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ABSTRACTS

STRUCTURE AND RHEOLOGY IN POLYPROPYLENE NANOCOMPOSITES

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The development of nanocomposites gained much interest recently and it might develop into one of the latest evolutionary steps of polymer technology. This new class of materials offers promising potentials for the diversification and new application of conventional polymeric materials. Polymer/clay nanocomposites have a layered structure and each layer is 1 nm thick at least in one dimension. Hundreds or thousands of layers are stacked together and form a silicate particle. The aim of developing nanocomposites is to break down clay particle agglomerates and improve the adhesion between matrix polymer and clay particles by the introduction of maleic anhydride functionalized PP (MAPP). In the nanocomposite containing individual particles, we can achieve significant reinforcement with a low level of filler loading. However, not only exfoliated structures (with individual particles) but several other structures can build up during the processing. Articles demonstrate the partial delamination, but in our oppinion the existence of exfoliated structure is not proved properly yet.

In our earlier research we studied the effect of different matrices, fillers and compatibilizers. We analysed the structures of nanocomposites by WAXS, TEM. Rheology is a new possibility to study the changes of structures.

In this study we deal with the rheological behaviours of polymer composites containing different amount of layered silicate and MAPP. Our goals are to prove the presence of exfoliation and quantitative evaluation of the results. We found

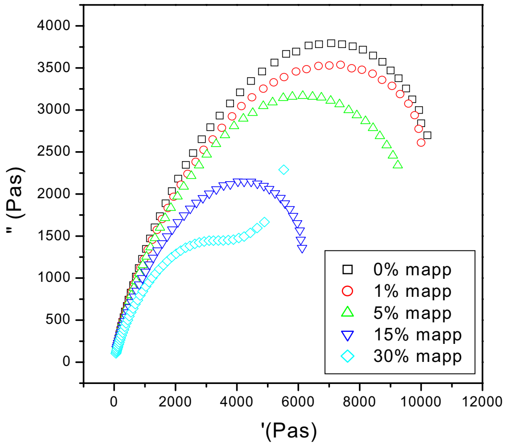

Fig. 1. Cole-Cole plot at 2 ν/ν% silicate content

strong correlation between the structure and the frequency dependence of complex viscosity and modulus in the case of different nanocomposite samples. This is even more apparent in the lower frequency range where the effect of molecular structure is predominated. To prove the changes of the structure we plotted the rheological parameters in Cole-cole diagram. In lower silicate content series, the changes in curves occurred at higher MAPP content. Thus, stacked layers need more MAPP to shear off them. With the alteration of MAPP content not only the shape of the curves but also the area of the curves changed. These behaviours indicate the presence of exfoliation.

ISOMERIZATION REACTIONS OF ALLYL AND CYCLOPROPYL PSEUDOHALIDES

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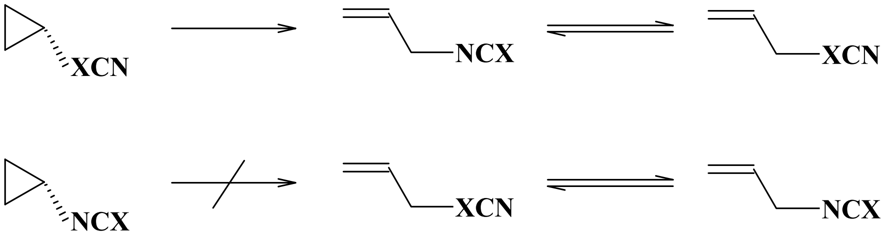
The isomerization reactions of allyl and cyclopropyl cyanate, thiocyanate and selenocyanate have been investigated both experimentally and theoretically. The gas phase pyrolysis of allyl derivatives leads to a 3:1 mixture of NCX and XCN isomers. In the case of the cyclopropyl pseudohalides ring opening and the appearance of a mixture of both allylic compounds were observed only in case of XCN derivatives:



Quantum chemical calculations were carried out at the MP2 and B3LYP levels of theory with the cc-pVTZ basis set using Gaussian 98 program package. All the reactants, products and transition states were studied and characterized. The calculated electronic structure of the molecules and the observed UV photoelectron spectra are in good correlation.

The theoretical calculations provide evidence for the reaction pathway via a [3,3] sigmatropic rearrangement. According to the calculations the ring opening of cyclopropyl NCX derivatives requires much larger activation energy than that of the XCN isomers.

SILOXANES: FROM THE Si-O BONDING TO THE STRUCTURE OF GLASS

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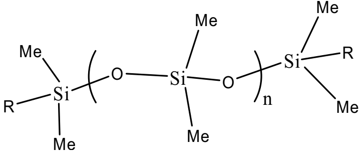
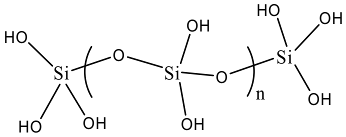
The siloxanes are molecules that alternating contain Si and O atoms. The substituents of the Si atom highly influence the properties of the siloxanes: changing the acidic hydrogen atoms of the silica to metal ions gives asbestos, mica and other silicates. Silicates containing Na, K, Ca ions are glasses which are often used as structural elements in various applications (ion-selective electrodes, lamp envelopes, substrate in microelectronics). In silicones organic substituents are on the Si atom. These compounds highly differ from those, mentioned before, being more similar to organic compounds like oils, and rubbers.



dimethylpolysiloxane



poly(meta)silicic acid

In my work I examine and compare the structure and stability of compounds containing Si-O bonds, using quantum chemical methods. The applied model compounds are linear and cyclic siloxanes containing 1-6 Si atoms with a number of substituents. Varying these substituents, and extending these molecules I seek for clusters which can describe the structure and reactivity of larger systems. One aim is to get acquainted with the structure of soda-glasses that being amorphous, can not be described by calculations containing periodic boundary conditions. In the literature amorphous silica is often examined by different membered siloxane rings. In order to analyse soda-glass I use rings, similar as in the literature, extended by anionic and smaller compounds to calculate the coordination of sodium-ions. In the glass the sodium-ion bounds to oxygen anion and coordinates to further oxygen atoms of the siloxane chain. The highest stabilization is obtained upon the coordination to the anionic and further three chain-oxygen atoms. According to the calculations a more stable structure is given, if the anionic oxygen is coordinated to an additional Si atom in the chain, resulting in a pentavalent structure. Na^+ can co-ordinate these anionic systems in various ways, the stability of these conformers does not differ significantly. Thereupon, if the transition state energies are not too high between these coordination types, a possibility is given to examine the migration of sodium-ion, and the rearrangement of the glass structure. Understanding these mechanisms, it can be explained that processes, like recrystallization, and diffusion of alien ions cause difficulties in industrial applications.

THERMAL AND STRUCTURAL ELUCIDATION OF TRANS-1,4,5,8-TETRAAZODECALIN CRYSTALS OCCURRED IN ETHYLENEDIAMINE

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We have recently prepared several supramolecular lattice compounds containing theophylline [1, 2, 3] in analogy of aminophylline, a drug with ethylenediamine, and studied their thermal and structural properties by several analytical methods.

Now, we have observed the spontaneous crystallization of translucent prisms of crystals from ethylenediamine from standing in closed vessel. We have decided to determine the composition and structure of these crystals of unknown origin by element analysis (C, H, N), FTIR, ^{1}H- and ^{13}C-NMR spectroscopy, simultaneous thermal analysis (TG/DTA) online coupled with evolved gas analyses (TG-FTIR, TG/DTA-MS) and X-ray diffraction methods [4]. In this way we could describe a potential contamination, that might appear also in the solid samples of aminophylline.

Molecular formula of crystals has been unambiguously calculated as $C_6H_{14}N_4$ from results of combustion analysis. More than 40 molecules with this formula having two double bound equivalents can be found in Beilstein database [5]. The number of potential candidates has been decreased on the basis of FTIR spectrum of crystals. At about 3200 cm^{-1} only one υ(NH) band occurs, so the compound contains only NH group(s), but not NH_2 groups. Above 3000 cm^{-1} υ(CH) bands do not appear, i.e. it does not include unsaturated $=$ CH groups. NMR spectra do not show any double bonds, and the two ^{13}C signals refer to a highly symmetric double-ring structure. Between the two possible types of bisimidazolidines and tetraazodecalins we have tried to distinguish by mass spectra of degradation products of the crystals measured by TG/DTA-MS. The biggest observed fragments ($m/z =$ 80, 81 and 82) may correspond to aromatic pyrazine which have been evolved most probably from tetraazodecalins. ^{1}H- and ^{13}C-NMR spectra of crystals have been compared with published data of 2,2’-bisimidazolidine [6, 7], *cis*- and *trans*-1,4,5,8-tetraazodecalin [8, 9, 10], and the spectra of unknown compound has been assigned as *trans*-1,4,5,8-tetraazodecalin. The final proof has been achieved by comparison of the powder X-ray diffraction pattern and unit cell parameters of our crystal with those of *trans*-1,4,5,8-tetraazodecalin calculated from previous data of its single crystal’s structure [11, 12].

We have examined also the possible thermal decomposition ways of *trans*-1,4,5,8-tetraazodecalin by online coupled evolved gas analyses (TG/DTA-MS and TG-FTIR). In the EGA-FTIR spectrum of released gaseous species measured at the highest evolution rate by TG-FTIR instrument ethylenediamine can be identified as another decomposition product of *trans*-1,4,5,8-tetraazodecalin.

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ENVIRONMENTAL EVALUATION AND COMPARISON OF WASTE SOLVENT TREATMENT ALTERNATIVES

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Due to the limited natural resources, more and more attention is paid to the concepts of sustainable development and consumption. According to regulations and social expectations, environmentally conscious engineering has to be met by designers and decision makers. The problem of treating the huge amount of industrial waste solvents focuses on the concept of sustainability since they are associated with significant amount of raw material and energy consumption. Today's environmental principles prefer the recovery and recycling of waste solvents to the end-of-pipe treatment alternatives. Waste solvent treatment is generally possible with several alternative processes and the selection has to be made on the basis of environmental evaluation beside economic analysis, since the aim of the treatment activity is to reduce the total environmental impact and not to increase it. A widespread acceptable and applied tool for the quantitative evaluation of the environmental impact of a process and for ranking process alternatives is the life-cycle assessment (LCA). It is used to assess the environmental impact of products or processes over the entire product life cycle.

In our work the environmental impacts of several waste solvent treatment options are assessed by LCA and their economic features are also estimated. The aim of the investigation is to compare the results of the LCA with economic evaluation data. The industrial processes are

(1) the recovery of a quaternary solvent mixture coming from a printing company with the so called ternary cut structure [1];
(2) the recovery of the same quaternary solvent mixture with novel hybrid structure based on heteroextractive distillation (HED) [2], [3];
(3) the recovery of tetrahydrofuran from a binary and a ternary mixture with several solvent treatment alternatives.

Beside the special HED, extractive distillation, ordinary distillation, pervaporation are also considered at the different recovery steps. As an end-of pipe treatment, incineration is investigated. The environmental evaluation of the different solvent treatment options is carried out with the Eco-indicator 99 life cycle impact assessment weighting methodology supported by the software SimaPro 5.1.

The methodology contains a weighting step making possible the expression of the environmental impact with a single score that makes the comparison of several processes easier. The dependency of the results on the weighting factors is also investigated. LCA models for each solvent recovery process are determined. Based on the LCA models optimization of the environmental impact is carried out in the case of simultaneous operation of incineration and recovery of processes (1) and (2). Economic features of the alternatives are also estimated.

The results show that economic features do not always have the same tendency like the results of the environmental evaluation. In the cases of processes (1) and (2), where simultaneous incineration and recovery of the waste solvents is possible, an optimal split rate of the waste solvent stream between the two treatment options can be determined based on the environmental evaluation. The optimal split rate highly depends on the efficiency of the recovery process. The novel hybrid separation structure based on HED has better environmental features than those of the less effective ternary cut alternative, and suggests more fractions of the waste solvent stream to recover. However, total recovery is recommended on the basis of the economic evaluation in every case.

In case (3) which involves pervaporation as well, the environmental and economic analyses give the same result that is: total recovery is recommended. Pervaporation answers better the expectations of the sustainable development: lower energy consumption and higher separation efficiency feature the membrane separation, therewith, lower operational but higher capital costs characterize the process.

The results obtained show the clear message that modern, effective, and also cheap recovery processes, the so called ‘clean technologies’, are needed to bring economic and environmental optima closer to each other, therewith encouraging the realization of sustainable development.

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REGIOSELECTIVE NUCLEOPHILE SUBSTITUTION OF 4-MESYLOXYMETHYLAZETIDINONES. LACTAM OR AZIRIDINE DERIVATIVE?

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Several compounds containing heteroatoms in 1,4 or 1,5 position to each other are effective antidepressants (Paroxetine, Reboxetine, Fluoxetine, Ifoxetine). We attempted to synthesize azetidinyl analogues of the above compounds containing two or more heteroatoms in defined distances, according to the reaction method indicated in *Fig. 1*.

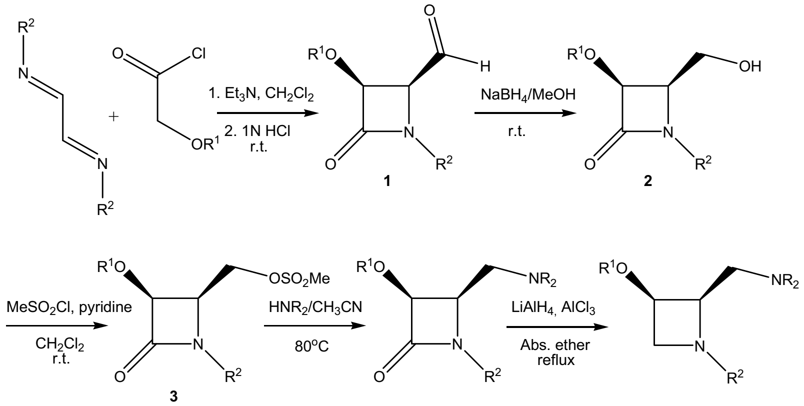

Fig. 1. Synthesis of 4-aminomethylazetidiones

Such a regioselective reaction of azetidinone derivatives containing more reaction centers is quite rare, as nucleophile substitution of the β-lactam ring results in most cases in cleavage of the four-membered ring. When substituting the mesyloxymethyl derivative (**3**), depending on the applied reagent, the starting compound reacts at two different electrophile centers, in a regioselective manner. (*Fig.2*)

According to our studies, derivatives (**3**) react with cyclic or open-chained secondary amines at the side chain, while with primer amines and ammonia at the lactam carbonyl, in the latter case giving an aziridine. When applying NaOMe as the reagent, the supposed open-chained intermediate (**5**) of the reaction (*Fig.2*) was also isolated.

As azetidinone-aziridine ring transformations like this were not widely investigated so far, we found it necessary to study the influence of the applied reaction conditions, like the solvent and the temperature, and the substituents of the starting azetidinone (**3**) on the ring transformation.

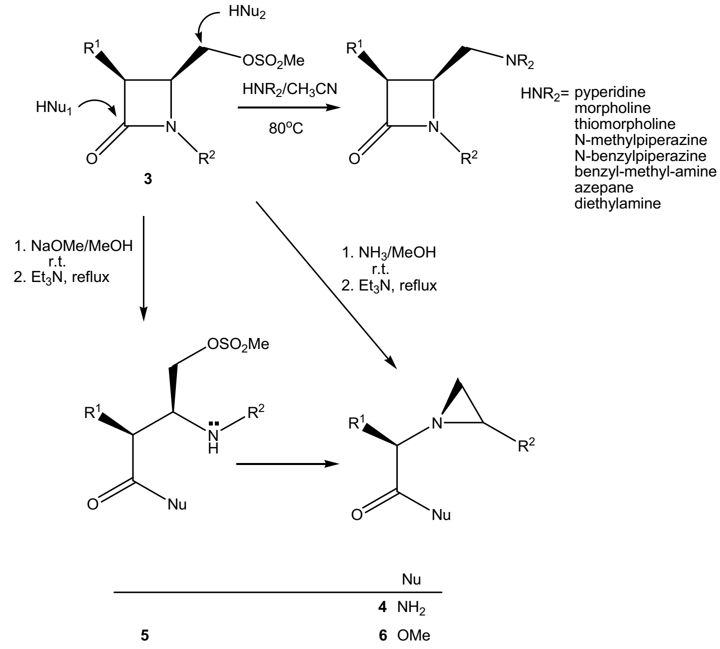

Fig. 2. Reaction of azetidinones **3** with nucleophiles

It was found that the reaction conditions influence only the reaction rate and the yields, while the substituents of azetidinone (**3**) have significant effect on the course of the reaction and on the products.

As being analogues of the recently evaluated carboxypeptidase A inhibitor 2-(2-aziridinyl)-3-phenylpropanoic acids, azetidinyl acetic acid products (**4**, **6**) of the ring transformation can be promising drug candidates.

PREPARATION OF BIMETALLIC Rh CATALYSTS BY ORGANOMETALLIC GRAFTING AND THEIR CHARACTERIZATION IN METHYLCYCLOPENTANE TRANSFORMATION

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The understanding of preparation methods and the improvement of bimetallic catalytic systems are important research areas, since the way by which the additive component modifies the properties of the pure metal is not well elucidated yet. The behaviour of bimetallic catalysts are obviously different from monometallic ones in various reactions [1], [2]. Chemical industries need more precisely prepared – so called 'tailor-made' – catalysts for cleaner, safer processes, producing less waste. Two types of 'Controlled Surface Reaction (CSR)' exist for the preparation of such tailored catalysts: redox processes [1] and organometallic grafting [1], [3]. These methods lead to specific metal – metal interactions and these catalysts appeared to be particular in various reactions, such as selective hydrogenation of unsaturated aldehydes [3] or in transformation of hydrocarbons [4], [5].

Our research aimed at developing new bimetallic M – M' catalysts, where M = Pt, Rh, M' = Ge, Sn, Pt, Rh, Au, etc... The samples were prepared in international cooperation at the University of Poitiers. In this presentation I would like to discuss in detail the developed preparation method I used during my stay in Poitiers last year. Briefly, the pre-reduced (H_2 flow, $T = 473$ K, 2 h, cooling in Ar flow) parent sample was immersed in heptane (anhydrous) solution in Ar atmosphere. After hydrogen adsorption (293 K, 1 h), the organometallic compound – $Ge(nC_4H_9)_4$ – was anchored in Ar, at 343 K for 6 h. Then the samples were washed with heptane and dried in Ar flow at 293 K for 1h and finally reduced in H_2 flow (473 K; 4 h). The preparation of Pt-Ge catalyst can be written by the following equations:

$$\mathrm{Pt-H_{ads} + Ge(nC_4H_9)_4 \rightarrow xnC_4H_{10} + Pt-Ge(NC_4H_9)_{4-x}}$$
$$\mathrm{Pt-Ge(nC_4H_9)_{4-x} + (4-x/2 \rightarrow (4-x)nC_4H_{10} + Pt-Ge}$$

The effect of different amounts of Ge added to Rh/Al_2O_3 sample was presented last year at the Department of Chemical Technology. In this presentation the effect of germanium and tin will be compared on the example of Rh/Al_2O_3 catalyst in methylcyclopentane transformation. The reaction was carried out in a closed loop reactor system in the temperature range 468 K – 513 K.

We found that the increasing amounts of Ge in the sample did not decrease noticeably the catalytic activity of the sample while adding large amounts of Sn lowered the catalytic activity. This fact may be explained by the formation Sn rich Sn − Rh surface alloy also supported by ^{119}Sn-Mössbauer spectroscopy. We found that in both cases the addition of small amount of the second metal resulted in a catalyst that behaved similar to large Rh ensembles while the presence of high amount of modifying compound caused behaviour similar to that of small Rh particles.

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SYNTHESIS OF A HEPARANASE INHIBITOR MOLECULE POSSESSING AN AZASUGAR COMPONENT

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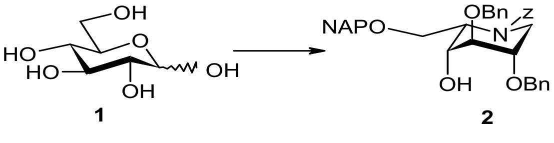
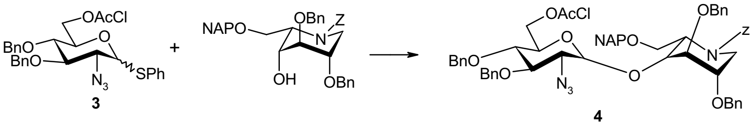
It has been recognized that tumor metastasis occurs via complex multistage processes, which involve tumor cell adhesion to various basement membrane components and degradation of the extracellular matrix and basement membranes. Glycosaminoglycans, such as heparin and heparan sulfate, are important constituents in these structures. Cleavage of heparan sulfate by the enzyme, heparanase, plays an important role in cell invasion of some malignant solid tumors through basement membranes. The expression level of this enzyme could be correlated with survival time of cancer patients. Antimetastatic cancer therapies may be based on the inhibiton of heparanase.

Heparanase is an endoglycosidase. Azasugars are well-known inhibitors of various glycosidases. As monosaccharide azasugars inhibit several glycosidases to incorporate specificity for heparanase inhibition we have designed pseudooligosaccharide derivatives mimicking the structure of heparin and heparan sulfate.

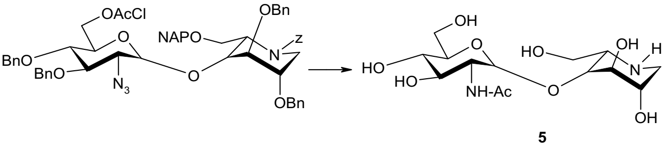
We now report the preparation of a heparanase inhibitory molecule and a protected azasugar derivative, which can serve as glycosyl acceptor in the synthesis of further heparanase inhibitors. Starting from D–glucose (**1**) a simple, efficient route was developed for the preparation of the 1,5-dideoxy-1,5-imino-L-iditol derivative (**2**).



Glycosylation of **2** with the glycosyl donor (**3**) afforded the protected pseudodisaccharide derivative (**4**).



Deprotection of **4** resulted in the free heparanase inhibitor (**5**).



INTERFACIAL INTERACTIONS IN POLYPROPYLENE/WOOD FLOUR COMPOSITES

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Thermoplastics reinforced with different natural fillers have received considerable attention in recent years because of their advantages. These composites are light, they have reasonable strength and stiffness, low cost and can be processed by conventional techniques such as extrusion and injection molding. Wood is one of the most common natural reinforcement used in thermoplastics industry. Wood flour composites are commercially attractive for high volume applications. Potential applications of these composites are automotive interior parts, furniture components, window and door profiles, fencing, siding, railing, flouring, decking, pallets, crates and marine components.

The properties of these wood flour reinforced materials, just like those of all other heterogeneous polymers, depend on four factors: characteristics of the components, composition, structure and interfacial interactions. The appropriate adhesion of the components is a basic requirement for the preparation of all fiber reinforced composites. Without sufficient interaction the matrix cannot transfer the external load to the fibers thus they cannot fulfil their function of carrying the load. Adhesion and coupling is especially important in thermoplastic matrices, because they usually contain very few reactive groups, if any. Various kinds of coupling agents are used to improve the adhesion between wood flour and polymeric materials.

In this study polypropylene/wood flour composites were prepared, and maleic anhydride modified polypropylene (MAPP) was used as a coupling agent to improve the adhesion between filler and matrix. Filler content, chemical structure of the coupling agent and the amount of coupling agent were changed in order to determine quantitative correlation between these factors and the strength of interfacial interactions. These interactions were followed by the measurement of mechanical properties in the composites. The stiffness and the tensile strength of polypropylene/wood composites increased with wood content. Introduction of MAPP increased the strength of interfacial interactions leading improved mechanical properties. Chemical structure of MAPP has also a significant effect on the mechanical properties of the composites.

INVESTIGATION OF SILICA THIN LAYERS PREPARED BY WET COLLOID CHEMICAL ROUTE

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Wet colloid chemical methods for thin film preparation offer a very promising alternative to the expensive physical techniques. Dip coating and spin coating are widely used to prepare structured coatings from nanoparticles on solid supports. Using the Langmuir-Blodgett (LB) technique truly monoparticulate layers can be prepared, and in the case of multilayers the properties of each individual layer can be influenced separately.

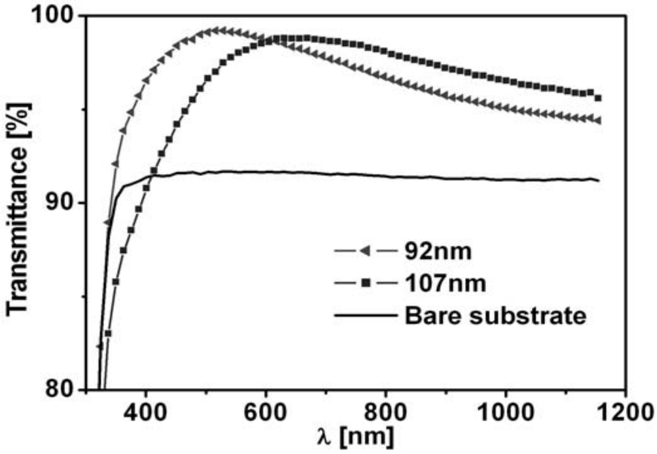

Fig. 1. Transmittance of the monoparticulate layers prepared from Stöber-silica nanoparticles of 92 nm and 107 nm diameters as the function of wavelength.

In this presentation the preparation and investigation of mono and multiparticulate thin films of Stöber-silica nanoparticles will be shown. The films were prepared by the LB-technique both from hydrophilic and hydrophobic Stöber-silica nanospheres of 92 and 107 nm diameters on glass substrate. The thin layers were investigated using Brewster angle microscopy (BAM), atomic force microscopy (AFM) and optical spectroscopy.

The BAM investigations highlighted the structural differences of the samples during continuous layer formation in the Wilhelmy film balance. The AFM images reflected continuous, highly ordered layers on the solid support, however, depending on particle hydrophobicity, unambiguous differences could be observed in the smoothness of the film surface.

The effective refractive index and the film thickness were determined from the transmission spectra (300–1200 nm) by evaluating interference peaks by Hild's method [1] and by parameter fitting. The spectra were notably different depending on particle sizes, number of layers transferred and particle hydrophobicity [3].

The monolayers showed expressed antireflection properties. The effective refractive indexes were in good agreement with the values predicted by the *effective medium approach* [2]. The film thickness values obtained for multiparticulate LB films indicated that the particles arrange themselves in a close-packed array during the preparation of LB films.

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CHEMICAL FINISHING OF LIQUID AMMONIA TREATED LINEN FABRICS

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Liquid ammonia treatment induces intracrystalline swelling of cellulose and it is very effective in enhancing certain end-use properties, such as dimensional stability, tensile strength, resistance to abrasion, crease recovery, as well as handle and appearance. Liquid ammonia treatment has also considerable influence on the rate and degree of conversion of the subsequent heterogeneous cellulose reactions. Although a number of shorter studies and comprehensive reviews have been published regarding the swelling with liquid ammonia, most of them concentrated on cotton and only a very few publications focused on liquid ammonia treatment of linen and linen-containing fabrics. Our starting assumption is that liquid ammonia treatment can be an appropriate technology for manufacturing of linen and linen-containing woven fabrics with excellent easy-care and wearing properties, as well as for producing high quality and luxurious tablecloths and apparel textiles from linen.

The objective of this research work is to evaluate the influence of liquid ammonia treatment on the properties of linen and linen/cotton fabrics. Recently, we have demonstrated that liquid ammonia treatment improves the dimensional stability, appearance after washing, wrinkling and hand-related properties, and abrasion resistance of linen and linen-containing fabrics significantly, however, the final properties of the fabrics are still unsatisfactory. For further improvement, the fabrics are crosslinked with a commercial modified glyoxal-based resin product by the wet fixation process. This presentation concentrates on the resin finishing process of the liquid ammonia treated linen and linen/cotton fabrics.

THERMAL CHARACTERIZATION OF CYCLODEXTRINS AND THEIR COMPLEXES USING COMBINED THERMOANALYTICAL TECHNIQUES

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Due to their reliability and simplicity thermoanalytical methods are frequently used techniques in the pharmaceutical technology. Unfortunately none of these techniques gives further information about the composition of the products evolved on heating. This deficiency can be eliminated using the combination of conventional thermoanalytical techniques (DTA, TG/DTG) with mass spectrometry and FTIR. The application of these simultaneous techniques allows the identification of the composition of gaseous products during degradation (fragmentation) and the evaluation of the desolvation evaporates as a function of time under the thermal process.

The application of cyclodextrins and their complexes have been of great importance in many fields as food industry, cosmetics, agriculture, chemistry, analytical chemistry and pharmaceutical technology. These substances are commonly used to prepare inclusion complexes in order to improve such important properties as stability and solubility, modify the release of drug substances and turn liquid substances, as essential oils into stable and free flowing powders. This last modification makes storage and handling easier, what is more suitable for manufacturing.

One example of the advantages of preparing inclusion complexes is observed for the essential oils, which are volatile liquids obtained from a large variety of plants, but when exposed to the oxygen of the air, light, moisture and high temperatures, they are oxidized, decomposed, become resinous or evaporate.

In the present study we aimed to carry out the thermoanalytical characterization of the cyclodextrin inclusion complexes of *Lippia sidoides* and *Mentha oil x villosa* essential oil extracts, and also to develop an experimental procedure to follow the escape of the volatile compounds from their inclusion complexes. The obtained results using conventional termoanalytical methods were compared to the results provided by the TG-MS combined technique. Complementary investigations were carried out with X-ray powder diffractometry. (The amount of the entrapped guests was determined using UV spectrophotometry.)

The application of TG-MS combined thermoanalytical techniques is an effective tool to prove the complex formation between guest and host, since both the evolution of the free and/or loosely bound guest and then at higher temperatures the entrapped guest evolving from its inclusion complex could be detected.

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MWD DESIGN WITH TUBULAR AND CASCADE REACTORS

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The aim of the work is to develop an inverse process model of a living polymerization in order to predict the production parameters from a predefined molecular weight distribution (MWD). The calculation methodology has been previously published [1], and it has been shown that the residence time distribution of the reactor and the input profiles dominate the MWD, and the dispersion effect of chain growth can be neglected. It has been demonstrated that the method with the applied simplifications results precise MWDs [2].

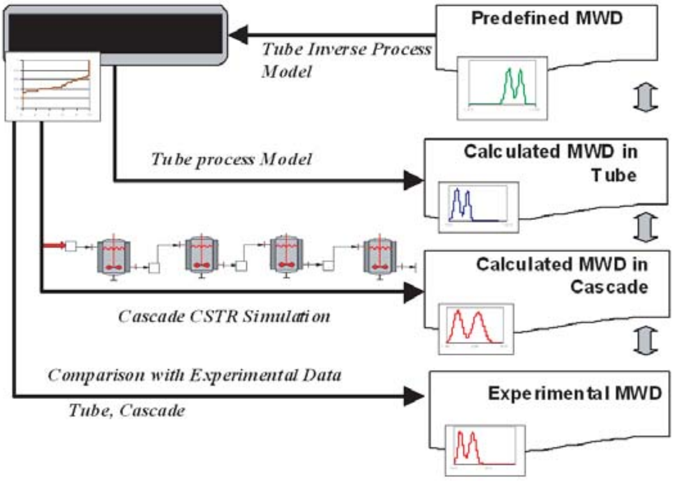

Fig. 1. MWD design strategy

The algorithm has been tested for different reactor types [3], and it has been found that periodic input functions applied for a long period of time to a continuous stirred tank reactor (CSTR) restrict the possible shapes of the MWD. For this reason, calculations have been carried out for a plug flow tubular reactor to demonstrate its much wider possibilities in MWD design. In tubular reactors, however, long chains can be deposited on the wall causing flow disturbance or occlusion. In order to solve this problem the tubular reactor is substituted with a reactor cascade.

The effect of the number of units and the input profile has been tested. 10 cascade units have been found sufficient to give a good fit to the target MWD. After experimental tests the algorithm is expected to be a continuous production alternative to the blending of polymers.

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R-GRAPH-BASED DISTILLATION COLUMN SUPERSTRUCTURE AND MINLP MODEL

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Synthesis of optimal process structures including distillation columns involves optimal design of each column as part of the structure. Thus, design of a column is also a synthesis task. The design and the optimization of a column can be executed in one step, simultaneously optimizing all the design and operation parameters, with structure-oriented process synthesis. First a superstructure which includes all the considered structures is generated. Then a mathematical model of the superstructure, usually a Mixed Integer NonLinear Programming (MINLP) problem, is formulated. Finally, this mathematical model is optimized.

Two MINLP models can be found in the literature for distillation column synthesis: VISWANATHAN and GROSSMANN, [1] and YEOMANS and GROSSMANN [2]. In the latter paper a Generalized Disjunctive Programming (GDP) model is given but an MINLP model is applied in the solution procedure. In these papers the superstructure contains by-pass streams or multifunctional units in order to maintain the possibility of representing the distillation column with different stage numbers. How easy the solution of an MINLP model of a superstructure is, has usually been analysed according to the shape (linearity, convexity, relaxation, scaling) of the equations [3].

Use of supergraphs instead of process networks decreases structural multiplicity. First FRIEDLER et al. [4] defined graphs (P-graph) for synthesizing structures. For representing structures, here we apply R-graphs, [5] which are extended bipartite graphs in mathematical sense. The nodes are identified as the input and output ports of the units; the edges are identified as the streams always connect output ports to input ports. Use of mixer or divider units is not suggested. Additionally, we defined the binarily minimal MINLP representation, [6] which applies a minimum number of binary variables to make distinction between structures. In the case of k different structures, the smallest whole number n of binary variables has to be used that satisfies $n \geq \log_2 k$.

In my presentation a new superstructure and MINLP model for distillation column synthesis is presented, which uses minimum number of binary variables in each column section for representing the different structures. R-graph superstructure representation is used for generating the MINLP model. The model is tested on the problem of separating equimolar benzene-toluene mixture. The required purity is 0.98 in both products. Constant molar overflow is assumed. The maximum number of trays is 31 in the example superstructure, the location of the reboiler (1^{st}), the feed plate (16^{th}), and the condenser (31^{st}) is fixed. Our model is compared to the models of VISWANATHAN and GROSSMANN, and YEOMANS and GROSSMANN. The MINLP model of VISWANATHAN and GROSSMANN, and YEOMANS and GROSSMANN contains 28 binary variables, but our model contains only 8. In case of a simple objective function ($\text{obj} = 5 \times R + N$, where N is number of stages, R is reflux ratio) the new model runs 30% faster than the model of YEOMANS and GROSSMANN, and 87% faster than the model of VISWANATHAN and GROSSMANN.

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DETERMINATION OF THE LIMITING FLOWS OF BATCH EXTRACTIVE DISTILLATION USING AN INTERVAL ARITHMETIC OPTIMIZER

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My research work is to investigate hybrid distillation systems; within this field I research the batch extractive distillation, the continuous extractive distillation and the reactive distillation. Using a new, interval arithmetic based optimizer I localize the singular points of the differential-algebraic system describing the process.

The batch extractive distillation (BED) can be realized in many ways. In my study I considered the simple BED, in which case the near azeotrope mixture is put in the vessel and the entrainer is added into the column. The process has two main parameters: the feed ratio (F/V), which is the ratio of the entrainer feed and the vapour in the column, and the reflux ratio (R). The feasibility domain, which is a part of the composition space from where the extractive profiles can reach the rectifying profile (*Fig. 1*), can be determined based on the phase portrait of the system of differential equations (1) describing the process. Localizing the singular points (UN, SN, S_2) this domain can be determined.

Localizing singular points means finding the roots of a system of equations. Searching for the roots of a system can be easily transformed to an optimization problem, using the sum of squares of the equations. The use of interval optimization guarantees that all solutions of a system will be found, and their existence (and in case of only one solution the uniqueness) is proved. Our optimization programme was developed at the University of Szeged. The programme uses interval branch and bound technique to minimize the objective function.

Two problems were investigated, the value of the minimal reflux ratio at zero feed, and the minimal feed rate at finite and infinite reflux ratios. The model mixture was acetone and methanol, which form minimal boiling azeotrope; the entrainer was water. The new method was successfully applied, the method found all the stable and unstable nodes, and the saddles. We found that the minimal flows depend on the appearance and disappearance of the singular points therefore to determine the exact minimal parameter values, i.e. the locus of the bifurcation points, a new condition was added.

Using interval optimization to compute the singular points of the system we could localize the minimal parameter values and found that at finite reflux

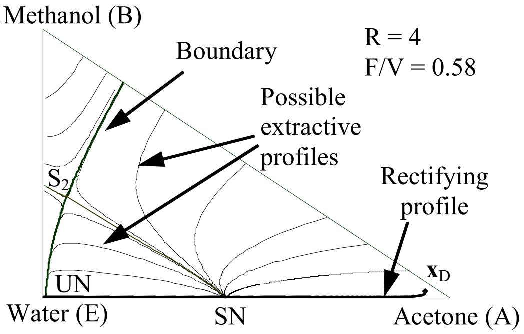

Fig. 1. Profile map and the singular points

$$\frac{\mathrm{d}x}{\mathrm{d}h} = \pm\frac{V}{L}\left(y(x, x_D, x_F, R, F/V) - y^*(x, T, p)\right) \tag{1}$$

where
x_D: composition of the distillate (specification)
x_F: composition of the entrainer
T: temperature
p: pressure
V/L: ratio of the vapour and the liquid in the column
h: dimensionless height

ratio the stable node jumps outside the meaningful composition space. Adding the bifurcation criteria the exact minimal parameter values were determined.

EXPERIENCES IN FOOD SENSORY TESTING SUPPORTED BY ProfiSens

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The researchers of the Department of Chemical Information Technology (BME) and of the Sensory Laboratory of Faculty of Food Sciences (BCU) created a profile analysis supporting software, the ProfiSens, whose main functions are the following [1, 2, 3, 6]:

- Creates kitchen lists and score sheets for the assessors,
- Collects data from the completed score sheets,
- Performs statistical data evaluation, and presents diagrams of the results.

We have used the first version of the ProfiSens since 2002/2003 academic year in research and in education as well [4, 5, 7]. The latest version was completed in summer 2004. This version was used in the evaluation of a cheese profile analysis series, where our goal was to investigate the effect of different storing circumstances on sensory properties of the most popular cheese in Hungary, the Trappist cheese [8]. In the shopping centres there are often this type of cheese on sale. Customer usually buy a large amount of it, and a part of it will be deep-frozen stored. It is well-known for cheese-experts, that deep-frozen stored cheese loses a lot of its good sensory properties.

In this paper I show the results of two cheese profile analysis series, one of them covers a 3-weeks storing experiment, the other one was carried out on the Íz-Feszt Exhibition (BCU, October 8–10), and compares two different Trappist cheeses, an ‘on sale’ type and a ‘not-on sale’ type. Discussing the profile analysis results of these two cheese-experiment series I show the newly developed parts of the ProfiSens software, as well.

I wish to express my gratitude to the Veszprémtej Ltd, supporting our cheese experiments, to my PhD supervisor, Klára Kollár-Hunek, to the leader of the Sensory Laboratory, Zoltán Kókai, to the head of Postharvest Department (BCU) Gábor Kollár and to the voluntary student researcher, Eszter Papp.

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FRACTIONATION OF CORN FIBER TO PRODUCE BIOETHANOL AND CORN FIBER OIL

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Corn Fiber is the by-product of the corn wet milling procedure, it adds up to 10% of the processed dry corn. It contains several valuable components, like starch, cellulose, and corn fiber oil. The fiber oil contains cholesterol-lowering and antioxidant substances. However, corn fiber is recently utilized as a component of the so called Corn Gluten Fiber (CGF), which is a cheap feed for cattle. Corn is the most convenient and rational substrate for bioethanol production in the temperate zone, so its production will prospectively increase. The steady demand for CGF will probably cause the deflation of corn fiber. Thus, many scientific papers deal with alternative, more rational utilization of corn fiber.

We measured the composition of corn fiber and proved that the usually reported oil and lignin contents are not accurate. The determined composition of corn fiber is: 15–22% starch, 40% hemicellulose, 12–15% cellulose, 15% protein, 5% oil, 1% ash, and minor components (lignin, nuclein acids, etc.). We developed a technology for utilizing corn fiber, which consists of the following steps:

1. The wet, SO_2-steeped (native) corn fiber is treated with water at the temperature of 120 °C, thus the starch is extracted.
2. The screened fiber is treated with 1% dilute sulphuric acid at 120 °C, thus the hemicellulose is extracted.
3. The screened fiber is treated with cellulase enzymes (enzmye power: 5 IU/g dw.), thus the cellulose is extracted.
4. Screening in two steps: a fine, white powder (lipoprotein), and a coarse, brown fiber can be separated.

The advantages of the technology as follows:

1. The starch is extracted without any chemical reagents, in a simple way.
2. The second step (dilute acid hydrolysis) pretreats the cellulose, thus decreased enzyme power is enough to reach high ($>$ 90%) conversion rate in the third step. The optimization of the second and the third steps resulted in low sulphuric acid and cellulase enzyme demand. The advantages of dilute acid pretreatment were previously reported (‘Dilute acid pretreatment of corn stover at long residence times’, G. KÁLMÁN et al., CABEQ Journal, 2002.)

3. The separated fine fiber adds up to about 10% of the original dry corn fiber, and contains 45% corn fiber oil. Such a high concentration of corn fiber oil was previously not reported.

Thus the determined technology can make the extraction of corn fiber oil economical. The technology yielded two and a half times more corn fiber oil than direct extraction of corn fiber. The reason of this is that the lipoprotein and lipopolisaccharide fractions were hydrolyzed during the second and third steps, thus all lipids became accessable for the extracting agent. Gas chromatografic analysis showed that the technology yields more phytosterols then direct extraction. The coarse fiber consists of unhydrolyzed polisaccharides, lignin, and some minor components (ash, etc.). If the cellulose content of the coarse fiber is high, it is recommended to recirculate it to the beginning of the third step (cellulose hydrolysis).

RESOLUTION OF DIFFERENT PHENYLISOPROPANOL DERIVATIVES

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The asymmetric compounds formed in the common chemical syntheses are usually obtained as racemic molecules. As the racemic compounds are the mixtures of two enantiomers, the separation of these enantiomers is very important from both scientific and practical point of view. The enantiomers of the biologically active racemic compounds have different biochemical properties, thus the separation of the more favourable enantiomer has an increasing importance. Nowadays, the most frequently used method among the preparation techniques of optically active compounds is the chemical, especially the optical resolution *via* diastereoisomeric salt formation using the improved method described by POPE and PEACHEY [1]. The systematized investigation of the existing methods [2] and the development of new ones (e.g. the formation of different molecular complexes [3] as well as coordination complexes [4]) are dynamically progressing research areas. In the last years the environmentally friendly and very selective biocatalysis became more and more important.

We examined the separation of the enantiomers of phenylisopropanol derivatives substituted in the aromatic ring using the methods of the enzyme-catalysed kinetic resolution and the chemical resolution *via* diastereoisomeric salt formation (*Fig. 1*). We found that when the appropriate solvent, enzyme and acylating agent have been added to the racemic alcohol and the reaction mixture was stirred for a given time at room temperature, the enzyme stereoselectively acylated the (R)-enantiomer. The (S)-enantiomer remained as free alcohol.

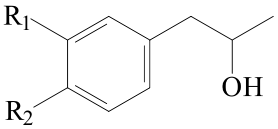

Fig. 1. Phenylisopropanol derivatives

In case of the resolution *via* diastereoisomeric salt formation we prepared the monoesters of the phenylisopropanol derivatives (maleic acid monoester, phthalic acid monoester and succinic acid monoester) (*Fig. 2*). Different chiral bases have been added to the monoesters and the rate of the separation was examined.

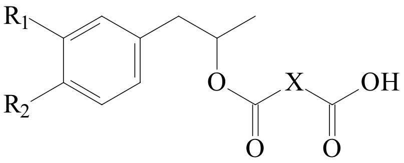

Fig. 2. Monoesters of phenylisopropanol derivatives

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IMPROVEMENT OF THE STATISTICAL MODEL OF STABILITY STUDY

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The purpose of the stability studies of pharmaceutical products is to provide evidence on how the quality of a drug product varies with time under the influence of a variety of environmental factors. With the knowledge of the behaviour and properties of the drug product the shelf-life can be established, which is an essential condition for the registration and the marketing of the drug product.

During the stability study at least three batches should be tested. The tablets are stored under adequate conditions and periodically assayed for their physical, chemical and biological attributes. For the statistical evaluation the ICH Guideline recommends the analysis of covariance (ANCOVA) model applying the batch factor as fixed effect and the degradation rate as covariate [1].

The improvement of the ICH Guideline model is a controversial question in the literature. Connected to this field we studied two issues.

1. The statistical method of the Guideline leaves out of consideration the extra variability caused by different dates of analysis. Thus, a new factor, the dates of analysis is added to the model [2]. The modified model divides the original error term into two parts: the reproducibility caused by the different analytical circumstances, considered as a random factor, is separated from the remaining variability consisting of the inhomogeneity of the tablets and the repeatability of the analysis.
   It must be highlighted that we have two time scales. The date scale is fixed to the calendar time and refers to the random effect attributed to the interval-to-interval variability. The storage period is defined as the time interval which has passed from the start of the stability study and belongs to the degradation rate. The two time scales do not coincide when the batches are put to storage at different time points.
2. The effect of the different batches is handled in a contradictory way in the Guideline. In the statistical model the batch factor is considered as a fixed effect, but according to the other part of the Guideline the estimated shelf-life should be applicable to all future batches manufactured under similar circumstances. This later requirement corresponds to the random effect approach. In this case the random effect approach is more justified, because our

aim is not to compare the batches involved in the stability study, but to draw conclusions for the future batches. Applying the random effect approach a random coefficient model is given, which fits linear function to the data with different slopes and intercepts.

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KINETICS AND PHOTOCHEMICAL STUDY ON THE ATMOSPHERIC FATE OF FLUORO-ALCOHOLS AND ACETONE

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As a result of the Montreal Protocol (1987), the fluoro-alcohols have gained an increasing importance proposed as replacement industrial materials for freons. These compounds degrade in the atmosphere via a series of reactions initiated by OH radicals, thus their atmospheric lifetime is essentially determined by the reaction rate coefficients with OH.

The kinetics of the reactions of OH radicals with ethanol as well as with its di- and trifluoro derivatives have been studied by using the laser flash photolysis-resonance fluorescence experimental technique. Application of this method involves the generation of free radicals by the laser flash followed by monitoring of the concentration change of the transient free radicals on the μs or ms time scale. The experimental parameters have been varied in a wide range of conditions what is a prerequisite for obtaining reliable rate coefficients. The rate coefficient value we determined for the OH + 2,2-difluoro-ethanol reaction is the first result obtained by direct kinetic means.

Acetone – next to methane – is the second most abundant organics in the atmosphere. In contrast to fluoro-alcohols, its atmospheric lifetime is determined not only by the reaction with OH, but also photolysis. The significance of photolysis is of particular importance in the upper troposphere and lower stratosphere and in the tropical region. Although the photochemistry of acetone has been one of the most studied photochemical systems, its renewed atmospheric interest has emerged new questions concerning its photochemistry at low temperature and in the presence of high oxygen and water vapour concentration. The answer on these questions has important implications for the whole chemistry of the atmosphere.

As a first step of a detailed research program, the UV-absorption spectrum of acetone has been determined in the absence and also in the presence of water vapour. An experimental method has been developed for the determination of photolysis quantum yield of acetone in synthetic air. The photolysis light source was an excimer laser operated at 248 nm (KrF line). The quantum yield has been obtained by measuring the rate of light absorption and that of the acetone consumption by GC. Within the experimental uncertainties, the quantum yield has been found to be unity. In contrast to a recent report in the literature, the water vapour apparently has no effect on the photolysis.

The work to be presented has been a contribution to the EU Integrated Project SCOUT-O3.

THE POTENTIAL ROLE OF dUTPase INHIBITION IN CHEMOTHERAPY

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The homotrimer deoxyuridine triphosphate nucleotidohydrolase (dUTPase) is unique in prevention from the mistake of uracil incorporation into DNA. The enzyme catalyzes pyrophosphorolysis of dUTP, the products are dUMP and inorganic pyrophosphate. By means of the catalyzed reaction, the enzyme regulates intracellular dUTP levels and produces the precursor for dTTP. Lack of dUTPase leads to an elevated dUTP/dTTP ratio which results in highly uracil-substituted DNA. Uracil-DNA induces the transformation of base excision repair into a hyperactive futile cycle leading to chromosome fragmentation and finally, thymine-less cell death [1].

Comparative structural studies of *E. coli*- and *Drosophila melanogaster* dUTPases (as prototypes for pro- and eukaryotic enzymes) by a variety of methods have revealed the followings:

(i) Differential schedule of ordering of the C-terminus along the catalytic cycle: ordering only in the presence of the triphosphate substrate-analogue in *E. coli* dUTPase, but ordering in the presence of dUMP, dUDP and dUTP-analogue in *D. mel.* dUTPase.

(ii) Structural effect of Mg^{2+} in the absence of nucleotides, observed exclusively with the *D. mel.* enzyme, argues for a structural metal-binding site only in eukaryotic dUTPase.

(iii) Allosterism in the *D. mel.* enzyme: nucleotide binding induces conformational change at a site 20 Å away from the ligand binding pocket.
The results indicate that antagonist design against dUTPases should take into account species-specific differences [2]–[4]

First, the substrate dUTP was replaced by the substrate analogue α,β-imino-dUTP, as antagonist. Imino analogues of nucleotide phosphates are commonly used as isosteric mimics of the natural substrates. The lower electronegativity (EN) of the nitrogen atom results in less reactivity of the phosphate ester imino analogues. It was demonstrated that dUTPase is capable of hydrolyzing the imino-linkage of α, β-imino-dUTP, while no detectable hydrolysis of the $\beta-\gamma$ bond occurs [5]. This substrate analogue is not a good antagonist, but it seems to be useful for structural investigations of dUTPases. Crystal structures of substrate (dUTP and α, β-imino-dUTP) and product complexes of wild type and mutant dUTPases were determined to reveal the catalytic mechanism of phosphate ester hydrolysis by dUTPase [5].

Methylene analogues of nucleotide phosphates are also used as isosteric mimics of the natural substrates. The EN of the oxygen replacing carbon atom is lower than the EN of nitrogen, so the α, β-methylene-dUTP can be a less hydrolizable, better antagonist of the enzyme, than the imino analogue. The crystal structure shows that the conformation of the phosphate chain at the active site of dUTPase is different in the methylene-derivative as compared to the substrate dUTP or the dUDP ligand. The location of the α-phosphorus is shifted by 4 Å where this atom is no longer available for attack from the catalytic water molecule.

The dUTPase gene silencing by RNA interference can be a good method to eliminate dUTPase functioning in human cancer cell lines, like HeLa cells. Four different small interfering RNAs (siRNAs) were designed for degradation of dUTPase mRNA. The siRNAs were formed in the cells by DICER from short hairpin RNAs (shRNAs) after transfection of an expression vector containing the corresponding gene sequence. The elimination of the mitochondrial isoform of dUTPase from HeLa cells caused phenotypical change.

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ECOTOXICITY TESTING FOR RISK ASSESSMENT OF CONTAMINATED SOILS

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The harmful effect of the contaminants on the ecosystem is measured by the science of ecotoxicology. To get a realistic view on the actual risk of the contaminant depending on its bioavailability, it is necessary to complement the chemical analysis with biological methods and ecotoxicity testing. The ecotoxicity testing methods consider the interaction between contaminants, soil matrix and biota. The integrated approach can be used for risk assessment, establishment of the target quality criteria, decision-making on the best possible technology and planning of a monitoring system during and after site remediation.

Two approaches are introduced for the characterization of the actual risk of the soil-contaminants. Some tests use water- or acidic water-extract of the soil to get information about the effect of the toxicants on the environment. These tests give a realistic picture only on the effects evolved upon the ground water but not in the whole soil. Direct contact ecotoxicity tests and their applications have been developed recently (GRUIZ, [2]; BISPO, [1]; VAAJASAARI, [3]). These solid phase methods give information about the whole soil and ensure direct contact between the soil and the testorganism.

The aim of this study was to assess sensitivity of several ecotoxicity testing methods in case of three different contaminated soils. Besides the standardized or widely used methods some new, interactive ecotoxicity tests have been developed and introduced in our laboratory, which are useful for the estimation of the risk of contaminated soils.

Tetrahymena pyriformis, a protozoon has been used as testorganism to produce a new, sensitive ecotoxicity test applied for soil suspension. This testorganism is a primary consumer in the food chain; therefore it has an important role within the methods that use microbial and animal testorganisms.

A new microcosm test has also been developed. The risk of the contaminated soil is estimated by the nitrification activity of the soil microflora. In this test the nitrification activity is ensured by an uncontaminated reference-soil. The decrease of this activity can be measured when the reference soil as a ‘testorganism’ is mixed with contaminated soil in different concentrations.

On the other hand we have compared the sensitivity of the interactive methods to some standardized methods applying soil extract. The testorganisms are as follows: *Vibrio fischeri, Azotobacter agile, Pseudomonas fluorescens, Tetrahymena pyriformis, Folsomia candida, Sinapis alba*.

The results of the experiments proved that both of the new methods are suitable for the requirements of ecotoxicology: reliable, sensitive, reproducible, fast and cheap. The main advantage of the direct contact between soil and testorganisms is that the bioavailability of the contaminant is included into the result. The interactive ecotoxicity tests indicated the effect of the contaminated soils on the ecosystem more effectively than the tests using soil extracts.

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THE SODIUM LOSS AND TRANSPORT THROUGH THE WALLS OF THE CERAMIC DISCHARGE TUBE OF HIGH PRESSURE SODIUM LAMPS

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The High Pressure Sodium lamps belong to the group of High Intensity Discharge lamps, nowadays they are considered to be a very advanced lamp type. HPS lamps have an advantage over the incandescent lamps because they utilize a higher portion of the consumed electrical energy. Its light efficiency can reach even the 150 lumen/W value, while its rated lifetime can be 28500 hours. This lamp is a special discharge lamp in which the light is emitted from a discharge zone formed between two tungsten electrodes. The discharge is produced in an arc tube, which is made of Al_2O_3 ceramics [1]. The arc tube has to resist to the additives in the discharge, to the hot sodium and metalhalogen vapors in the lamp ($1100 - 1200°C$). Neither the corrosion of ceramic arc tube, nor the processes leading to the bonding of the additives are allowed during the use of the lamp. Due to sodium loss the composition of additives changes in the discharge, the discharge voltage increases and so the emitted light intensity decreases and the lamp will switch off [2].

A black precipitation appeares on the internal surface of the glass outer jacket in the lamps burnt for several thousand hours. The scope of my work was to study the cause of this precipitation related probably to the sodium transport through the walls of the arc tube. For this purpose ceramic arc tubes originating from lamps burnt for different times were examined by XPS (X-ray Photoelectron Spectrometry) and SIMS (Secunder Ion Mass Spectrometry), in order to determine the amount of sodium accumulated on the internal and external surface of the ceramic wall. As the mechanism of sodium loss is complex, model tests were also needed to map the diffusion mechanism of sodium.

According to the XPS measurements high amount of sodium accumulates on the internal surface of the arc tube during the operation of the lamp. Sodium was identified also on the external surface of the arc tube suggesting the sodium diffusion through the wall. The indentification of the sodium source for the glass outer jacket needs further analyses as the glass itself also contains sodium. In the middle of the glass outer jacket surface aluminium was found too. In the edge of the glass outer jacket aluminium could be indentified, but its amount was smaller than that in the middle. The reason of this effect can be the evaporation of the aluminium(sub)-oxide(s) in the middle of the arc tube.

The planned experiments to find out the mechanism of sodium diffusion in Al_2O_3 are in progress. From the measured sodium concentration profile I want to determine the mechanism of sodium diffusion, the diffusion coefficient, and its temperature-dependence.

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INVESTIGATION ON OSMITIC DEHYDRATION OF APPLE

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Osmotic dehydration (OD) is a water removal process. It is a pre-drying step in the production of dried fruits. It gives the possibility to form ‘minimal processing’ type production by correct optimization of the OD factors. The theoretical background of this technological step is described by the physical laws of diffusion and osmosis. The conventionally used osmotic solutes are the sucrose, glucose and fructose [1].

The aim of this study is the investigation of the use of fructo-oligosaccharides (*Fig. 1*) that are important from dietetics aspect.

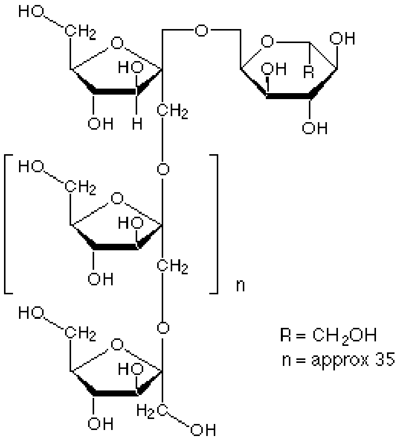

Fig. 1. The structure of fructo-oligosaccharides

During this work the theoretical background of OD is developed by the mathematical description of the transport processes in the fruit tissue. In the beginning of the preliminary experiments it was proved, that solving and diffusion rate of fructo-oligosaccharides and sucrose are in the same order ($10^{-9} - 10^{-10}$ m^2/s).

These results give the possibility to use them in the OD without any technological difficulties [2].

In the second phase of our research we investigated the technological factors of conventional blanching and atmospheric osmotic dehydration on the sugar content, total solid content, texture and organoleptic properties of the products. Sucrose and fructo-oligosaccharides behave similarly by the changes of the factors, meanwhile the degrees of changes are different. We studied also microwave, vacuum and microwave-vacuum treatments as alternative pre-treatment methods. The measured parameters show significant difference at 95% confidence level. To verify the utilization of fructo-oligosaccharides in the food industry we made different fruit products, such as prunes, plum jam, plum preserves and sour cherry juice. The textural and organoleptic properties of the products were as good as that of the control, which were made with sucrose. On the basis of these results it can be established that fruit products can be prepared with the use of fructo-oligosaccharides. These products can contribute to the health protective human nutrition.

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THE EFFECT OF COMPATIBILIZER OF ISOTACTIC POLYPROPYLENE (iPP) AND POLYAMIDE-6 (PA-6) BLENDS BASED ON iPP AND ITS β-NUCLEATED FORM

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In the pervious study iPP/PA-6 blends were prepared. The iPP component was applied as matrix polymer. The phase structure of the iPP/PA-6 blend is heterogeneous. In the present study iPP/PA-6 blends and their β-nucleated forms were prepared, using iPP functionalized by maleic anhydride (MAPP) as compatibilizer. The melting and crystallization characteristic, as well as the structure of the blends were studied by differential scanning calorimetry (DSC), and polarised light microscopy (PLM). According to our previous study [1], the formation of β-iPP was suppressed in the presence of PA-6, but some details of this phenomenon remained unexplained. For example, individual β-spherulites can be observed in the iPP/PA-6 blend. However, in the presence of MAPP compatibilizer predominantly β-iPP matrix was formed. The main reason of this effect was made clear in this study, namely that the nucleating agent was encapsulated selectively by the polar PA-6 phase.

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DEVELOPMENT OF CONTINUOUS MEASURING METHOD FOR ADSORBABLE ORGANICALLY BOUND HALOGENS IN WATERS (AOX MONITOR)

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AOX = **a**dsorbable **o**rganically bound **halogens**.

This parameter of water quality is an analytical convention, which can describe the contamination of waters.

This measuring procedure can determine the amount of chlorine, bromine and iodine content in the adsorbable organic components (organic fluoro compounds can not be measured in this way).

AOX is a very dangeorous group of materials because it has toxic, mutagenic and carcinogenic effects and strong bioaccumulation property in fat containing tissues. They are generated in almost every reaction of organic matters and reactive halogens (even in household cleaning by hypochlorite containing fluids). The reaction products can go through the waste water treatments to the rivers and lakes. So we have to measure it not only at the end of pipes, but in rivers and lakes too. If our drinking water comes from river or lake we drink these dangerous materials. Even if there is a clean water source not polluted by industrial effluents, its organic trace components will produce AOX components when the required chlorination (desinfection) is applied before usage in a tap water pipe-line network.

> Up to date there is not any continuous mesaurement method of AOX. We have not any realtime data on the amount of AOX what we are drinking day by day.

Only a laboratory method is known, which takes long time, and it is a complicated measuring procedure. There is a standard (Determination of adsorbable organically bound halogens (AOX), EN 1485: 1996) which describes the measuring method.

We have studied this procedure and designed a revolutionary new technique to establish a miniaturized and automatizable method, which is principally a variation of the standard method. In this invention we introduce a novel, miniature and very effective plasma incinerator process which runs with low power consumption and uses ambient air instead of noble gases. The electrochemical detector is also redesigned to fit to the small sample amount used in the absorption unit.

Our instrument has two parts, a microcoulometer (which can absorb the halogen-acids coming from the incinerator unit), and an incinerator cell.

While the laboratory microcoulometer can measure 0.1 μg to 300 μg chloride, our microcoulometer can measure near *500 pg* chloride.

We have made:

- a microcoulometer
- an assistant utility integrated with computer
- control software for this integrated system.

Next R&D step: absorption and incinerator cell.

The target specifications for the prototype AOX Monitor:

- Measurement frequency: 1–6 measurement/hour (depends on concentration)
- Measuring range: 0.1–1000 μg halogen/litre water
- Unattended period: 7 days

DYEING OF POLYESTER WITH DISPERSE DYE – CYCLODEXTRIN INCLUSION COMPLEXES

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The long range industrial application of cyclodextrin is one of the successful stories of the last decades. Initially cyclodextrins have only been applied in the pharmaceutical industry.

Recently, however, their use was introduced in the cosmetical-, food- and textile industry too.

Among the requirements in the industry the environment-, processing- and customer-friendly production has become dominant.

The importance of inclusion complexes formed by cyclodextrins are increasing by time.

Disperse dyes are practically insoluble in water. Additives or/else application under high pressure used to be necessary. Most of the additives are risky to the environment, in the processing and for the consumers. Cyclodextrins however are environment-friendly products and do not bring about any risks to the producers and consumers.

If inclusion complex formation between cyclodextrins and disperse dyes might be expected and if the produced complexes would show satisfactory water solubility new dyeing technology for hydrophilic and lipophilic fibers might be elaborated.

Three disperse dyes of different chromofor groups (C.I. Disperse Orange 30, C.I. Disperse Yellow 42, C.I. Disperse Red 60) were the target of our studies.

Subsequent to preliminary studies the randomly-methylated-β-cyclodextrin (RAMEB) proved to be most suitable for the planned experiments.

Solubility isotherms have been established at five different temperatures beside constant dye content and six different RAMEB concentrations. Based upon the solubility isotherms the most suitable dye to RAMEB ratio could be calculated and produced for the dyeing experiments.

Six dyeing procedures have been performed on polyester fabric samples in dye baths containing optimized RAMEB to dye ratios under atmospheric pressure at 98 °C as well as under elavated pressure at 130 °C.

The results of the dyeing experiments have been evaluated after comparison with the respective fabric samples dyed according to traditional disperse dyeing procedures.

EFFECTS OF SULFADIAZINE ON BIOLOGICAL MODEL MEMBRANES

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Sulfadiazine is one of the veterinary drugs used in the treatment of bacterial infections and toxoplasmosis. Sulfadiazine can occur in different compartments of the environment (e.g. in soil and groundwater) and can affect the microorganisms harmfully. Especially the membranes of bacteria are damageable against this 'foreign' substance.

The toxic effect of sulfadiazine on the cell membranes was studied on liposomes as model systems. The dipalmitoyl-phosphatidylethanolamine(DPPE)/dipalmitoylphosphatidylglycerol(DPPG)/water and the dipalmitoylphosphatidylcoline (DPPC)/water systems were investigated for mimicking the membranes of bacteria and human cells.

The thermotropic behaviour, the structural characteristics and the surface morphology of the lipid/sulfadiazine/water systems were examined in wide lipid/sulfadiazine molar ratio range [5/1–1000/1] by using differential scanning calorimetry (DSC), small and wide angle x-ray scattering (SAXS, WAXS) and freeze-fracture (FF).

The sulfadiazine caused significant alteration in the lamellar structure depending on the lipid/sulfadiazine molar ratio as it was observed by SAXS, however, these changes did not indicate defined characteristic changes in the layer periodicities. The changes in the thermotropic behaviours are more expressed; a new phase transition (located at about 65 °C) appeared. The changes in the WAXS curves correlated with the thermotropic effects indicating that the sulfadiazine did not have a strong effect upon the lipid packing inside the double layers of the liposomes. The morphological investigations revealed that the characteristic regular spherical shell forms are drastically affected by the presence of the sulfadiazine as beside the spherical liposomes non spherical but layer-structured domains begin to appeare in the electron micrographs.

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INVESTIGATION OF DIFFERENT HYDROCARBON COMPOUNDS

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Steam cracking of hydrocarbons to olefins is the largest petrochemical process. The chemical reactions in the course of the steam cracking are well known; the maximum olefin quantity can be retrieved from the usual feedstocks. Because the environment protection comes to the front, more types of feedstock can be applied in the pyrolysis industry: the huge amount of plastic waste is a potential feedstock because of its high energy and mass content. This is lost by the usual waste treatment processes (landfill, burning). These waste treatments are becoming more and more expensive due to the rigorous regulations.

In our earlier work [1] we built a laboratory steam-cracker. The apparatus is appropriate to steam-crack complex mixtures: a gasoline sample which was stemmed from an industrial plant was steam-cracked under different conditions; the results followed the trends found in literature. We examined another gasoline which was cracked at an industrial plant as well and accomplished a comparative study.

Polyethylene (PE) and polypropylene (PP) compose the largest amount of wastes. Actually PE and PP are mixtures of straight chain paraffin resp. branching paraffin molecules. Paraffins, naphtenic compounds and aromatics compose the usual feedstock; the paraffins produce the most olefin. A plausible idea is to recycle the PE and PP wastes with steam-cracking. However, steam-cracking of materials with such consistency that can not be converted to low viscosity fluid raises some issues.

First of all we have to find a method to get the material into the reactor. We built in a heatable storage vessel and a pump. The apparatus was appropriate to steam crack solid paraffins (mol mass=360-480 g/mol). The paraffins produce olefins at high yields.

In the TVK at the polymerization plant a low polymerization grade PE arises (LPPE). A relative low viscosity fluid can be obtained if LPPE is mixed into heated gas oil. The viscosity of the fluid which contained 10 m/m% LPPE was low enough to dosage into the reactor. The parameters were varied and at every point pure gas oil was steam-cracked as well. The result showed that the yields of the mixture and the pure gas oil were scarcely different. Coking and depositing inside the reactor were not observed.

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STUDIES ON β-LACTAM SYNTHESIS VIA 4-*exo* RADICAL CYCLIZATION USING CuBr-COMPLEXES FROM SECONDARY α-BROMO ENAMIDES[1]

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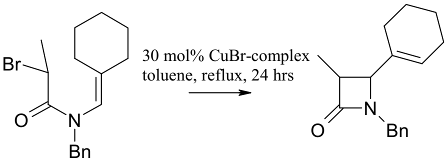
The β-lactam ring moiety is contained in a large number of biologically active compounds, mainly ones with antibacterial effects. The use of radical cyclization methods to prepare heterocyclic compounds, particularly γ-lactams, is widespread. Cyclization of secondary α-halo-enamides with a method using Bu_3SnH proved to be efficient [1], but suffers from technical difficulties (e.g. toxicity of the reagents, difficulty in workup). In the case of tertiary α-halo-enamides, cyclizations mediated by CuBr-complexes gave extremely good yields (96–98%) with the additional advantage of simple workup, ambient reaction conditions, short reaction times and relatively cheap reagents [2]. However, the usage of this method for secondary α-halo-enamides appears in the literature only in one single case (*Fig.1*) [2].



Scheme 1.

Fig. 1.

We have therefore planned to investigate the scope and limitation of the applicability of the copper mediated cyclization method to this type of compound. A general overview of the expected reaction is depicted in *Fig.2*.

The following enamides were prepared, and cyclized under various conditions, (see *Fig. 3*).

If we compare the results achieved using secondary α-bromo enamides to those achieved using tertiary α-bromo enamides, we see that we need higher temperatures and longer reaction times. Moreover, the probability of side reactions

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[1] This research was done at the Chemistry Department of University of Warwick under supervision of A. J. Clark.

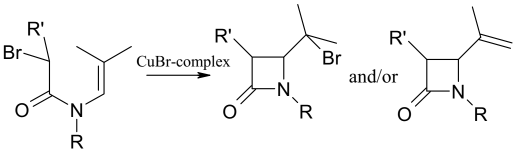

Fig. 2.

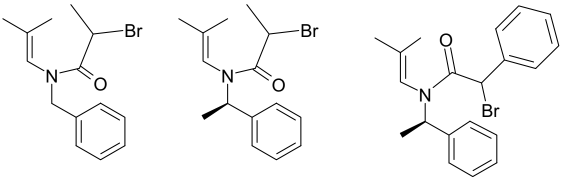

Fig. 3.

is higher. These observations are consistent with the fact that the stability of secondary radicals is less than that of the tertial radicals. It was also found that using 1 equivalent of CuBr-complex rather than catalytic amount, the reaction times become shorter and side reactions decrease. In two cases the reactions provided the expected β-lactams with high stereoselectivity favouring the *trans* isomers with medium yields. In none of the cases did we observe the formation of unsaturated β-lactams (cf. *Fig. 1*). In case of the phenyl substituted enamide, we found that the reaction took place on a different pathway and preferred the 5-*endo* rather than the expected 4-*exo* cyclisation.

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CONVERSION OF CYCLOALIPHATIC COMPOUNDS ON ALUMINA SUPPORTED Ir CATALYST

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Nowadays there are only a few percent of petroleum fractions which are used in original, non-transformed form as fuels. The steadily growing output of engines requires the production of high quality fuels, gasolines with high octane number and gas oils with high cetane number.

In gasoline production the high octane number is achieved by using reformate gasoline rich in aromatic compounds, and/or alkylate rich in isoparaffins.

The aromatic compounds are more or less toxic because of their carcinogenic effect. The environmental protection through the ever stricting rules forces the producers that they have to replace aromatic compounds with other high octane number materials, like isoparaffins and ethers. These compounds are harmless in comparison with the aromatics. The so-called straight-run gasolines contain naphtenic compounds in significant amount, those, which have longer side-chains should be converted into isoparaffins. The octane number increase is larger with longer side-chains.

The EXXON Research and Engineering Company conducted investigations, the results are patented, which proved that such conversion is possible and can be of economic advantage. (Int. Appl. Nr. PCT/US 96/14282, PCT/US96/14284). The main component of the catalyst was Ir beside other alloying metals, the supports were silica, alumina and zincoxide.

On the basis of these results we started our examinations in a laboratory reactor built by the experts of MOL Company.

The main part of this apparatus is the high pressure tubular reactor heated by a three-zone furnace. The hydrogen stream and the reactor pressure is automatically regulated. The experiments were carried out with a 1% Ir on alumina catalyst which was prepared in our laboratory with the impregnation of commercial alumina with $IrCl_3$ solution. The catalyst was reduced and activated in the reactor in hydrogen stream at 500 °C. The test material was methyl cyclohexane, the reaction temperature was $200 - 250$ °C, the liquid feed rate $0.1 - 0.2$ cm^3/min. Measurable conversion was at $240 - 250$ °C and at 0.1 cm^3/min liquid feed rate with 5 g catalyst.

According to these results the methyl cyclohexane was cleaved primarily at the secondary carbons affording 2- and 3-methyl hexane in more than 30%. The amount of 3-methyl hexane is the more, what means that the C-C bond being more

Table 1.

Reaction conditions				Main products						
entry Nr.	Temp. °C	Liquid feed rate cm^3/minute	H_2 ml/min	2Me-pent %	3Me-pent %	2Me-hex %	3Me-hex %	3Et-pent %	n-heptán %	Me-chex %
5	240	0.1	60	2.1	1.8	10.1	18.8	0.2	0.7	65.9
8	240	0.15	90	1.5	1.3	7.4	13.6	0.1	0.5	75.2
9	250	0.1	60	4.8	3.7	16.4	29.1	0.6	1.3	42.4

distant from the tertiary carbon was cleaved preferentially. 2- and 3-methyl pentane were also arisen in 4–10%, what presumes the simultaneous cleavage of two C-C bonds in the same molecule with the exit of methane.

Summarizing, it is worth to carry on further research with Ir catalyst, after optimizing the reaction conditions, and further substrates, support materials or alloying components can be investigated.

THE EFFECT OF THE NANO-ENVIRONMENT ON THE ACTIVITY OF SUPPORTED Au CATALYSTS

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In addition to the tin modified supported noble metal (Pt, Pd) catalysts gold supported on various metal-oxides has also high activity in low temperature (-40 – $+100$ °C) CO oxidation. It is suggested that CO oxidation takes place on highly dispersed gold nanoparticles (particle size: 2–6 nm), however, the role of the metal-oxide support is not really understood.

The aim of our studies is the elucidation of the role of oxides upon using nanogold supported on modified alumina support and finding a relationship between the method of preparation, structure and activity.

In this contribution we shall report on the influence of MgO and different transition metal oxides on the activity of Au/Al_2O_3 catalysts in CO oxidation. Two types of catalysts were prepared and tested: (i) gold on Al_2O_3 support modified by MgO, MnO_2, CoO, Fe_2O_3 and gold on different spinels ($MgAl_2O_4$, $MnAl_2O_4$, $CoAl_2O_4$, $FeAl_2O_4$).

Diluted solutions of the nitrates of the modifiers were used by adsorption, followed by drying and calcining to prepare Al_2O_3 modified by MgO, MnO_2, CoO and Fe_2O_3. Nitrate solutions of Al and the corresponding metals as well as the method of coprecipitation, followed by drying, calcining were used to prepare the spinel type supports. The structure of the support materials was investigated by XRD and BET methods. Diluted solution of $HAuCl_4$ was used to introduce gold by adsorption, followed by washing with water and drying. The metal contents of the catalysts were determined by ICP. Selected catalysts were characterized by XRD, TEM and FTIR. The CO oxidation was investigated in both preferential (in the presence of hydrogen) and non-preferential CO oxidation in a flow reactor using temperature-programmed oxidation (TPO) technique and time on stream (TOS) approach under isotherm conditions. TPO experiments showed that gold catalysts on spinel type supports were more active than Au/Al_2O_3 catalysts modified by metal-oxides. In TPO experiemtns in most of the cases the activity in the heating part was higher than in the cooling part. However, Au on spinel type support showed the opposite behaviour. The catalyst 3.5 % Au/$MnAl_2O_4$ showed the highest activity in CO oxidation. In TOS experiments the activity of the catalysts was always higher in preferential CO oxidation than in non-preferential cases. In preferential oxidation the S_{CO2}values were independent of the CO partial pressure, it showed slow variation with the type of modifier and a strong dependence of the temperature and conversion.

FITTING THE BORON PEAK AND RESOLVING INTERFERENCES IN THE 450–490 KEV REGION OF PGAA SPECTRA

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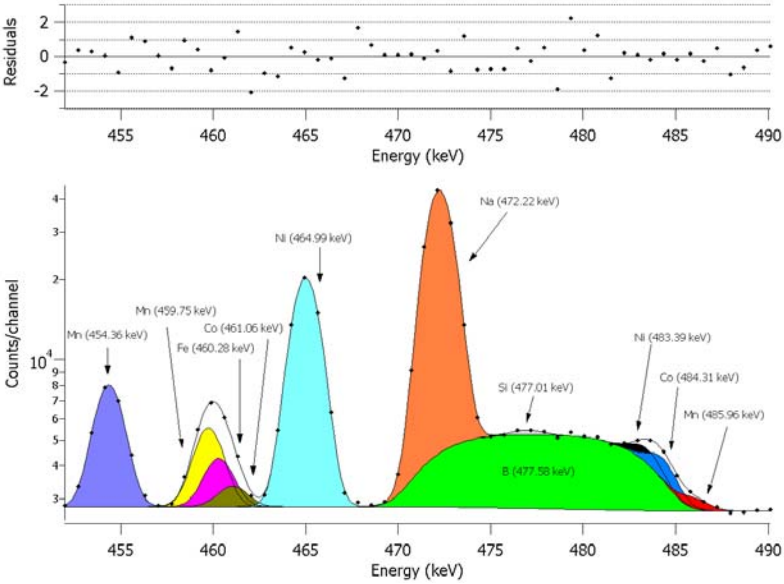
The sensitive and nondestructive measurement of boron concentrations using prompt-gamma activation analysis (PGAA) has already been utilized in numerous applications, including the analysis of water impurities, food, biological and geological samples.



The analytical line of boron at 477.6 keV originates from the $^{10}B(n,\alpha\gamma)^{7}Li^{*}$ reaction. Due to the recoil from the emission of the alpha particle, the energy of the detected γ-rays from the ^{7}Li* nuclei is significantly influenced by the Doppler-effect. As a result, the peak of boron is highly broadened in the energy spectrum, increasing the chance of interferences with peaks from other elements. The actual shape of the boron peak also depends on the ‘stopping power’ of the matrix; hence this region of PGAA spectra requires special techniques to evaluate.

We developed a model to describe the shape of the boron peak, which appears as a convolution of Doppler-broadened gamma-ray peak with the instrumental response function. A sophisticated instrumental response function has been used which consists of a Gaussian plus low and high energy tails. The decomposition of the boron and overlapping peaks becomes feasible in this way, using nonlinear least-squares fitting.

The procedure was tested first on model samples of boric acid, boron carbide and a solution of boric acid and sodium carbonate, to check the effects of the different matrixes on the peak shape. All these samples were measured with various combinations of detectors and electronics, having different instrumental response functions. Finally, the model was successfully applied to fit more complicated cases of real samples and found to be a useful tool in the determination of boron.

SYNTHESIS OF NEW ORGANOPHOSPHOROUS FLAME RETARDANT COMPOUNDS AND THEIR USE FOR REACTIVE MODIFICATION OF POLYMERS

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According to the latest legislation of European Union the most widely used flame retardant additives in the epoxy resins, the bromine containing additives are going to be banned from July 2006, so their replacement e.g. by organophosphorous flame retardants became crucial. The fire retardant properties of organophosphorous compounds have been recognized and investigated over a number of years and have thus found use as additives in a variety of polymeric materials. Many organophosphorous additives have low molecular weight and are therefore somewhat volatile, leading to the possibility of their loss from the polymer. Clearly, there was a need to increase the permanence of the additive within the polymer by incorporation of the organophosphorous functionality within the polymeric structure, in order to maximize the fire retardancy and to reduce the possibily evolution of toxic species.

Our aim was to synthesize phoshorous containing flame retardants which can be used as reactive flame retardants in polycondensation reactions due to their free functional groups and to incorporate them into polymers. A simple and cost-effective method was developed in order to introduce phosphorous moiety into the commercially available crosslinking agents for epoxy resins. This way phosphorus containing amines were synthesized (aliphatic: TEDAP, aromatic: TOPDAP), which function both as crosslinking agent and flame retardant.

According to the thermal behaviour of the synthesized compounds, it can be concluded, that their decomposition is endothermic, what is advantageous in the aspect of flame retardancy, just as the significant charring. Their further enormous advantage over the traditional additives is that they do not increase the viscosity of the epoxy resin.

The synthesized phosphorus containing amines were incorporated into epoxy resins. The enthalpy of the curing followed by DCS confirmed that they can replace the traditional curing agents. Furthermore they perform an excellent flame retardant effect evaluated by LOI, UL-94 and Cone Calorimeter measurements (*Fig. 1*).

The best results were achieved applying TEDAP: the Oxygen Index of the epoxy resin sample could be increased from 21 to 33, and it achieved the best, V-0

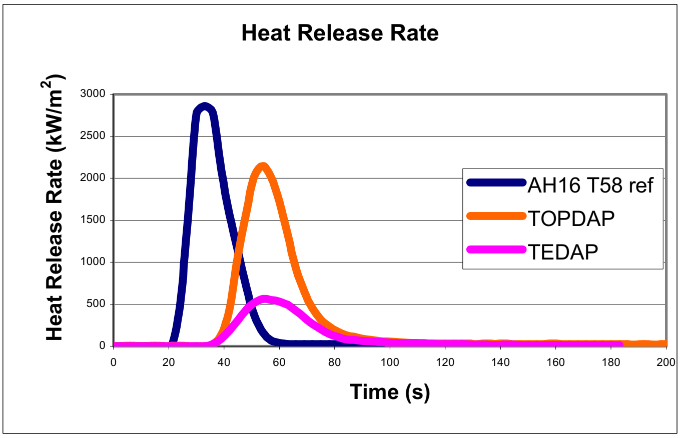

Fig. 1. Heat release rate during the burning in the function of time

classification according to UL-94 standard; the peak of the heat release rate was decreased to the fifth of the original value.

EFFECTS OF *Salmonella minnesota* DEEP ROUGH MUTANT BACTERIAL LIPOPOLYCASSHARIDE ON MODEL MEMBRANES

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Lipopolysaccharides (LPS), referred endotoxins, are the major components of the outer membrane of Gram-negative bacteria, located only on the outer leaflet of the membrane and also possessed of antigenic properties of the bacterial cells. The biological effects of endotoxins can be deduced from the interaction between the LPS molecule and the cell membranes. Salmonella minnesota R595 deep rough mutant bacterial lipopolysaccharide used in this study contain besides the lipid-A moiety only two KDO (2-keto-3-deoxyoctonic acid) entities.

To yield some information on the changes in the membrane structure caused by LPS molecule phospholipid-water fully hydrated liposomes (dipalmitoylphosphatidylcholine (DPPC)/water, dipalmitoylphosphatidylethanolamine-dipalmitoylphosphatidycacid (DPPE-DPPA)/water and dipalmitoylphosphatidylethanolamine-dipalmitoylphosphatidylglycerol (DPPE-DPPG)/water liposomes as model membrane systems containing different amounts of LPS) were studied by differential scanning calorimeter (DSC), small-angle X-ray scattering (SAXS) and freeze fracture (FF) methods.

The mass-ratios of the LPS in the liposome systems (related to the lipid) were varied in a range from 0.03 up to 3.5 mg LPS/ mg lipid. The changes in the thermal, structural and morphological behaviour of the liposome systems were strongly dependent on the LPS/ lipid ratios. In the DPPC systems the pretransition disappeared already at small LPS concentration. The behaviour of the systems containing DPPE was stronger affected by LPS than that containing DPPC. In the LPS ratio regime from 0.03 up to 0.7 mg LPS/ mg (DPPE-DPPG) a phase separation was effected by LPS in the DPPE-DPPG systems. This effect became more significant by increasing amount of LPS up to the mass ratio of 0.354 LPS/(DPPE-DPPG). In the DPPE-DPPA systems from the mass ratio of 0.362 mg LPS/ mg (DPPE-DPPA) cubic structure was formed as it was observed by SAXS and FF methods, too.

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RIDGE REGRESSION METHOD TO LOGIT MODEL

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Clinical investigations often result in binary data (e.g. whether a patient survived or not). When dealing with binary response logit regression is a widely used model. With this approach the binary response is considered as an outcome of a binomial random variable. The distribution parameter represents the probabilities of the two specific response outcomes. The logit model relates the probability of occurrence against the regressor variables. The most commonly used method of estimating the parameters of the logit model is the method of maximum likelihood. In some circumastances the variance of the estimated parameters is large. For example multicollinearity or small sample sizes inflate the variation. Our aim was to reduce the variance of the estimated parameters.

Ridge regression is an alternative to least squares with continuous response variable when multicollinearity exists. Ridge regression performs biased estimation to the regression parameters, but the bias of the estimator is over-compensated by the smaller variance.

Considering the concept of ridge regression we have modified the maximum likelihood estimator for logit regression. Computer simulation with four regression variables were performed to study the performance of the proposed regression method. The following regression situations were analysed: regression with

- continuous
- discrete
- correlated
- independent

regression variables. The effect of sample size (the number of data in a data set) was also studied.

In many regression situations the proposed method performs better than the original maximum likelihood estimation.

FEASIBILITY STUDY OF HETEROGENEOUS BATCH EXTRACTIVE DISTILLATION

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Separation of liquid mixtures to pure components is an important industrial task, involving both environmental and economical issues. These mixtures are commonly separated with application of batch or continuous rectification. However, azeotropes cannot be separated in a simple rectification process. Extractive distillation is an optional method for separating azeotropes.

In my research work I plan to study the separation of the minimum and maximum boiling azeotropes in batch extractive distillation using light, intermediate and heavy entrainers, applying a rectification column, a stripping column and a middle-vessel column.

In this presentation I would like to give a short look into my latest research results, showing clearly the applied methodology for studying the subject, namely into the feasibility of batch heterogeneous extractive distillation for separating a minimum boiling azeotrope. The studied mixture is acetonitrile and water, with butyl acetate as entrainer.

The candidate processes are operated in a distillation column at atmospheric pressure with a heated (boiled) vessel at the bottom, and a condenser together with a decanter at the top. The entrainer itself can be continuously fed (1) to the top of the column or (2) to some intermediate point in the column, or (3) into the still. It can also be premixed with the separating mixture in the still in advance (4). Whether the process is feasible and one or two column sections are needed was a question answered by the feasibility study. The results of the feasibility study have been validated by using ProsimBatch rigorous simulator.

First, isovolatility curves were computed for estimating which components can be produced from various domains. A limit distillate purity of water was then specified; this assigns a tie line in the liquid phase distribution area that limits the acceptable compositions in the top of the column.

Residue curves were computed; this roughly corresponds to total reflux and to the arbitrary number of stages. According to this map, a very narrow feasible region can be assigned where cases (3) and (4) are feasible with an enormous amount of entrainer premixed to the still.

Extractive profiles were then computed with total reflux for cases (1) and (2). It has been found that case (1) is feasible between $(F/V)_{min}$ and $(FV)_{trans}$ (transition point); whereas case (2) is feasible above $(FV)_{trans}$, too.

Such minimum and turning values exist in case of finite reflux ratios as well, but an infeasible region also appears near the acetonitrile-butyl acetate edge. Notwithstanding, good recovery is achieved, according to the validation with rigorous computation.

SMART COMPOSITES WITH CONTROLLED ANISOTROPY

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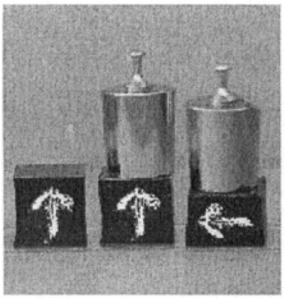
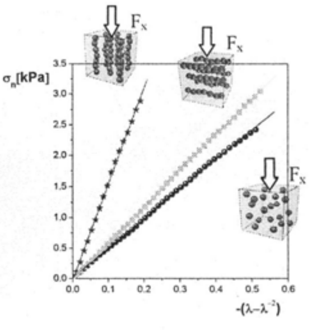
Many useful engineering materials, as well as living organisms have a heterogeneous composition. The components of composite materials often have contradictory, but complementary properties. Fillers are usually solid additives that are incorporated into the polymer to modify the physical properties. Fillers can be divided into three categories: those that reinforce the polymer and improve its mechanical performance, those that are used to take-up space, and thus reduce material cost. The third, more less common category is when filler particles are incorporated into the material to improve its responsive properties. Smart soft composites are valuable materials for several technological applications e.g. vibration control.

Composite materials, consisting of rather rigid polymeric matrices filled with magnetic particles, are long time known and called magnetic elastomers. These materials are successfully used as permanent magnets, magnetic cores, connecting and fixing elements in many areas. These traditional magnetic elastomers have low flexibility and practically do not change their sizes, shapes and elastic properties in the presence of external magnetic field.





The new generation of magnetic elastomers represents a new type of composites, consisting of small (mainly nano and micron-sized) magnetic particles dispersed in a highly elastic polymeric matrix. The combination of polymers with magnetic materials displays novel and often enhanced properties. The magnetic particles couple the shape of the elastomer to the external magnetic fields. All of the forces acting on the particles are transmitted directly to the polymer chains resulting in either locomotion or deformation. Shape distortion occurs instantaneously and disappears abruptly when external fields are applied or removed, respectively. Combination of magnetic and elastic properties leads to a number of striking phenomena that are exhibited in response to impressed magnetic fields. Giant deformational effect, tuneable elastic modulus, non-homogeneous deformation and quick response to magnetic field open new opportunities for using such materials for various applications.

Elastic materials with tailor-made anisotropy can also be prepared under external field. The anisotropy manifests itself in direction dependent elastic modulus. In this presentation I report the preparation and mechanical properties of anisotropic elastomers.