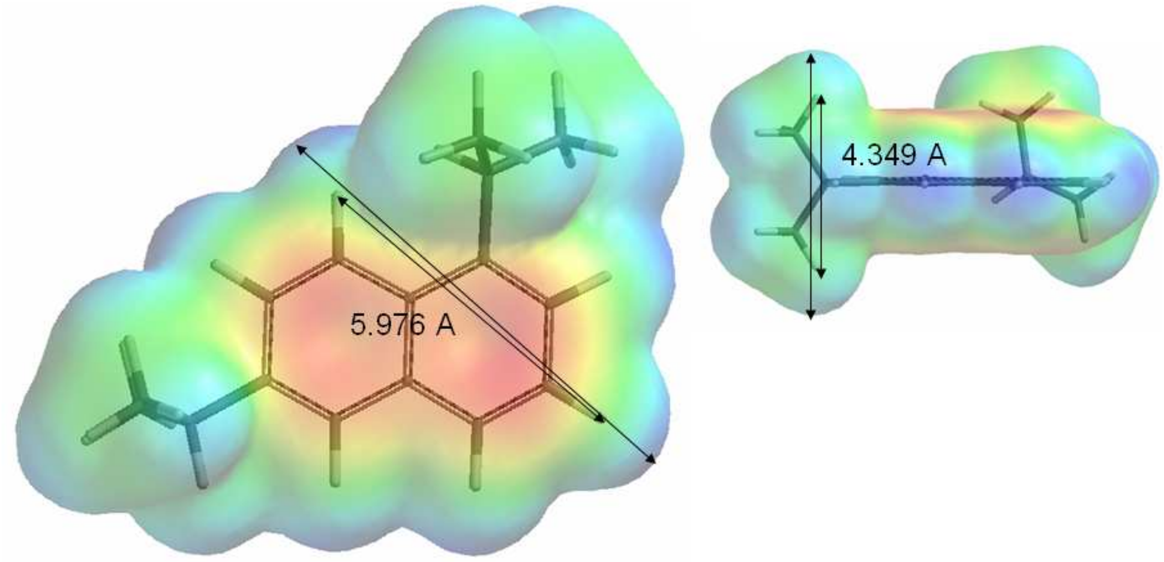


1,5-DIPN:

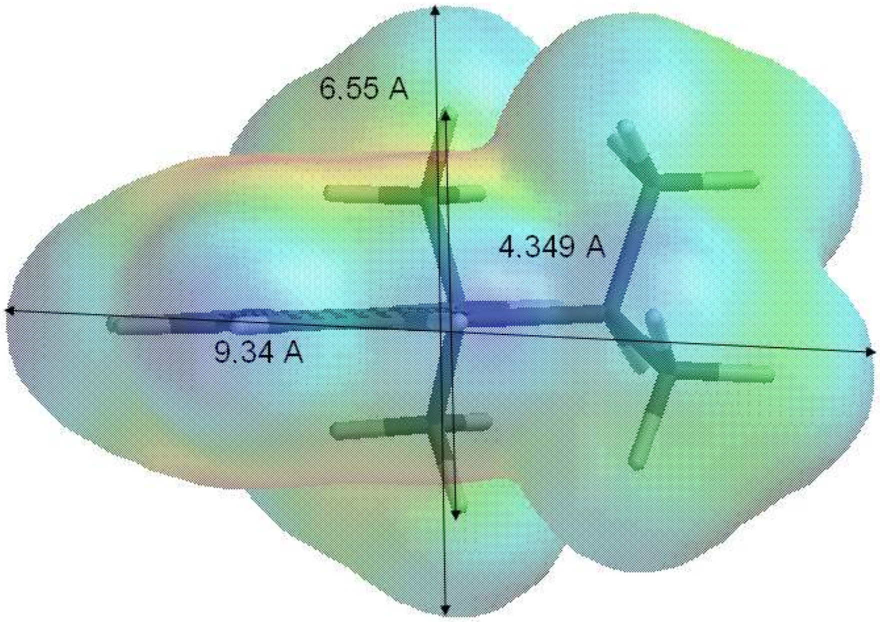


1,6-DIPN:

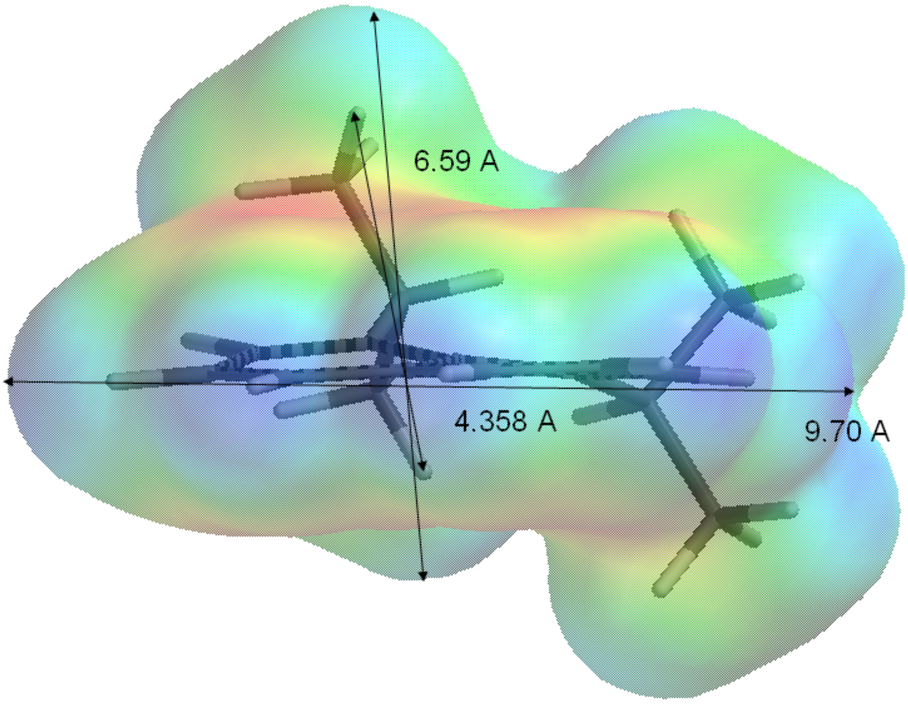




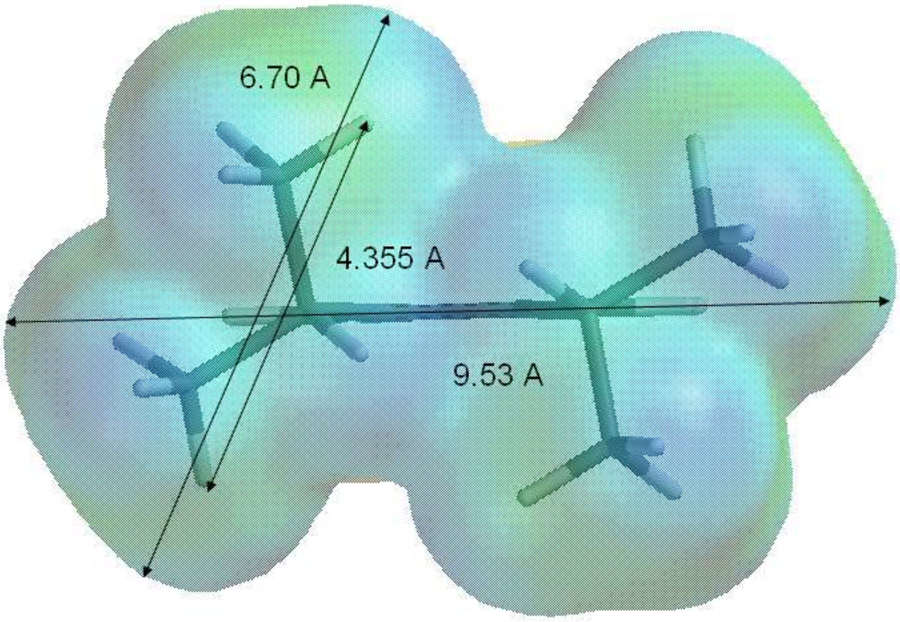
1,7-DIPN:



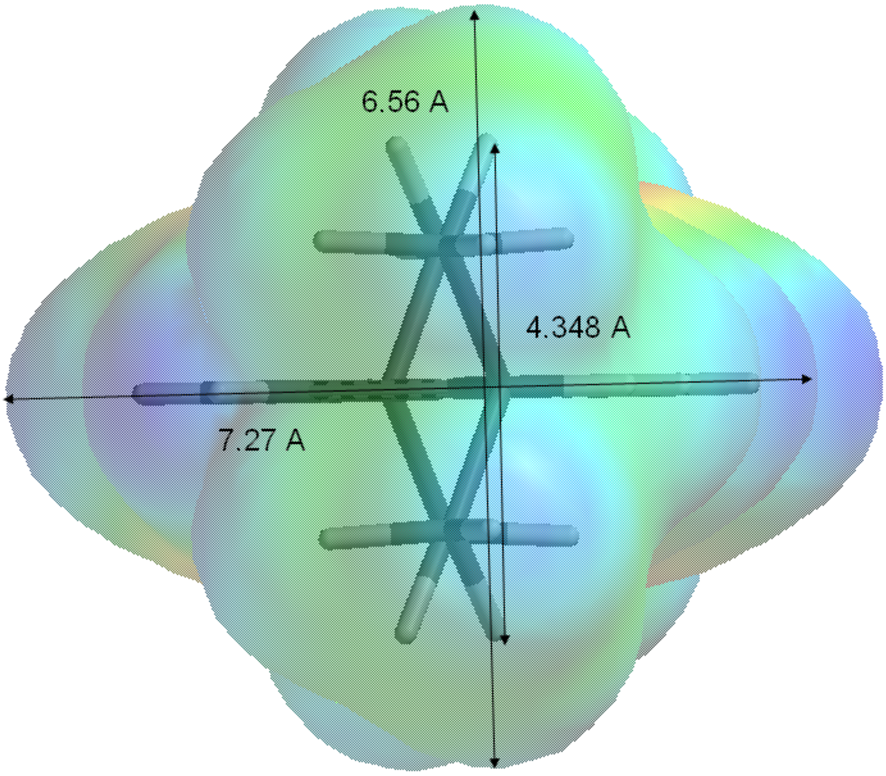
1,8-DIPN:



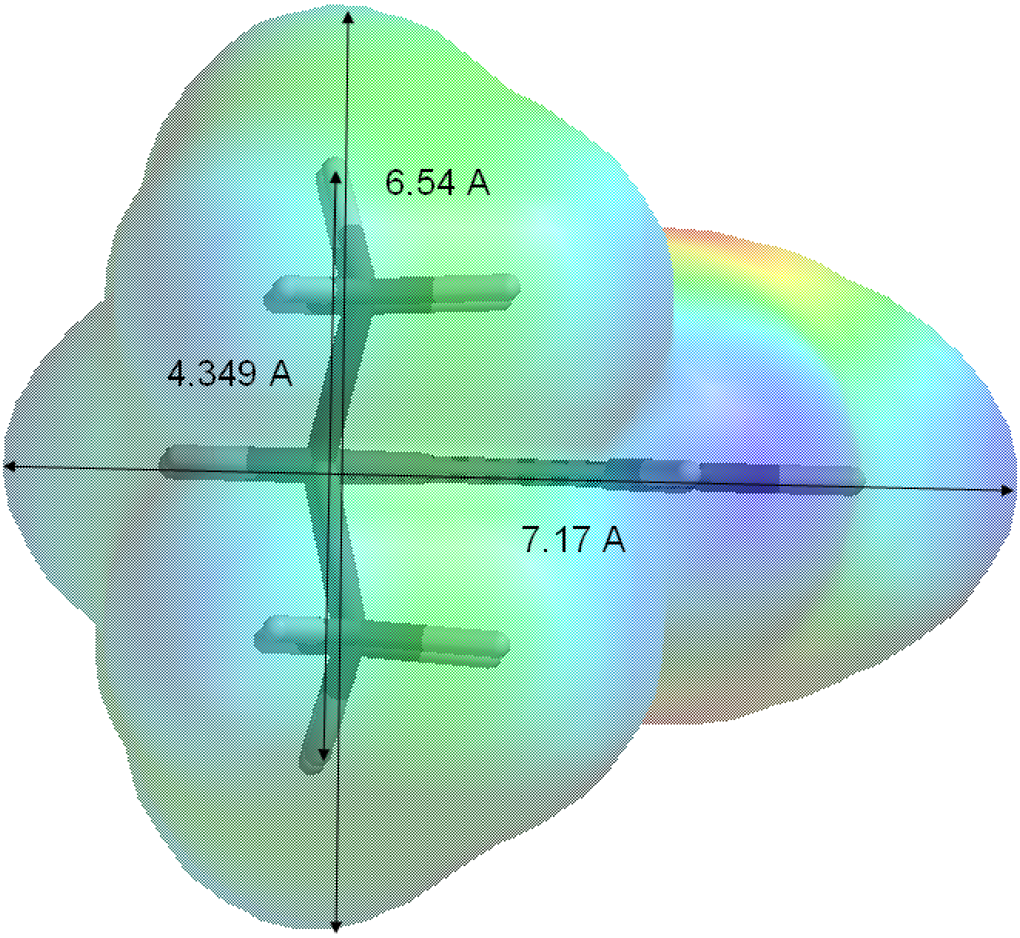
2,3-DIPN:



2,6-DIPN:

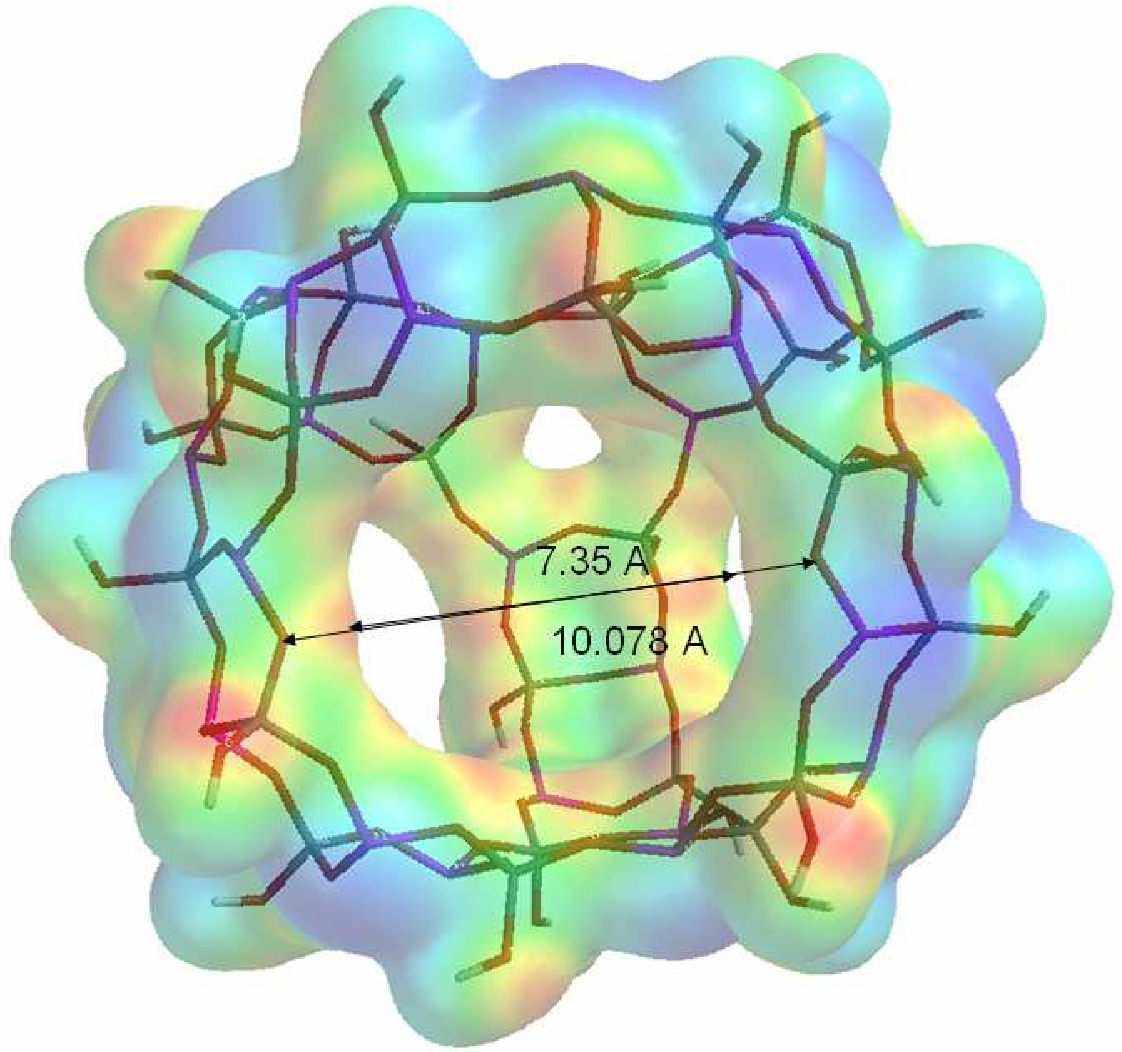


2,7-DIPN:



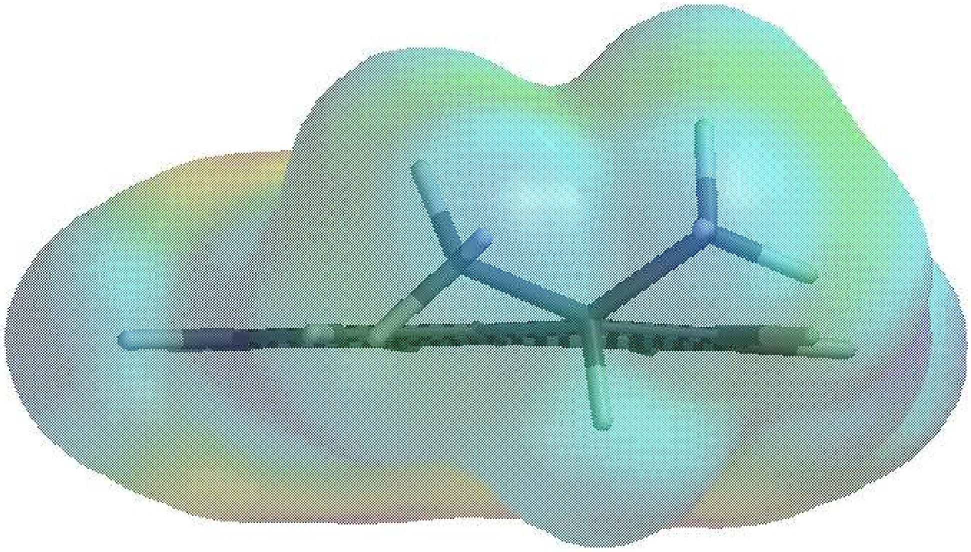
The same procedure was applied to the faujasite supercage. The dimension obtained for this well-described structure matches the one reported on the International Zeolite Association website and therefore confirms the validity of the approach.

Faujasite super cage:

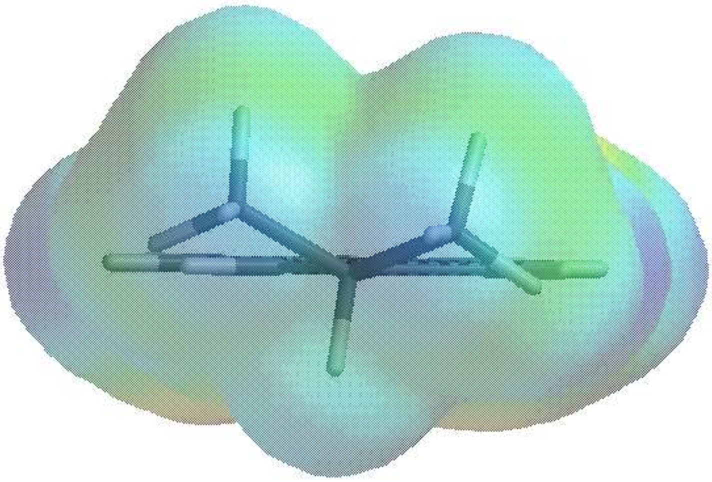


It is easy to realise that the shortest dimension is obtained when the rotation of the isopropyl group places it in such a way that the two methyl groups are above the aromatic plane and the hydrogen is below (or vice versa). Modelling shows that it should be considered as a transition state between the two different conformers. In the case of 1-IPN the energy difference between this transition state and the most stable conformer is 42.5 kJ/mol. It is only 11.7 kJ/mol for 2-IPN.

Smallest 1-IPN possible

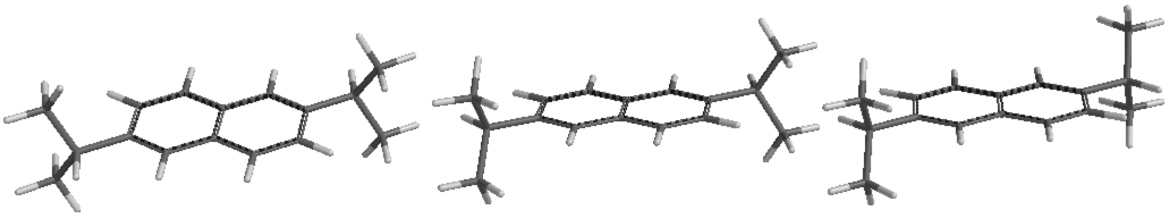


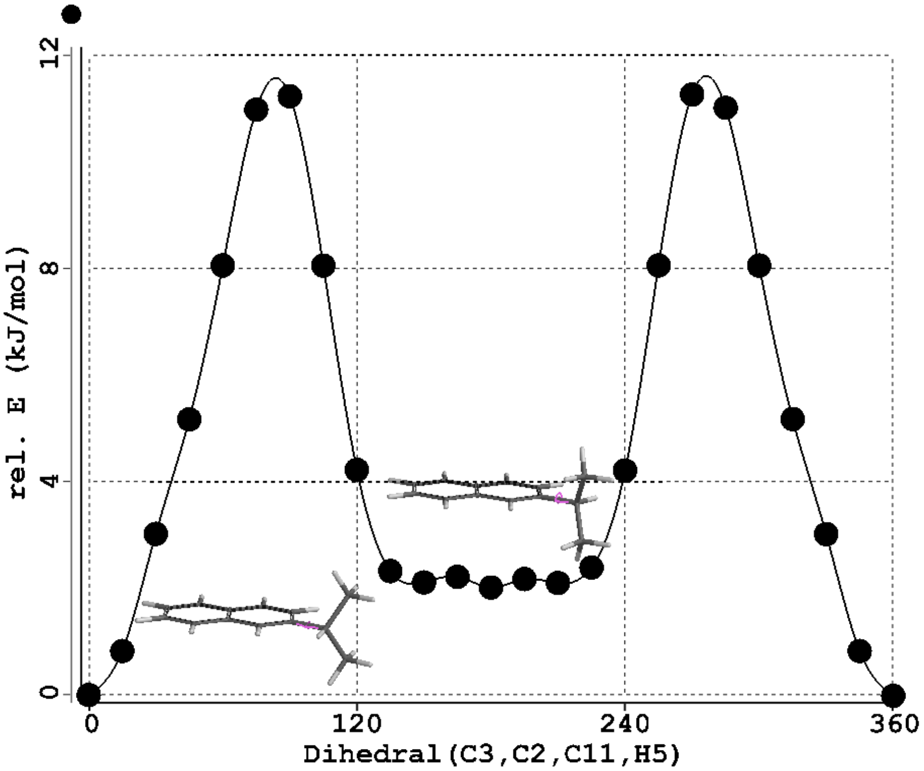
Smallest 2-IPN possible



Conformers

The 3 possible conformers of 2,6-DIPN: left (most stable) with both isopropyl-H in line with the α-H of naphthalene, middle: with one isopropyl-H in line with the α-H of naphthalene, and right (least stable) with both isopropyl-H in line with the β-H ‘s of naphthalene. The energy diagram displaying their relative stability is displayed below.





Energy diagram of complete rotation of the isopropyl group of 2-IPN (B3LYP/6-31G*) showing the 2 conformers, differing ~ 2 kJ/mol in stability, and separated by a rotation barrier of ~ 11 kJ/mol.

Outlook

This project originated with the development in Leuven of a new synthetic approach towards microporous zeolites. The objectives were to perform catalytic experiments in order to validate or not the principle, while addressing in the mean time sustainability issues. The results obtained should as well allow further development of these new catalysts.

These catalysts, called BImodal POrous Materials (BIPOMs), were synthesized by controlled built-up of the structure starting from small and well-defined entities. By opposition with dealumination or desililation, extra porosity was added by constructive way and not by destructing part of a zeolite structure. It is to the best of our knowledge the first attempt to create bimodal materials from the bottom-up approach. The BIPOM catalysts were expected to enhance catalysis due to their extra mesoporosity, therefore reducing the mass transfer limitations and easing the access to the active site. Achieving this would simply mean combining advantages of both homogeneous and heterogeneous catalysts.

With the only constraints to address acid catalysed reactions and to potentially impact the industrial unsustainable productions, a lot of possibilities were still open. By screening the relevant literature it was found that dialkylation of naphthalene was an interesting challenge. Numerous groups claim that shape-selectivity was observed over catalysts such as dealuminated Mordenite but reactions were frequently performed with low overall yields. For this reason it appeared interesting to try applying BIPOM catalysts to this reaction. In order to fully benefit from shape-selectivity isopropylation was chosen rather than methylation. Molecular dimensions were indeed more different and should afford an important discrimination towards one or several of the ten possible isomers. This could potentially compensate for the worse atom-efficiency compared to methylation. Particular interest was put on the selective formation of 2,6-diisopropylnaphthalene (2,6-DIPN), as it is an intermediate for the production of a relatively new and promising polymer, polyethylene naphthalate. Selectivity for dialkylation in general was also investigated.

As described in Chapters 2 and 3, it was found that this system was completely determined by the thermodynamic distribution of the isomers over classical commercial zeolites and that shape-selectivity was never needed to explain the experimental isomer distribution. This statement was made possible through very accurate measurements, confirming the hypothesis made by Brzozowski (see discussion in Chapter 2) that some literature claims may be false and create confusion.

With shape-selectivity ruled out, the main objective became to increase naphthalene conversion as the desired product was also the most abundant in the thermodynamic distribution. Performances were found to be best over wide pore zeolites such as ultrastable Y zeolite. This also seemed to favour the use of BIPOMs as catalysts for this reaction because of their expected better access to active sites and lower mass transfer limitations. Experiments, under the same standard conditions than those applied with classical zeolites, showed that the added mesoporosity in the BIPOMs was indeed allowing them to match closely the results of H-USY, in terms of conversion, selectivity and reaction rate. Besides this, these bimodal catalysts clearly outperformed their parent MFI catalysts. These results were seen as a proof-of-principle for the BIPOM concept. They showed that a bottom-up approach could compete with a top-down approach.

Further testing was made for the best classical zeolite, H-USY, and the best BIPOM catalyst, the ZG (50), in order to address more specifically the industrial perspective of this work. Both catalysts showed similar excellent stability with time. Differences arose when a temperature study was performed. It appeared that the Y zeolite was active at much lower temperature than the ZG (50). On the other hand, the BIPOM catalyst showed a wider operating temperature window, ranging from 150°C to 225°C. Selectivity towards 2,6-DIPN in particular was reasonably similar for both catalysts but the side-product distribution was clearly more in favour of the ZG (50) in the perspective of industrial recycling. When considering the potential industrial application, it was found that the highest yield for 2,6-DIPN (17%) was obtained at 150°C over H-USY and (20%) at 225°C over the ZG (50). This led to the conclusion that from now on the ZG (50) had to be considered as the Best Available Technique (BAT) as defined in the Integrated Pollution Prevention and Control document. Moreover, this catalyst belongs to the first generation of BIPOMs and was not designed specifically for this reaction. There is therefore good reasons to believe it can be potentially still improved.

By taking into account that, as described in Chapters 3 and 4, no shape-selectivity can be expected (and therefore no good selectivity towards 2,6-DIPN), being able to separate 2,6-DIPN from the other reaction products became crucial. If in analogy with the Kureha process, isolation of DIPNs in general is easy by applying several distillation, further purification to obtain pure 2,6-DIPN is generally described as difficult. Very recently, some work was performed on melt crystallisation of the 2,6-DIPN/2,7-DIPN binary mixture. These results have been reproduced with good agreement and further investigations on the commercial isomer mixture have been performed.

Distillation of a commercial mixture of isomers under vacuum did not allow separating or even enriching any isomer. It should still be noted that several groups report normal pressure distillation to enrich the mixture in 2,6-DIPN but this option was not considered in order to avoid high temperatures resulting in thermal decomposition. It would also generate higher energy consumption because of the huge reflux ratio.

Direct crystallisation on the other hand provided great results. Though operated in a very explorative way, crystallisation enabled to obtain 2,6-DIPN with above 95% purity and 1,5-DIPN as the main impurity. Interestingly 1,5-DIPN was also obtained pure, therefore suggesting that 2,6-DIPN could be potentially obtained pure by adequate crystallisations.

These results consist in a huge breakthrough as so far the main purification issue was about how to separate 2,6-DIPN from 2,7-DIPN. This separation is very difficult, both products being very similar regarding most of their physical or chemical properties. Being able to shift the problematic to how to separate 2,6-DIPN from 1,5-DIPN offers a lot more possibility to achieve a higher 2,6-DIPN purity and clearly makes it possible to foresee an industrial process solely dedicated to 2,6-DIPN.

Though not existing under the form we proposed, it is still possible to find relevant literature on a potential process. Alkylation was derived essentially from the Kureha process operated in Germany to yield the DIPN mixture. The oxidation part was initially inspired by the process run by Amoco for the oxidation of 2,6-dimethylnaphthalene, but the DSM process for toluene oxidation was found more interesting. Direct comparison is however difficult as the important oil price variations in the last months generate huge production cost differences and do not allow comparison before price indexation.

The process described in this thesis offered a small increase in overall yield and the loss of one step but the recycling step is very important. Oxidation was not studied in this work and process conditions were derived from the relevant literature. Foreseen oxidation side-products are naphthalene and naphtoic acid.

The overall process despite its little improvement regarding sustainability has very limited chances to be implemented industrially as its return on investments is very low, even for large volume, at high conversion and selectivity. This is mainly due to the spill of 4 carbons during the oxidation of 2,6-DIPN. Besides its not sustainable aspect, this is clearly damaging in an important way the profitability of the whole process.

If one wants to see this process applied industrially, several options can be investigated.

In a first step, real shape-selectivity towards 2,6-DIPN can be targeted. This would result in a process approaching the Kureha one but with 2,6-DIPN production instead of the DIPN mixture. For economic comparison the case described in this work with naphthalene and isopropanol conversions at 90% can be used. The main cost saving will appear in the equipment investment as this would strongly diminish the recycling and separation. However, the spill of 4 carbons in the oxidation would still strongly reduce the profit.

A second and clearly more economically interesting approach would be to improve the atom-efficiency by applying methylation instead of isopropylation. For this purpose, there is a real need for a shape-selective catalyst, as thermodynamic does not favour the formation of 2,6-dimethylnaphthalene over the other isomers. If achieved, this would mean a strong equipment reduction (and therefore a lower investment) in the alkylation part, combined with an atom-efficient oxidation. Based on prices described in Chapter 7, this would considerably impact the production cost in a positive way.

Finally, in a more ideal way, a complete different route may be investigated. This could be best done in the case of methoxycarbonlyation of naphthalene, as this would result in a one step synthesis, therefore considerably reducing the plant size, the amount of feedstock, the purification operations and the volume needed for them.

Summary

This thesis summarises the PhD work on catalysis over specific acidic zeolites in order to aim for a more sustainable chemistry.

Even if industry is improving its processes both in terms of efficiency and sustainability, production of bulk chemicals still widely uses Lewis or Brønsted acids when an acid catalysed step in required. Being able to deliver efficient heterogeneous acid catalysts is therefore a necessity if one aims at improving the way chemistry is interacting with the environment (*Chapter 1*). Diisopropylation of naphthalene for the industrial production of dimethyl naphthalene-2,6-dicarboxylate (NDC) was chosen as a model system. Numerous claims can be found in the literature for shape-selective dialkylation in general with higher selectivity when bulky alkylating groups are used. Diisopropylation was chosen to balance between atom efficiency and shape-selectivity. Reported shape-selective catalysts are usually slow due to transport limitations. Controlled mesopority as in BImodal POrous Materials (BIPOMs) might overcome this. Furthermore, though actually no industrial process does exist, SRI has published a process cost study on Amoco technology leading to NDC.

It has been shown in the case of naphthalene isopropylation that shape-selectivity, either at the substrate level, the transition state level or the product level cannot be seen as a realistic explanation for the product distribution. Large pore zeolites, such as H-USY, yield, as expected, a mixture very close in terms of composition to the thermodynamic one obtained computationally. Zeolites like Mordenite, supposed to have pore sizes matching very closely some molecular dimensions (*Chapter 2*) and therefore expected to exclude the formation of some isomers, are in practice solely slower and not more selective. High selectivity observed in the literature with such catalysts can in most cases be explained by analytical difficulties to measure accurately low amounts of products rather than by the discrimination of particular isomers. At relatively high temperatures, these smaller pore zeolites are still operating under kinetic conditions and the time needed to reach the thermodynamic equilibrium is therefore too long (*Chapter 3*) when the same equilibrium is reached within a few hours over wide pore zeolites.

Studies performed with the BIPOMs in naphthalene diisopropylation showed that the bottom-up approach for creating better access to the zeolite active sites can be achieved (*Chapter 4*). It is hard to compare the results obtained this way with those obtained with a top-down approach such as dealumination or desilylation as the latest have been widely studied while the BIPOMs seem to be the first positive attempt of structural building. Results belonging to this thesis should therefore be considered as a proof-of-principle for the concept but extra efforts and new catalyst generations are still needed to compete totally with the top-down approach as only MFI structure have been achieved so far, while dealumination or desilylation are possible on most of the structures. Still, MFI zeolites obtained by controlled growth clearly outperformed their parent structure and showed reactivity comparable with or better than reference wide pore zeolites (*Chapters 4 and 5*). This also shows that for isopropylation of naphthalene the key factor lays in the ease to reach the active sites thanks to wide pores or super-micropores rather than in the potential shape-selectivity generated by small pores.

With such a complex reaction mixture, separation issues are very important. Results presented in this thesis show that GC separations are possible but that a very careful analysis is needed. Reliable and accurate results can however be achieved by combining at least 2 different columns either in parallel or with a GC x GC system (*Chapter 2*). Crystallisation and recrystallisation results, on the other hand, open a new possibility for the industrial production of 2,6-diisopropylnaphthalene (2,6-DIPN). As it seems to be impossible to generates very pure 2,6-DIPN at low temperature through synthesis since shape-selectivity has no influence on the reaction outcome, being able to purify 2,6-DIPN from its isomer mixture is crucial. Results from recrystallisations in methanol indicate that very pure 2,6-DIPN can be obtained from a kinetic isomer mixture, along with very pure 1,5-DIPN. Though slightly different, it is assumed that recrystallising a thermodynamic mixture would allow the same range of purity (*Chapter 6*).

Taking all this into account, it seems possible to implement a new process for the industrial production of dimethyl naphthalene-2,6-dicarboxylate (NDC). Production around 45 kt/y could be realised for a sell price set at 5.5 €/kg (about the required market price for the polymer industry) while still generating a profit around 4% in the base case

(*Chapter 7*). However, higher yields in principle can be achieved, mainly by feeding propene more properly. Still, even the highest yield possible combined with a shape-selective catalyst (leading to the lowest investment cost) does not generate a clear economically attractive process, though in the latter case the Amoco process is clearly outperformed. The loss of 4 carbons out of 6 in the oxidation step is simply too much.

This process is, however, slightly more sustainable than the route from *ortho*-xylene. Yields are higher and a smaller number of different chemicals are needed.

Samenvatting

In dit proefschrift wordt het promotieonderzoek naar de toepassing van een specifiek soort zure katalysatoren voor de ontwikkeling van duurzame chemische processen samengevat.

Hoewel op dit moment de industrie bezig is met het verbeteren van zijn processen, zowel in termen van rendement als duurzaamheid, worden er bij de produktie van bulkchemicalieen nog altijd op grote schaal Lewis- of Brønsted-zuren toegepast als katalysator. De ontwikkeling en beschikbaarheid van efficiente heterogene katalysatoren is dientengevolge een noodzaak als men zich als doel heeft gesteld de interactie tussen de chemische industrie en het milieu te verbeteren (Hoofdstuk 1). De diisopropylering van naftaleen tot 2,6-diisopropylnaftaleen, een intermediair voor de industriele productie van dimethyl naftaleen-2,6-dicarbonzuur (NDA) werd gekozen als modelsysteem. In de literatuur kunnen talloze claims worden gevonden met betrekking tot de shape-selective (= vorm-selectieve) dialkylering van naftaleen. Doorgaans neemt de vormselectiviteit toe als grotere alkylerende groepen worden gebruikt. Diisopropylering werd gekozen als compromis tussen de tegenstrijdige eisen: atoomefficientie en vormselectiviteit. De tot nu toe uit de literatuur bekende vormselectieve katalysatoren zijn echter doorgaans te langzaam tengevolge van transportlimiteringen. Gecontroleerde mesoporositeit zoals in BImodale POreuze Materialen (BIPOMs) zouden dit probleem kunnen oplossen. Verder is het zo, dat hoewel er tot op dit moment geen goede industriële route voor dit product bestaat, SRI wel een proceskostenstudie heeft gepubliceerd gebaseerd op Amoco-technologie die leidt tot naftaleen-2,6-dicarbonzuur dimethylester (NDC).

In het geval van de isopropylering van naftaleen is het duidelijk geworden dat vormselectiviteit, hetzij op substraatnivo, overgangstoestandnivo, of produktnivo, geen goede verklaring biedt voor de experimentele produktverdeling van de isomeren. Zeolieten met grote porien, zoals H-USY, leiden zoals verwacht, tot een isomerenmengsel dat wat samenstelling betreft dicht bij de berekende thermodynamische komt. Zeolieten zoals Mordeniet, waarvan werd aangenomen dat de poriegrootte goed overeenkwam met de moleculaire afmetingen van sommige isomeren (Hoofdstuk 2), en waarvan dus werd verwacht dat andere isomeren niet zouden worden geproduceerd, bleken in de praktijk slechts langzamer te zijn maar niet selectiever! De in de literatuur gerapporteerde hoge selectiviteit met deze katalysatoren kan in de meeste gevallen worden verklaard door analytische problemen bij het accuraat meten van zeer kleine hoeveelheden i.p.v. selectiviteit voor bepaalde isomeren. Zelfs bij relatief hoge temperaturen werken deze zeolieten met kleinere porien nog in het kinetisch regime, en is de benodigde tijd om het thermodynamisch evenwicht te bereiken te lang (Hoofdstuk 3), terwijl het thermodynamisch evenwicht wordt bereikt binnen enkele uren met de zeolieten met grote porien.

Onderzoek naar de naftaleen diisopropylering uitgevoerd met de BIPOMs, maakt duidelijk dat de bottom-up benadering om een betere toegang tot de katalytisch actieve plaatsen te verkrijgen, succesvol is (Hoofdstuk 4). Het is moeilijk om de verkregen resultaten met deze methode te vergelijken met die van een top-down benadering zoals dealuminering of desilylering, daar deze laatst genoemde methoden uitvoerig onderzocht zijn, terwijl het bij de BIPOMs gaat om een eerste poging een structuur te bouwen met beheersing vanaf de moleculaire schaal tot en met het micrometernivo. De in dit proefschrift beschreven uitstekende resultaten met een MFI-zeoliet dienen daarom te worden beschouwd als een proof-of-principle en hoogstens als een indicatie van de potentie van deze benadering. Extra inspanningen met nieuwe generaties katalysatoren zijn echter hard nodig om de uiteindelijke competitie aan te gaan met top-down benaderingen als dealuminering en desilylering, toepasbaar voor de meeste zeolietstructuren. Blijft staan dat de MFI zeolieten, verkregen door gecontroleerde groei en kristallisatie, in prestatie de moederstructuren duidelijk overtroffen, en nu al een reactiviteit laten zien direct vergelijkbaar met, of beter dan de referentie grote porie zeolieten (Hoofdstukken 4 en 5). Het laat tevens eens te meer zien dat voor de isopropylering van naftaleen de key success factor de toegankelijkheid is van de katalytisch actieve sites, en niet de vermeende vormselectiviteit van de kleine porien.

Met een complex reactiemengsel van in principe 10 sterk op elkaar gelijkende isomeren, is zorgvuldige analyse van groot belang. De resultaten gepresenteerd in dit proefschrift laten zien dat scheiding op basis van GLC mogelijk is, maar zorgvuldigheid en voorzichtigheid is vereist. Betrouwbare en accurate resulaten konden echter worden verkregen door de combinatie van 2 verschillende GC-kolommen, parallel of eleganter met een GCxGC systeem (Hoofdstuk 2). Een belangrijke potentiele doorbraak voor de industriele produktie van 2,6-diisopropylnaftaleen (2,6-DIPN) werd bereikt in directe (smelt)kristallisatie experimenten met een diisopropylnaftaleen isomerenmengsel. Daar het er naar uitziet dat vormselectieve synthese van 2,6-DIPN met een zeolietkatalysator een hersenschim is, is selectieve afscheiding van 2,6-DIPN uit het isomerenmengsel cruciaal. Rekristallisatie in methanol suggereert dat zeer zuiver 2,6-DIPN kan worden verkregen al uit een kinetisch mengsel, tezamen met zeer zuiver 1,5-DIPN. Verwacht mag worden dat met een thermodynamisch mengsel, waarin een veel grotere percentage 2,6-DIPN aanwezig is, een vergelijkbare zuiverheid kan worden bereikt (Hoofdstuk 6).

De integratie van alle verkregen resultaten heeft geresulteerd tot een nieuw processchema voor de industriele produktie van naftaleen-2,6-dicarbonzuur dimethyl ester (NDC). Bij een schaalgrootte van 45 kt/jaar, naar directe analogie met het door SRI geanalyseerde Amoco proces, bedraagt de verkoopprijs in het base case scenario ongeveer 5.5 €/kg, overeenkomend met de vereiste minimum voorwaarde vanuit de polymeerindustrie (Hoofdstuk 7). De winst voor belasting en afschrijving bedraagt dan echter een schamele 4%. Een hoger rendement lijkt echter zeer wel realiseerbaar door gecontroleerde stapsgewijze voeding van propeen, nu naar een directe analogie met het bestaande industriele proces van Kureha in Duitsland, dat een mengsel van diisopropylnaftalenen produceert. Helaas wordt zelfs het proces met het hoogste rendement en de kleinste recycles (bv. door aan te nemen dat er wel duidelijk een vormselectieve katalysator zou kunnen worden gevonden) economisch niet attractief, d.w.z. met een winst groter of gelijk dan 15%, hoewel in het laatste geval het Amoco proces wel wordt overtroffen. De oorzaak ligt erin dat het noodzakelijke verlies van 4 C-atomen van de oorspronkelijke 6 uit 2 moleculen propeen, simpelweg een te grote concessie is aan de atoomefficientie.

Overigens kan het nieuwe procesvoorstel, al in het base case scenario wel als enigzins duurzamer worden beschouwd dan de Amoco route gebaseerd op ortho-xyleen. De opbrengsten zijn hoger, en er zijn minder verschillende chemicaliën nodig.

Acknowledgements

Now is the time to put a final end at this PhD. Of course after slightly more than 4 years the amount of people I have met or interacted with is impressive but I would like to thanks some of them for some precise reasons related to work and/or my life outside work.

First of all I would like to thank Wim for offering me the opportunity to work on this topic. I believe we were quite an unusual student/supervisor couple in the way we worked together but when I look at the final result I know we did a good job. I really enjoyed the freedom you gave me (even if it came with the drawback I did not see you as much as I would have liked in the last months) and liked our long discussions both scientific and non scientific. I wish we could have been more than just the two of us, always belonging to one group without really working on the same things than the others, but I guess none of us could have done anything regarding to that. I am confident in the fact that we will meet again, somewhere.

I would like to thanks as well all my committee members for accepting to take part in my defence. Among them I'd like to thank particularly: Prof. Van Bekkum for his interest in my work since the very beginning and the interesting suggestions and discussions that even led me to write one of my propositions, Prof. Walter for his enthusiasm in participating in this committee, the nice and friendly interaction we have for about 10 years and the very nice words about my work (it made me feel so much better!) and Prof. Kreutzer for accepting the unrewarding position of reserve member.

My thanks go as well to Ulf Hanefeld and Guido Mul for accepting to be my "daily supervisors". You both came out with interesting remarks on my articles and/or manuscript drafts.

During this project I had to work with some equipment I had no knowledge about before. Remco, thank you so much for the time you spent explaining me out to handle an autoclave, for the numerous hours we spent together trying to fix it or looking for stupid leaks, without having to ask twice for some support. It seems people consider me as

capable to solve minor problems when you are away and that's doubtless because of what you taught me. Thanks as well for having taking care of the GCs so well. Considering that most of my work relies on GC analysis, I can say you help putting this work on tracks. But above this, thank you for the nice discussions besides work during the practicles, when I was just coming along for a break or even overnight. Thanks you for your friendship along these years, I'm confident we will keep in touch wherever I end up.

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Publications and oral presentations

Publications

C. Bouvier, W. Buijs, U. Hanefeld, B.C. Gagea, P.A. Jacobs, J.A. Martens, "Diisopropylation of naphthalene over acid mordenite and ultrastable Y zeolites: shape-selectivity or thermodynamic control?", submitted to *J. Catal.*

C. Bouvier, W. Buijs, G. Mul, B.C. Gagea, P.A. Jacobs, J.A. Martens, "A new type of catalysts for the isopropylation of naphthalene", to be submitted to *Angew. Chem. Int. Ed.*

C. Bouvier, N. Reumkens, W. Buijs, "Differences in Gas Chromatography analysis of the diisopropylnaphthalene isomeric system", to be submitted to *J. Chromatogr. A.*

C. Bouvier, W. Buijs, G. Mul, B.C. Gagea, P.A. Jacobs, J.A. Martens, "Influence of the temperature on the product distribution of the diisopropylation of naphthalene over ultrastable Y zeolites and Zeogrids", to be submitted to *J. Mol. Catal. A.*

C. Bouvier, W. Buijs, "Evaluation of an industrial process for the production of dimethyl naphthalene-2,6-dicarboxylate through diisopropylation of naphthalene with respect to sustainability and economics", to be submitted to *Int. J. Environ. Technol. Manage*.

Oral presentations and posters

C. Bouvier, U. Hanefeld, W. Buijs, “Heterogeneous acid catalysts for sustainable Friedel-Crafts and aldol reactions”, NWO meeting of the study groups Design and Synthesis, Structure and Reactivity, Biomolecular Chemistry, Lunteren, the Netherlands, November **2004**, poster.

C. Bouvier, U. Hanefeld, W. Buijs, “Differences in product distribution in the isopropylation of naphthalene with various acid catalysts”, NWO meeting of the study groups Design and Synthesis, Structure and Reactivity, Biomolecular Chemistry, Lunteren, the Netherlands, November **2005**, poster.

C. Bouvier, W. Buijs, U. Hanefeld, “Differences in product distribution in the isopropylation of naphthalene with various acid catalysts”, NCCC VI, Noordwijkerhout, the Netherlands, March 7-9, **2005**, poster.

C. Bouvier, W. Buijs, U. Hanefeld, “Isopropylation of naphthalene over several zeolitic catalysts: HY and BIPOMs”, NCCC VII, Noordwijkerhout, the Netherlands, March 6-8, **2006**, poster.

C. Bouvier, W. Buijs, “Isopropylation of naphthalene over several zeolitic catalysts: HY and BIPOM’s”, XVII International Conference on Chemical Reactors, Athens, Greece, May 15-17, **2006**, oral presentation.

C. Bouvier, W. Buijs, “Diisopropylation of naphthalene over several zeolitic catalysts: HY and BIPOMs”, NCCC VIII, Noordwijkerhout, the Netherlands, March 5-7, **2007**, oral presentation.

C. Bouvier, W. Buijs, G. Mul, “Diisoproplyation of naphthalene over zeolite catalysts”, International Symposium on Catalysis Engineering, Delft, the Netherlands, June 14-15, **2007**: poster.

Curriculum vitae

Christophe Bouvier was born on March 23rd 1979 in Casablanca, Morocco. In September 1997, he started his university studies at the Université de Haute-Alsace, Mulhouse, France. In 1999, he entered the Ecole Nationale Supérieure de Chimie de Mulhouse, France. During this formation he worked 10 months for the Commissariat à l'Energie Atomique, in Mons, France. He graduated in June 2003 with a specialisation in organic and bioorganic chemistry. He received his Diplôme d'Etudes Approfondies in 2003. His final project was carried out under the supervision of Prof. Dr. Ir. Serge Neunlist (Université de Haute-Alsace). In May 2004, he started his Ph.D. research first at the Laboratory of Applied Chemistry and Catalysis and then in 2006 within the Catalysis Engineering group of the Technische Universiteit Delft, the Netherlands, under the supervision of Prof. Dr. Wim Buijs on an "Exploration towards a more sustainable process for dimethyl naphthalene-2,6-dicarboxylate over acidic zeolites". The results of this research are described in this thesis.