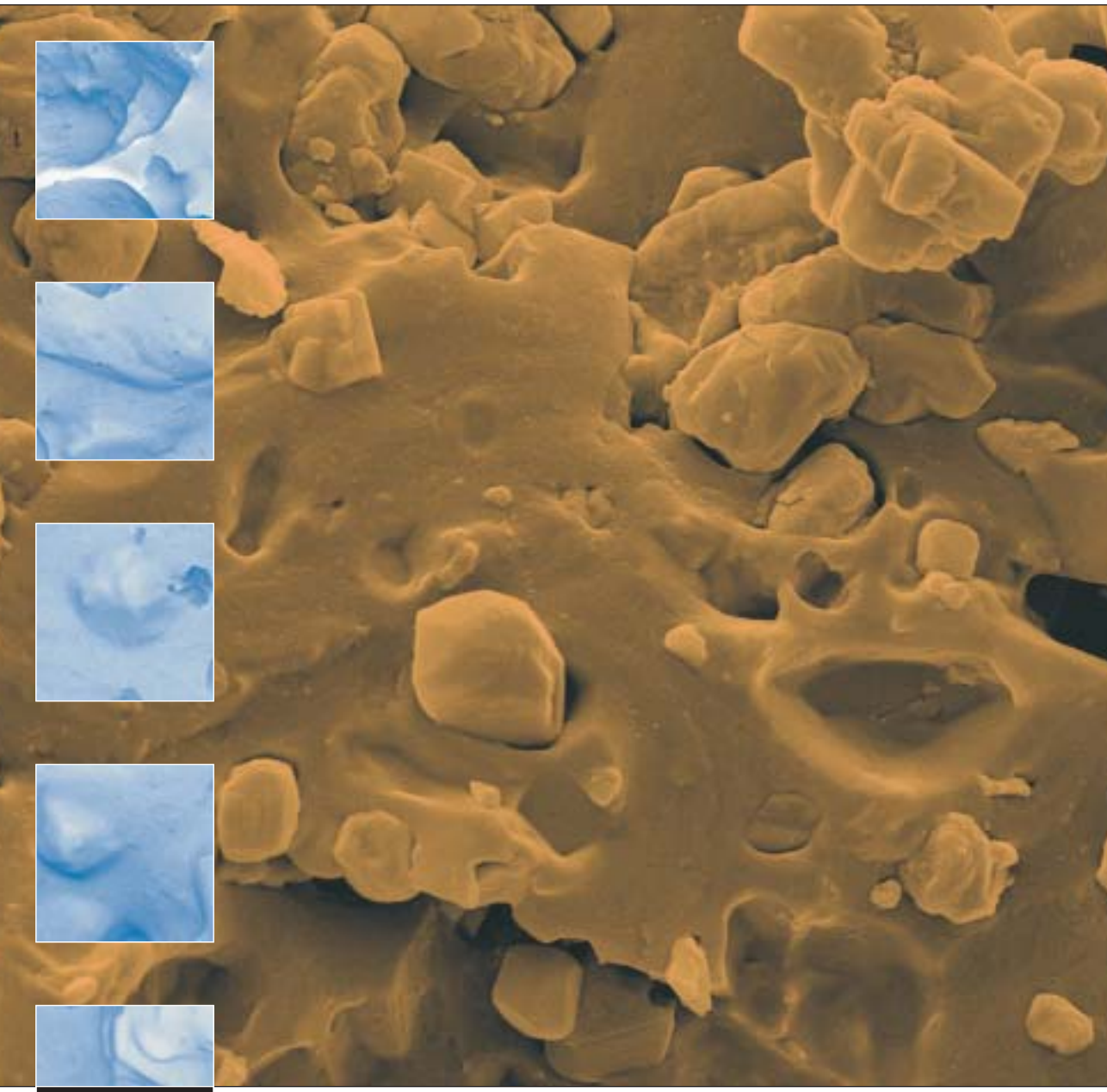
2002 - 2006

IZVJEŠĆE O ZNANSTVENOJ DJELATNOSTI

SCIENTIFIC ACTIVITIES REPORT



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University of Zagreb // Faculty of Chemical Engineering and Technology

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University of Zagreb / Faculty of chemical engineering and technology

IZVJEŠĆE O ZNANSTVENOJ DJELATNOSTI 2002. - 2006.

SCIENTIFIC ACTIVITIES REPORT 2002 - 2006

FAKULTET KEMIJSKOG INŽENJERSTVA I TEHNOLOGIJE

Maruličev trg 19
telefon: 01 4597 281
telefaks: 01 4597 260
E-mail: office@fkit.hr
URL: www.fkit.hr

Fakultet kemijskog inženjerstva i tehnologije je visoko tehničko učilište koje izvodi sveučilišne studije, znanstveni i visokostručni rad u znanstvenom području tehničkih znanosti (polje kemijsko inženjerstvo i polje druge temeljne tehničke znanosti) te u znanstvenom području prirodnih znanosti (polje kemija). Široko obrazovanje te poduka o metodologiji analiziranja dijelova uz sagledavanje cjeline osnova su moderne problemski orijentirane nastave. Na Fakultetu studenti stječu znanja bitna za istraživanje, razvoj i projektiranje održivih kemijskih procesa te unapređivanje postojećih konvencionalnih procesa, čime se osigurava kvalitetna, pouzdana i sigurna proizvodnja uz uvažavanje kriterija ekonomičnosti, djelotvornosti i zaštite okoliša te znanja bitna za razvoj lijekova, polimernih i anorganskih nemetalnih materijala, razvoj alternativnih puteva sinteze kao osnove novih procesa, kao i za razvoj metoda osiguranja kvalitete.
Temeljne organizacijske jedinice Fakulteta su zavodi u kojima se obavlja nastavni, znanstveni i visokostručni rad iz jednog ili više znanstvenih područja. Znanstvenoistraživački rad ustrojava se i provodi putem projekata. Bibliotečno-informacijski centar, Računalne učionice te priključak na Internet važna su infrastrukturna potpora nastavnom i znanstvenoistraživačkom radu na Fakultetu.

UPRAVA FAKULTETA

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Dr. sc. Antun Glasnović, redoviti profesor

Prodekanica za nastavu i znanost
Dr. sc. Vesna Tomašić, izvanredni profesor

Prodekan za upravu i poslovanje
Dr. sc. Stanislav Kurajica, izvanredni profesor

Prodekanica za međunarodnu suradnju
Dr. sc. Sandra Babić, docent

FACULTY OF CHEMICAL ENGINEERING AND TECHNOLOGY

Marulićev trg 19
phone: +385 1 4597 281
fax: +385 1 4597 260
E-mail: office@fkit.hr
URL: www.fkit.hr

Faculty of Chemical Engineering and Technology is a university-level institution specialized in teaching, scientific and professional work in the field of technical sciences (chemical engineering and other technical sciences), as well as in the field of natural sciences (chemistry). Teaching and education is based on modern, problem-oriented methods and provides students with analytical methodology in solving problems, but always keeping in mind the synthetic overview. Students of the Faculty gather contemporary knowledge on the research, development and design of new, sustainable chemical industrial processes as well as on the improvement of the existing ones, to ensure the high-quality, reliable and safe production that takes into account criteria of economy, efficiency and environmental protection. In addition, students of the Faculty may specialize in drug design, design and development on new polymeric and inorganic materials, development of novel synthesis routes as a basis for new processes, as well as in the quality management.

FACULTY MANAGEMENT

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Dr. sc. Antun Glasnović, full professor

Vice-dean for education and science
Dr. sc. Vesna Tomašić, associate professor

Vice-dean for organization and financing
Dr. sc. Stanislav Kurajica, associate professor

Vice-dean for international colaboration
Dr. sc. Sandra Babić, assistant professor

Poštovani čitatelji,

Dobrodošli na stranice *Izvješća o znanstvenoj djelatnosti 2002.–2006.* Fakulteta kemijskog inženjerstva i tehnologije na kojima su istaknute najvažnije istraživačke aktivnosti i postignuća naše institucije u zadnjih nekoliko godina.

Fakultet kemijskog inženjerstva i tehnologije (preimenovan 1991.) sastavnica je Sveučilišta u Zagrebu. Utemeljen je 1919, kao prvi Kemijsko-inženjerski odjel u Hrvatskoj – dio Tehničke visoke škole u Zagrebu, u cilju provođenja znanstvenog istraživanja i obrazovanja mladih znanstvenika i inženjera u području kemije i kemijskog inženjerstva. Danas obuhvaća 16 Zavoda na kojima se izvodi nastava, znanstveni rad te stručne i savjetodavne aktivnosti u području kemijskog inženjerstva, kemije i srodnih polja. Fakultet raspolaže s velikom centralnom bibliotekom sa približno 22.000 naslova knjiga, monografija i sl., a obuhvaća i oko 330 naslova stranih i domaćih znanstvenih časopisa. Fakultet, neposredno ili putem međusveučilišne suradnje ostvaruje međunarodnu suradnju s brojnih znanstvenim institucijama. Fakultetom upravljaju dekan, tri prodekana i Fakultetsko vijeće.

Nastavno osoblje, koje u ovom trenutku obuhvaća 63 profesora, 8 asistenata i 52 znanstvena novaka, djeluje u približno 40 laboratorija te na površini od 9,000 m^2.
Više od 5.500 diplomiranih studenata, više od 1.100 poslijediplomskih studenata sa stupnjem magistra znanosti i više od 590 sa stupnjem doktora znanosti današnje su brojke koje naglašavaju našu intenzivnu nastavnu djelatnost.

Naša misija je uglavnom određena specifičnim potrebama društva u kojem živimo. Ukratko, cilj nam je predložiti, primijeniti i provoditi kvalitetne dodiplomske i poslijediplomske studijske programe. Prioriteti prema ostvarenju tih ciljeva obuhvaćaju: (a) predlaganje novih obrazovnih programa koji će biti nacionalno prepoznati po izvrsnosti; (b) pripremu studenata za rad u struci, pristupanje naprednijim obrazovnim programima, vodstvo u profesiji, pripremu za cjeloživotno učenje; (c) poticaj otkrivanja, razvoja i širenja znanja kroz izvrsnost u istraživanju; (d) doprinos ekonomskom razvoju države, regije, nacije.

Ovo *Izvješće* opisuje istraživačke znanstvene programe Fakulteta kemijskog inženjerstva i tehnologije provedene od 2002. do 2006. Tijekom tog perioda znanstveni i stručni rad na Fakultetu provodio se uglavnom na projektima uz poticaj i potporu Ministarstva znanosti, obrazovanja i športa u području tehničkih znanosti (kemijsko inženjerstvo) te u području prirodnih znanosti (kemija i fizika). Svako poglavlje obuhvaća kratak opis projekta i postignute rezultate. Istraživači i ostali suradnici na projektu naznačeni su na početku, a popis objavljenih radova dan je na kraju svakog poglavlja. Popis radova pripremljen je na temelju završnog izvješća o projektima primjenom podataka iz nacionalne baze podataka (internetska stranica: http://bib.irb.hr). Na kraju izvješća nalaze se tri priloga: popis nagrada i priznanja, popis umirovljenih profesora i popis znanstvenih projekata koji su trenutno u tijeku.

Na kraju, ugodna mi je dužnost da mogu zahvaliti fakultetskom znanstvenom i administrativnom osoblju na iskrenom trudu i marljivosti kao i na njihovim izuzetnim ostvarenjima postignutim od 2002. do 2006. Iskrena dobrodošlica svima onima koji će otkrivati Fakultet kemijskog inženjerstva i tehnologije putem *Izvješća o znanstvenoj djelatnosti 2002.–2006.*, u nadi da će Vaša razmišljanja o Fakultetu, bez obzira o kojem području aktivnosti se radi, biti ugodna i korisna. Konačno, željela bih pozvati čitatelje da nam pošalju kritični osvrt i sugestije za daljnja poboljšanja te prijedloge za buduću suradnju.

Vesna Tomašić
Prodekanica za nastavu i znanost

Savršenstvo ne nastaje onda kad se nema što dodati, već kada se ne može ništa oduzeti.
Antoine de Saint-Exupéry

Dear readers,

Welcome to the *Scientific Activities Report 2002-2006* of the Faculty of Chemical Engineering and Technology, which highlights the most important research activities and achievements of our institution in the last few years.

Faculty of Chemical Engineering and Technology (renamed so in 1991) is a constituent of the University of Zagreb. It was founded in 1919, as the first Department of Chemical Engineering in Croatia – a part of the Technical Institute Zagreb, with the aim to do scientific research and educate young scientists and engineers in the field of chemistry and chemical engineering. Today it is organized in 16 departments that perform teaching, scientific work, professional and consulting activities in Chemical Engineering, Chemistry and related fields. Faculty has a large central library with about 22.000 titles of books, monographs, etc., and is subscribed to about 330 titles of the foreign and domestic scientific journals. The Faculty has developed valuable international cooperation with various scientific institutions in the world, either directly or through inter-university cooperation. Faculty is governed by a Dean and three vice-Deans, and the Faculty Council.

The present educational staff comprises 63 professors, 8 teaching assistants and 52 researchers operating in about 40 laboratories and area of 9,000 m^2.
More than 5.500 graduate students, more than 1.100 postgraduate students who received the Master degree and more than 590 students with Doctoral degree are today's total numbers, which highlights our highly spirited activities in teaching.

Our mission is mainly determined by the specific needs of the society in which we live. In summary, our mission is to develop, implement and maintain high quality undergraduate and graduate programs. Priorities towards accomplishing those goals include: (a) proposing new educational programs nationally recognized for educational excellence; (b) preparing students for professional practice, admission to advanced degree programs, leadership in the profession, and lifelong learning; (c) promoting the discovery, development, and dissemination of knowledge through excellence in research; (d) contributing to the economic development of the state, region, and nation.

This *Report* describes research scientific programs at the Faculty of Chemical Engineering and Technology for the period from 2002 to 2006. During this period, scientific and professional work at the Faculty has been carried out mostly on projects promoted and funded by the Ministry of Science, Education and Sports in the field of technical sciences (chemical engineering) and in the fields of natural sciences (chemistry and physics). Each chapter includes the summary of research efforts for research projects listed. Research staff and others who participated in these projects are identified at the beginning, while the list of references is given at the end of each item. The list of references is prepared according to the final status of the 2002-2006 project term using data from the National Bibliography database (web address: http://bib.irb.hr). There are three appendices at the end of the *Report:* list of honors and awards, list of retired researchers and list of current scientific projects.

In closing, I have a pleasant duty to thank the Faculty's scientific and administrative staff for their honest efforts and enthusiasm as well as their many excellent achievements throughout the period from 2002 to 2006. I extend a warm welcome to those discovering the Faculty of Chemical Engineering and Technology through the *Scientific Activities Report 2002-2006* and hope your association with the Faculty, in whatever sphere of activity, will be enjoyable and profitable. Finally, I would like to invite the readers to send us critical opinions and suggestions for further improvements and proposals for future collaboration.

Vesna Tomašić
Vice-Dean for Education and Science

Perfection is reached not when there is nothing left to add,
but when there is nothing left to take away.
Antoine de Saint-Exupéry

Izvješće o radu na znanstvenim projektima u razdoblju od 2002.-2006.

Znanstveno nastavni djelatnici Fakulteta kemijskog inženjerstva i tehnologije Sveučilišta u Zagrebu su u razdoblju od 2002.-2006. sudjelovali u radu dvadeset i četiri znanstvena projekta financirana od Ministarstva znanosti, obrazovanja i športa. U tom vremenu objavili su 4 knjige, 8 udžbenika i 2 skripta. Također su bili autori 27 poglavlja u raznim knjigama te održali 41 pozvano predavanje na domaćim i inozemnim znanstvenim skupovima. Objavili su ukupno 280 znanstvenih radova u časopisima citiranim u bazi Current Contents, 5 patenata, kao i 77 članaka u ostalim časopisima.
Aktivno su sudjelovali na 474 savjetovanja u zemlji i inozemstvu, a u zbornicima skupova objavljeno je 186 radova, od toga 128 radova u zbornicima s međunarodnom recenzijom. U istom je razdoblju pod mentorstvom djelatnika fakulteta izrađeno 37 disertacija, 38 magistarskih radova i 181 diplomski rad.
Treba napomenuti da su također dali veliki doprinos unapređenju gospodarstva kroz brojne elaborate, stručne radove i studije izvodljivosti.

Vesna Gržetić
Voditeljica Bibliotečno-informacijskog centra

Scientific activity report summary in the period of 2002-2006

The members of the Faculty of Chemical Engineering and Technology of the University of Zagreb have collaborated in 24 scientific projects funded by the Ministry of Science, Education and Sports of the Republic of Croatia in the period of 2002-2006. In the same period they have published 4 books, 8 university and 2 internal textbooks. They have authored 27 chapters in various scientific monographs and held 41 invited lectures in domestic and international conferences. They have published 280 scientific articles cited in Current Contents, 5 patents and 77 other articles. They have participated to 474 conferences. They have published 186 conference papers, 128 of which with international reviewing. They have mentored 37 PhD theses, 38 MSc theses and 181 graduation works. They have contributed to the Croatian chemical industry and public sector via numerous reports, professional papers and feasibility studies.

Vesna Gržetić
Head of the library and information center

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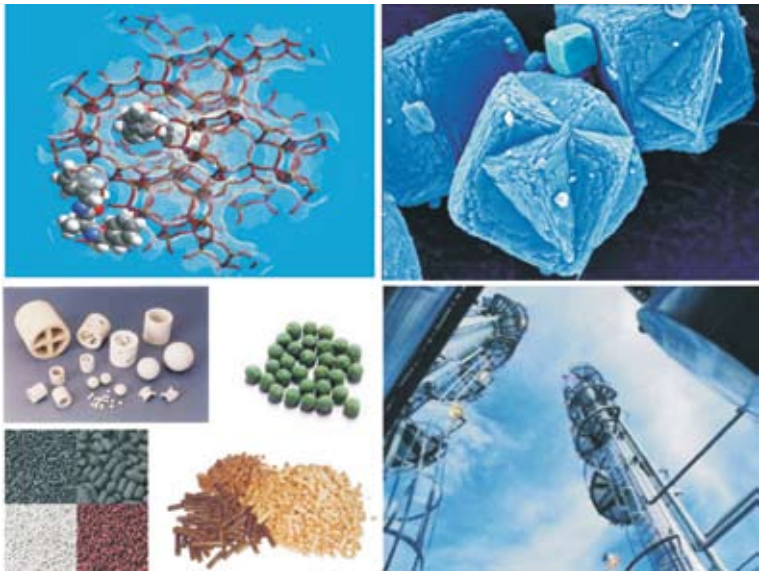

Različiti tipovi katalizatora korišteni u procesima.
Different types of catalysts used in processes.

GLAVNI ISTRAŽIVAČ

Stanka Zrnčević 01 4597 102 / szrnce@fkit.hr
Zavod za reakcijsko inženjerstvo i katalizu

SURADNICI

Vesna Tomašić
Ljubica Matijašević
Karolina Maduna Valkaj
Franjo Jović
Igor Dejanović

VANJSKI SURADNICI

Goran Šmit
(Pedagoški fakultet, Osijek)
Maja Fabulić Ruszkowski
(INA Industrija nafte, Zagreb)
Tatjana Glavanović
(PLIVA, Zagreb)

OPIS PROJEKTA

Kataliza je kamen temeljac kemijske i srodnih industrija, ali i integralni dio mnogih važnih procesa kojima se uklanjaju emisije štetne za okoliš. Zbog svog velikog utjecaja na globalnu ekonomiju i zaštitu okoliša, kataliza i nadalje predstavlja značajan poticaj za istraživanja u tom području.
Stoga je cilj projekta identificiranje ključne varijable potrebne za izvedbu aktivnijih, selektivnijih i stabilnijih katalizatora. Aktivnosti koje to omogućavaju su: sinteza i karakterizacija katalizatora, izučavanje zavisnosti između strukturnih i kemijskih značajki katalizatora i njihovih katalitičkih značajki, oblikovanje katalizatora, istraživanje kinetike i mehanizma reakcija, optimiranje procesa prijenosa tvari i topline u katalitičkom procesu te izbor odgovarajućeg reaktorskog sustava.
Istraživanjima u okviru predloženog projekta stvorit će se osnove za izvedbu novih, te unapređenje postojećih katalizatora koji pridonose razvoju katalitičkih procesa za uklanjanje za okoliš štetnih tvari, te razvoju ekološki prihvatljivih procesa.

KLJUČNE RIJEČI
kataliza u zaštiti okoliša, sprječavanje onečišćenja, pročišćavanje otpadnih voda, katalitičko spaljivanje

>> POSTIGNUTI REZULTATI

U okviru projekta objavljeno je tridesetak znanstvenih i stručnih radova. Korištenjem sredstava znanstvenog projekta izrađeni su uređaji te nabavljeni instrumenti što je omogućilo izvođenje laboratorijskih istraživanja predviđenih ovim projektom. Rezultati znanstvenih istraživanja objavljeni u radovima odnose se na:

- pripremu katalizatora (zeoliti, zeoliti modificirani metalima, monolitni keramički katalizatori, katalizatori na bazi zlata)
- karakterizaciju katalizatora prije i nakon uporabe
- ispitivanje utjecaja pripreme te prethodne obrade katalizatora na njihovu aktivnost, selektivnost i vijek trajanja
- izučavanje kinetike i mehanizma redukcije NO_x, niskotemperaturne oksidacije CO, te oksidacije fenola
- predloženi su matematički modeli potrebni za simulaciju procesa
- korišteni su moderni alati za simulaciju procesa (Chem CAD, HYSYS).
- određene su optimalne vrijednosti procesnih parametara.

Provedena istraživanja doprinijela su stjecanju novih spoznaja, te stvaranju osnova za izvedbu novih katalizatora koji pridonose razvoju katalitičkih procesa za uklanjanje tvari štetnih za okoliš. Dano je tehnološko rješenje za smanjenje emisije otpadnih plinova, te smanjenje potrošnje energije i količine otpadnih voda na postrojenju NPK gnojiva (Petrokemija, Kutina).

+385 1 4597 102 / szrnce@fkit.hr
Stanka Zrnčević
Department of Reaction Engineering and Catalysis

Principal investigator

PROJECT DESCRIPTION

Catalysis is the backbone of the chemical industry. It is also an integral part in some of the most important pollution control and environmental cleanup processes. Because of its substantial impact on the global economy and environmental protection, catalysis remains an active and vital area of research and development.
The principal aim of the proposed research project is to identify the key catalyst design variable in order to obtain more active, selective and stabile catalysts for development of more sustainable and less damaging manufacturing processes. The range of activities cover synthesis and characterization, studies of interrelationship between structural and chemical properties of solid materials and their catalytic properties, tailoring of the textural properties, kinetics, selection of suitable reactor system and the optimization of heat and mass transfer involved in the catalytic process.
The research activities will provide a basis for the advancement of processes that make efficient use of energy and raw materials with minimal impact on the environment. Also, catalytic solutions will be developed for the abatement of pollutants that are detrimental to the environment.

KEY WORDS
environmental catalysis, pollution prevention, wastewater purification, catalytic combustion

RESEARCH ASSOCIATES

Vesna Tomašić
Ljubica Matijašević
Karolina Maduna Valkaj
Franjo Jović
Igor Dejanović

CONSULTANTS

Goran Šmit
(Faculty of Pedagogy, Osijek)
Maja Fabulić Ruszkowski
(INA Industrija nafte, Zagreb)
Tatjana Glavanović
(PLIVA, Zagreb)

PROGRESS SUMMARY

Approximately thirty scientific and professional papers have been published within the project. Using the funds of research project, the laboratory equipment has been developed and the instruments purchased which provide opportunity for laboratory experimentation in the proposed project. The results of scientific researches published in the papers were related to:

- catalyst preparation (zeolites, zeolites modified by metals, monolithic ceramic catalyst, gold-based catalyst
- characterization of catalyst before and after tests
- investigation of catalyst synthesis and pretreatment on catalyst activity, selectivity and stability
- investigation of kinetics and mechanisms of NO_x reduction, phenol and low-temperature CO oxidation
- mathematical models for process simulation were developed
- modern simulation tools were used (Chem CAD, HYSYS)
- the optimal values of process parameters were identified

The research contributed to gathering new knowledge and providing a basis for the successful development of new catalysts for pollution control and environmental cleanup processes. The technological solution for the reduction of energy consumption as well as waste gases and wastewaters emission from the NPK fertilizing facility is proposed (Petrokemija, Kutina).

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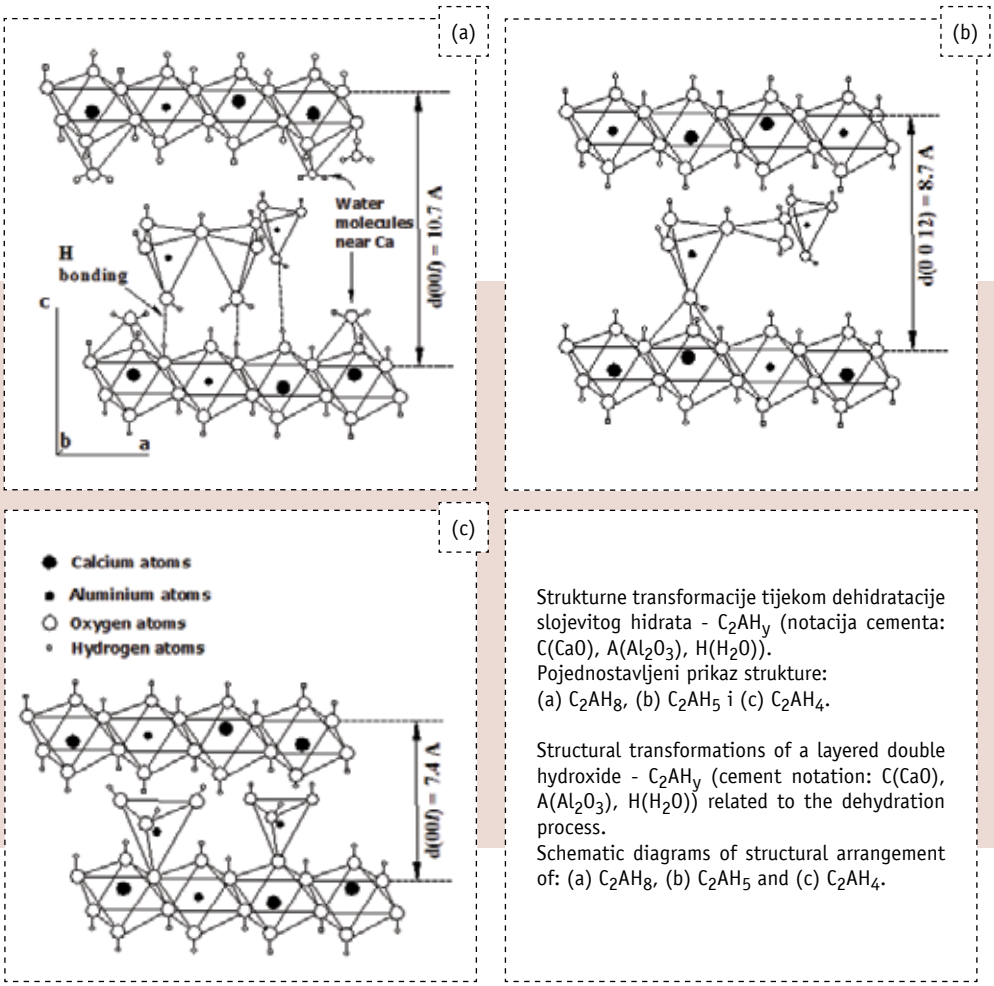

Strukturne transformacije tijekom dehidratacije slojevitog hidrata - C_2AH_y (notacija cementa: C(CaO), A(Al_2O_3), H(H_2O)).
Pojednostavljeni prikaz strukture:
(a) C_2AH_8, (b) C_2AH_5 i (c) C_2AH_4.

Structural transformations of a layered double hydroxide - C_2AH_y (cement notation: C(CaO), A(Al_2O_3), H(H_2O)) related to the dehydration process.
Schematic diagrams of structural arrangement of: (a) C_2AH_8, (b) C_2AH_5 and (c) C_2AH_4.

GLAVNI ISTRAŽIVAČ

Tomislav Matusinović 01 4597 218 / tmatusin@fkit.hr
Zavod za anorgansku kemijsku tehnologiju i nemetale

SURADNICI

Stanislav Kurajica
Juraj Šipušić
Nevenka Vrbos
Nenad Bolf
Denis Stjepan Vedrina
Goran Galinec
Neven Ukrainczyk

OPIS PROJEKTA

Iako je hidratacija aluminatnog cementa proces od temeljne industrijske i komercijalne važnosti, kemijske reakcije pri hidrataciji nedovoljno su razjašnjene. Opći je cilj projekta prijenos znanstvenog znanja prema gospodarstvu. Znanja stečena našim dugogodišnjim znanstvenim istraživanjima mehanizma brzog vezanja i očvršćivanja aluminatnog cementa, znanja o faznom sastavu, odnosu struktura, svojstava i reaktivnosti te znanja o motrenju i vođenju procesa, omogućit će dodatno stjecanje znanja o procesu i kvalitetnijem studiju procesa hidratacije. Glavni je cilj istraživanja izrada modela procesa hidratacije, razvoj nove metode kontinuiranog određivanja izotermne topline hidratacije i toplinskih svojstava cementnog materijala, razvoj linearne korelacije između makroskopskih svojstava cementnog materijala i parametara ultrazvučnog signala kao posljedice interakcije vala i mikrostrukture te eksperimentalno istraživanje procesa proizvodnje aluminatnog cementa *in situ*. U predloženom projektu je znanstvenoistraživački rad u funkciji razvoja održivih tehnologija i proizvodnji kvalitetnijeg proizvoda, te je važan element za povećanje djelotvornosti procesa i poslovne učinkovitosti cjelokupnog nacionalnog razvoja i povećanja međunarodne konkurentnosti hrvatskog gospodarstva.

KLJUČNE RIJEČI
aluminatni cement, hidratacija, mehanička i toplinska svojstva materijala, modeliranje, ultrazvučna mjerenja

>> POSTIGNUTI REZULTATI

Brz razvoj čvrstoće aluminatnog cementa (AC) posljedica je hidratacije $CaAl_2O_4$, glavne hidratno aktivne faze. Kinetika hidratacije $CaAl_2O_4$ praćena je kvantitativnom rendgenskom difrakcijskom analizom i metodom mjerenja kemijskog skupljanja te je ustanovljeno da ne ovisi o vrsti nastalih produkata hidratacije, no značajno ovisi o veličini čestica. Na osnovi izmjerenih temperaturnih profila tijekom hidratacije cementnog materijala u cilindričnoj geometriji, rješenjem inverznog problema II Fourierovog zakona određena je volumna toplinska generacija i količina ukupno razvijene topline hidratacijom. Razvoj mehaničkih svojstava pripravljenih pasti i mortova praćen je ultrazvukom, bez razaranja uzorka te je ustanovljena proporcionalnost tlačne čvrstoće i parametara određenih obradom ultrazvučnog signala. Detaljno je istražena dehidratacija $Ca_2Al(OH)_6Al(OH)_4 \cdot 3H_2O$ koja se provodi u tri stupnja pri: 110, 175 i 300 °C. Produkti hidratacije AC uz dodatak klorida zemnoalkalijskih kovina pripadaju klasi AFm spojeva. Istraženi su dvofazni alumosilikatni gelovi, posebice tijek njihove kristalizacije, strukturne promjene i ugradnja niklja i kobalta te kinetika kristalizacije i staklotvornost ganitne ($ZnAl_2O_4$) staklokeramike sustava ZnO-Al_2O_3-SiO_2.
Rezultati rada na projektu: deset znanstvenih radova objavljenih u CC časopisima, jedan znanstveni rad objavljen u časopisu citiranom u SCI Expanded bazama, jedno znanstveno priopćenje u CC časopisu, četiri znanstvena rada prihvaćena za objavljivanje u CC časopisima, sedamnaest znanstvenih radova u cijelosti objavljenih u zborniku radova znanstvenih kongresa s međunarodnom recenzijom, jedan znanstveni rad u cijelosti objavljen u zborniku ostalih skupova, jedan rad u kategoriji ostali radovi, četiri obranjene doktorske disertacije, dva obranjena magistarska rada i dvadeset i dva obranjena diplomska rada.

+385 1 4597 218 / tmatusin@fkit.hr **Tomislav Matusinović**
Department of Inorganic Chemical Technology and Non-Metals

Principal investigator

RESEARCH ASSOCIATES

Stanislav Kurajica
Juraj Šipušić
Nevenka Vrbos
Nenad Bolf
Denis Stjepan Vedrina
Goran Galinec
Neven Ukrainczyk

PROJECT DESCRIPTION

Although the hydration process of calcium aluminate cement represents a process of industrial and commercial importance, the chemical reactions involved during hydration are not yet well understood. The general goal of the project is transfer of scientific knowledge towards industry. The knowledge achieved during the years of scientific investigation of rapid setting and hardening of calcium aluminate cement, the knowledge about its phase composition, relations between structure and properties as well as reactivity and knowledge about process control will enable competent study of hydration process. The main goal of research is development of a hydration process model, development of a new method for continuous determination of isothermal heat of hydration and thermal properties of cement materials, development of a linear correlation between macroscopic properties of cement materials and parameters of ultrasonic signals as a result of interaction of ultrasonic wave and microstructure and experimental research of calcium aluminate cement production process *in situ*. Scientific and research work in the function of development of sustainable technologies and production of higher quality product is an important element in the improvement of the process efficiency and the overall national development and enhancement of the international competitiveness of the Croatian economy.

KEY WORDS
calcium aluminate cement, hydration, mechanical and thermal properties of materials, modeling, ultrasonic measurements

PROGRESS SUMMARY

Rapid strength development of calcium aluminate cement (CAC) is a consequence of $CaAl_2O_4$ hydration. As revealed from the QXRD and chemical shrinkage measurements, its hydration kinetics does not depend on the kind of hydration products formed, but depends on the powder particle size. Temperature profiles obtained during hydration of CAC paste in cylindrical geometry were input parameters in the heat conduction and generation inverse problem, giving the rate and total heat of cement hydration. Compressive strength of the CAC paste and mortars has been successfully correlated with the parameters obtained by the analysis of ultrasonic signals. Dehydration of $Ca_2Al(OH)_6Al(OH)_4 \cdot 3H_2O$ proceeds in three steps at: 110, 175 and 300 °C. Hydration products of CAC obtained by the addition of earth alkali chlorides belong to the group of AFm compounds. Two-phase aluminosilicate gels crystallization kinetics, structural changes and incorporation of nickel and cobalt into the matrix have been investigated. Crystallization kinetics and glass forming ability of gahnite glass ceramics in the system $ZnO\text{-}Al_2O_3\text{-}SiO_2$ have been investigated as well.
Project achievements have resulted in: ten scientific papers published in journals cited in Current Content, one scientific paper published in journal cited in SCI Expanded database, four scientific papers accepted for publication in journals cited in Current Content, seventeen scientific papers published in international congress proceedings, one scientific paper published in congress proceedings, one paper published in other journals; four Ph.D. theses, two Mr.Sc. theses and twenty two B.Sc. theses have been completed.

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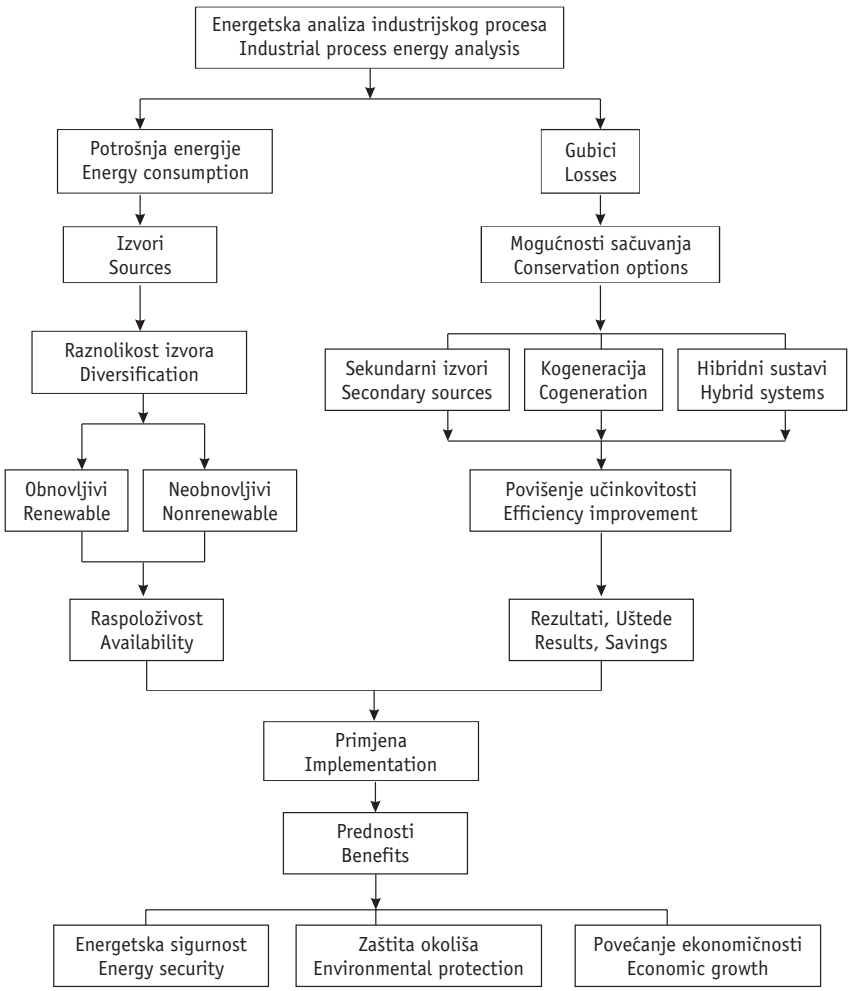

Blok shema metodologije istraživanja.
Research methodology scheme.

GLAVNI ISTRAŽIVAČ

Rajka Budin 01 4597 138 / rbudin@fkit.hr
Zavod za termodinamiku, strojarstvo i energetiku

SURADNICI

Veljko Filipan
Igor Sutlović

VANJSKI SURADNICI

Alka Mihelić-Bogdanić
(Tekstilno-tehnološki fakultet, Zagreb)
Vladimir Mikuličić
(Fakultet elektrotehnike i računarstva, Zagreb)
Željko Tomšić
(Ministarstvo gospodarstva, rada i poduzetništva, RH)
Vladimir Kramberger
(INA Industrija nafte, Zagreb)

OPIS PROJEKTA

Povećani interes usmjeren na industrijsku energetiku bio je neophodan u istraživanju i razvoju pristupa rješenju za ostvarenje programa boljeg gospodarenja energijom. Zbog toga su tehnički, ekonomski i ekološki aspekti planiranja i korištenja energetskih sistema ključni elementi u strategiji usmjerenoj na principe održivog razvoja. Proširena energetska istraživanja usmjerena na pitanja gospodarenja energijom uključila su današnje stanje i dala prijedloge za budućnost što je ukazalo na mogućnosti diverzifikacije izvora i sačuvanja energije. Uzimajući u obzir relevantne podatke industrijskih procesa utvrđen je program kontrole i proračuna, analiza energetskih bilanci te su određene granice analiziranog procesa. Svrha istraživačkog programa bila je utvrđivanje učinkovitosti energetski intenzivnih procesa i operacija, otpadnih energija kao i mogućnosti te akcije za primjenu alternativnih mogućnosti. Istraživanja su bila povezana s razvojem proizvodnje i potrošnje energije, gubicima kao i mogućnosti sačuvanja. Rezultati na području energetskih, ekonomskih i ekoloških prednosti postignuti predloženim istraživanjima pogodni su i imaju značajnu ulogu u procesnoj industrijskoj energetici.

KLJUČNE RIJEČI
gospodarenje, sačuvanje energije, gubici, diverzifikacija izvora

>> POSTIGNUTI REZULTATI

Prikazana istraživanja rezultiraju vrijednim prijedlozima na području sniženja potrošnje energije putem povišenja učinkovitosti i diverzifikacje izvora. Značaj energetske analize s ciljem promidžbe sačuvanja energije, tj. sniženja specifične potrošnje uključuje podatke o postojećim i novim tehnologijama. Metodologija istraživanja i rezultati dobiveni detaljnim proračunima objavljeni su u međunarodnim (3) i domaćim (5) časopisima, izloženi na simpozijima te tiskani u cijelosti u zbornicima radova međunarodnih (12) i domaćih (2) kongresa. U tom razdoblju obranjena je jedna doktorska disertacija. Nadalje, objavljen je udžbenik Osnove tehničke termodinamike, drugo izdanje, Školska knjiga 2002. Autorice R. Budin i A. Mihelić-Bogdanić dobile su nagradu J.J. Strossmayer za najuspješnije znanstveno djelo u području tehničkih znanosti 2002. U proteklom periodu objavljena su 3 poglavlja u međunarodnim znanstvenim knjigama.
Primjena sekundarnih izvora, tj. povrata kondenzata i dimnih plinova, kogeneracije i hibridnog solarnog sustava rezultira učinkovitostima između 10 i 80 %. S obzirom na zadovoljavajuća ulaganja i ekološke prednosti moguć je i očekuje se široki raspon primjene.

+385 1 4597 138 / rbudin@fkit.hr
Rajka Budin
Department of Thermodynamics, Mechanical Engineering and Energetics

Principal investigator

RESEARCH ASSOCIATES

Veljko Filipan
Igor Sutlović

CONSULTANTS

Alka Mihelić-Bogdanić
(Faculty of Textile Technology, Zagreb)
Vladimir Mikuličić
(Faculty of Electrical Engineering and Computing, Zagreb)
Željko Tomšić
(Ministry of Economy, Labour and Entrepreneurship, Republic of Croatia)
Vladimir Kramberger
(INA Industrija nafte, Zagreb)

PROJECT DESCRIPTION

An increased interest towards energy problems in industrial processes has taken place in research and development approaches to solution for realizing a better energy management policy. Therefore, technical economic and environmental aspects of energy systems planning and exploitation were the key elements of energy strategy focused on the principles of sustainable development. Expanded energy research of management questions by examining today trends and recommending proposals for future are major gains in resources diversification and energy conservation. Relating to relevant industrial process data establishment of audit accounting program, all process energy balances analyses and boundaries for process segments were studied. The scope of research program was the identification of efficiency of energy intensive processes and unit operations, energy wastes as well as of possibilities and actions for implementation and alternative forecast. This research was related with progress in the whole chain of energy production, consumption, losses and conservation. The results of energy, economical and environmental benefits derived from proposed investigation are suitable and have prominent role for process energy in industry.

KEY WORDS
management, energy conservation, losses, diversification sources

PROGRESS SUMMARY

The presented research results in valuable proposals directed on reducing energy consumption through efficiency increasing and sources diversification. The significance of energy analysis with purpose to promote conservation, i.e. lowering specific energy consumption includes information about existing and new technologies. The research methodology and results obtained using detailed calculation are published in indexed/abstracted international (3) and domestic (5) journals, presented on conferences and completely printed in proceedings of international (12) and domestic (2) congresses. Also, one dissertation was realized. In addition, the book *Osnove tehničke termodinamike* (Fundamentals of Engineering Thermodynamics, in Croatian), second edition, Školska knjiga 2002. is published. The authors R. Budin and A. Mihelić-Bogdanić received the J.J. Strossmayer award for the 2nd edition of the book – the book being the best scientific work in the field of technical science (2002). In this period 3 chapters in International Scientific Books were published.

By applying secondary sources, i.e. condensate and flue gases recovery, CHP and hybrid solar system efficiencies are between 10 and 80 %. With regard to reasonable investments and environmental advantages the vast range of applications is going to be opened up.

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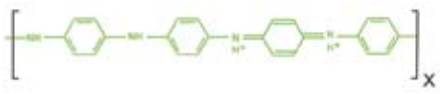
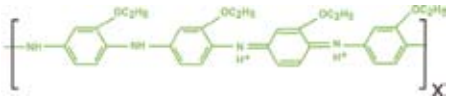
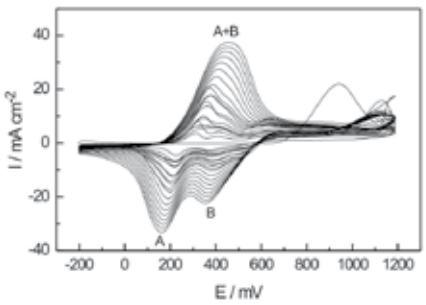


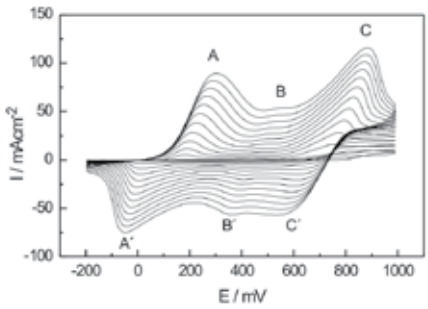
Polianilin
POLYANILINE (PANI)



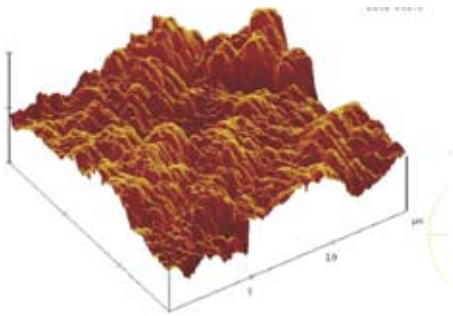
Poli(*orto*-etoksianilin)
POLY(*ortho*-ETHOXYANILINE) (POEA)



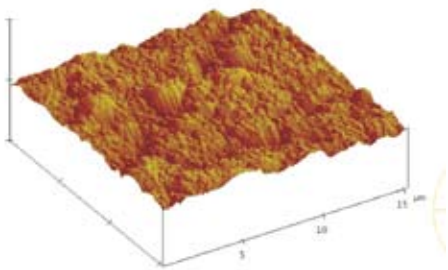
CV za rast polianilina
CV for polyaniline growth



CV za rast poli(*orto*-etoksianilina)
CV for poly(*ortho*-ethoxyaniline) growth



AFM za PANI sloj
AFM for PANI layer



AFM za POEA sloj
AFM for POEA layer

ELEKTROKEMIJSKA ISTRAŽIVANJA VODLJIVIH POLIMERA

GLAVNI ISTRAŽIVAČ

Ljerka Duić

01 4597 141 / lduic@fkit.hr

Zavod za elektrokemiju

SURADNICI

Sanja Grigić
(do 1.3.2003.)
Marijana Kraljić Roković
Zoran Mandić
(od 1.1.2006.)

OPIS PROJEKTA

Vodljivi polimeri su relativno nova vrsta organskih polimera zanimljivih svojstava. Njihova se električna provodnost može mijenjati u širokom području: od izolatora do vodljivosti bakra. Interdisciplinarno polje istraživanja vodljivih polimera otvara mnoge mogućnosti primjene u industriji i medicini. U okviru ovog projekta provođena je elektrokemijska sinteza vodljivog polianilina (PANI) i njegovih derivata metodom cikličke voltametrije (CV).
Studirana je sinteza polianilina (PANI) s ciljem upoznavanja utjecaja eksperimentalnih uvjeta na svojstva sintetiziranog sloja PANI na podlozi od Pt i nehrđajućeg čelika kao i utjecaja dodataka monomera supstituiranih anilina (*o*-, *m*- i *p*-fenilendiamina) na sintezu polimernog sloja i na svojstva rezultirajućih polimernih slojeva. Studirana je i elektropolimerizacija *orto*-etoksianilina.
Cilj je bio ispitati sintetizirane slojeve na katalitičko djelovanje u kvazireverzibilnoj redoks reakciji hidrokinon/kinon, kao i na učinkovitost u zaštiti od korozije elektrokemijski nanesene prevlake na podlogu od nehrđajućeg i mekog čelika.
Sve sinteze su provođene u otopinama raznih kiselina (HCl, H_2SO_4, H_3PO_4) za vrijednosti pH $\approx$ 0.

KLJUČNE RIJEČI
vodljivi polimeri, elektrokemijska sinteza, elektrokataliza, zaštita od korozije

>> POSTIGNUTI REZULTATI

Ustanovljen je utjecaj pojedinih fenilendiamina na brzinu polimerizacije i rasta sloja na Pt elektrodi. Slojevi su snimani pretražnim elektronskim mikroskopom (SEM), i mikroskopom atomske rezolucije (AFM). Utvrđen je utjecaj pojedinog tipa monomera, koncentracije i brzine polimerizacije na morfologiju slojeva. Provedena je elektrokemijska sinteza poli(*orto*-etoksianilina) (POEA). Razlike u odnosu na PANI sloj potječu od etoksi-skupine. Uspoređivanjem snimaka AFM, uočava se morfologija POEA kompaktnija od sloja PANI.
Karakterizacija slojeva provedena je i metodom elektrokemijske impedancijske spektroskopije (EIS). Ispitivanjima provedenim CV i voltametrijom na rotirajućoj disk elektrodi (RDE) u kvazireverzibilnoj reakciji hidrokinon/kinon (H_2Q/Q) ustanovljena je veza između stanja površine vodljivih polimera i katalitičkih svojstava polimera. Povećanjem dodataka *o*- i *p*-fenilendiamina dolazi do usporavanja katalitičkog djelovanja, zbog povećane kompaktnosti polimernog sloja. Uzorci nehrđajućeg čelika prevučeni polimernim slojem ispitivani su s obzirom na mogućnost zaštite od korozije praćenjem potencijala otvorenog kruga (POK) u otopinama raznih pH vrijednosti. Dokazano je da PANI slojevi učinkovito štite od korozije. Slojevi POEA također su učinkovita zaštita od korozije. Opisan je elektrokemijski mehanizam zaštite čelika od korozije putem polimera PANI tipa.
U okviru projekta objavljeno je 8 znanstvenih radova citiranih u CC, 1 znanstveni rad citiran u SCI, 2 rada prihvaćena za objavljivanje u časopisima citiranim u CC, 6 radova u zbornicima radova sa znanstvenih skupova, 1 magistarski rad je obranjen, obranjena je jedna doktorska disertacija te 4 diplomska rada.

+385 1 4597 141 / lduic@fkit.hr
Department of Electrochemistry

Ljerka Dujć

Principal investigator

PROJECT DESCRIPTION

Conducting polymers are a relatively new class of organic polymers with interesting properties. Their electrical conductivity can be varied from isolators to the conductivity of copper. The interdisciplinary field of the research of conducting polymers opens up many possible applications in industry and medicine. Within the frame of this project, the electrochemical synthesis of conducting polyaniline (PANI) and its derivatives has been carried out with the application of cyclic voltammetry (CV).

The synthesis of PANI was studied aiming to learn the influence of experimental conditions on properties of the layer synthesised on Pt and stainless steel (SS) substrates, as well as the influence of substituted aniline monomers (*o*-, *m*- and *p*-phenylenediamine) on the synthesis, and on the characteristics of the resulting polymer layers. The electropolymerisation of *ortho*-ethoxypolyaniline was also studied. The aim was to test the layers synthesised on catalytic acting on quasireversible redox reaction quinone/hydroquinone, as well as the efficiency in corrosion protection when the electrochemical coating of conducting polymers is applied on the SS and soft iron substrates. All the syntheses were carried out in solutions of different acids (HCl, H_2SO_4, and H_3PO_4) at pH $\approx$ 0.

KEY WORDS
conducting polymers, electrochemical synthesis, electrocatalysis, corrosion protection

PROGRESS SUMMARY

The influence of phenylenediamines on the rate of polymerisation and on layer growth has been established on Pt-electrode. The scanning electron micrographs (SEM) as well as atomic force micrographs (AFM) were taken. The influence of the each of different monomers, concentration and the rate of polymerisation on the morphology of layers was established. The electrochemical synthesis of poly(*ortho*--ethoxyaniline) (POEA) was also carried out. The difference in comparison to PANI layer is due to ethoxy-group. From the AFM micrographs it is evident that the layer of POEA is more compact compared to PANI layer.

The characterisation of the layers was also carried out with the electrochemical impedance spectroscopy (EIS) method. Through the investigations carried out with CV and the voltammetry with the rotating disc electrode (RDE) for the quasi-reversible reaction H_2Q/Q, the relation between the surface state of conducting polymers and catalytic properties of polymers has been established.

The samples of SS coated with the polymer layer were tested for the corrosion protection by monitoring the open circuit potential (OCP) in solutions of different pH. It has been proved that PANI layers are effective in corrosion protection. POEA layers are also effective protection from corrosion. The electrochemical mechanism of SS corrosion protection with PANI-type layers is described.

The investgations on this project resulted in 8 scientific CC publications, 1 scientific SCI publication, 2 accepted papers for publication in CC, 6 scientific publications in symposia proceedings, 1 Ph.D. disertation, 1 M.Sc. thesis and 4 B.Sc. theses.

RESEARCH ASSOCIATES

Sanja Grigić
(until March 1st, 2003.)
Marijana Kraljić Roković
Zoran Mandić
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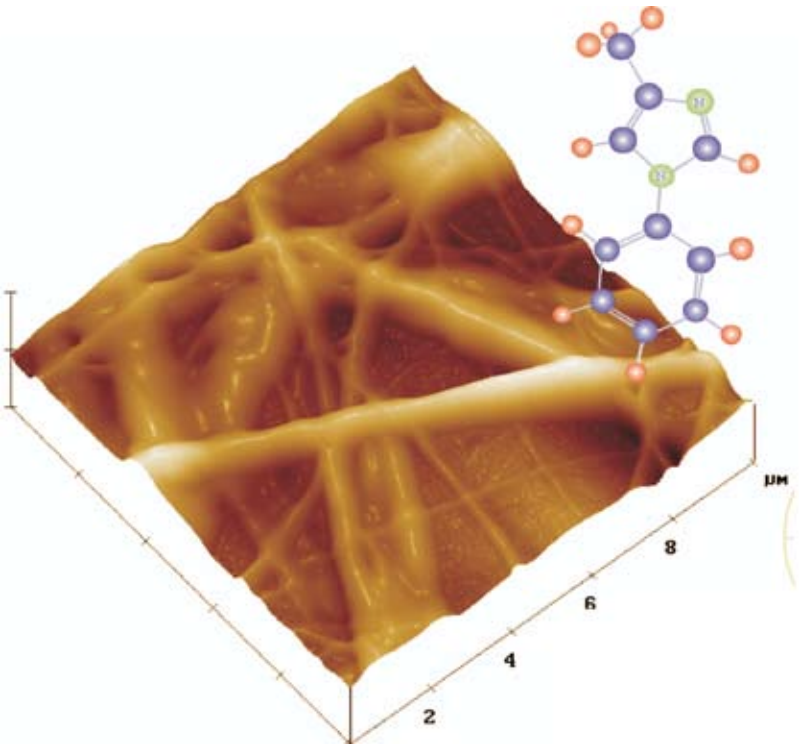

AFM snimka površine bakra prekrivenog zaštitnim slojem 1-fenil-4-metil imidazola.
AFM image of copper covered with 1-phenyl-4-methylimidazole.

GLAVNI ISTRAŽIVAČ

Ema Stupnišek-Lisac 01 4597 117 / elisac@fkit.hr
Zavod za elektrokemiju

SURADNICI

Ana Dunja Mance
Rahela Gašparac
Helena Otmačić Ćurković
Katarina Marušić

VANJSKI SURADNICI

Lujo Dvoraček
(PLIVA, Zagreb)
Darko Rajhenbah
(Ministarstvo poljoprivrede, šumarstva i vodnog gospodarstva)
Dražen Marijan
(PLIVA, Zagreb)

OPIS PROJEKTA

Korozija je proces nenamjernog razaranja konstrukcijskih materijala (uzrokovan fizikalnim, kemijskim i biološkim čimbenicima) koji je odgovoran za gubitak 1 % nacionalnog bruto proizvoda. Prema tome, od velikog značaja je razvoj metoda i tehnika za smanjenje tog procesa. Među ostalim tehnikama zaštite od korozije, primjena inhibitora korozije zauzima posebno mjesto i po specifičnosti zaštite kao i po raširenosti primjene.
Cilj ovog projekta je razvoj novih, djelotvornih i ekološki prihvatljivih inhibitora korozije. Dosadašnja istraživanja utjecaja sastava i strukture molekule na zaštitna svojstva heterocikličkog organskog spoja pokazala su da je moguće dizajnirati molekulu organskog spoja dobrih inhibitorskih karakteristika. Sintetizirani su novi derivati imidazola s fenilnom skupinom koji su pokazali znatno bolja inhibitorska svojstva. Postupak sinteze ovih spojeva kao i njihova inhibitorska svojstva su u postupku dobivanja patentnih prava.

KLJUČNE RIJEČI
korozija metala, netoksični inhibitori korozije metala, imidazoli, elektrokemijske metode, zaštita okoliša

>> POSTIGNUTI REZULTATI

Rezultati istraživanja provedenih na projektu pokazali su da su derivati imidazola dobri inhibitori atmosferske korozije bakra kao i korozije bakra u otopinama anorganskih kiselina i u morskoj vodi.
Za potrebe elektrokemijskih i spektroskopskih ispitivanja ponovno su sintetizirani 1-fenil-4-metilimidazol i 1-(p-tolil)-4-metilimidazol, a sintetiziran je i novi derivat 1-(o-tolil)-4-metilimidazol. Na osnovi dosadašnjih iskustava nastavit će se modificiranje molekule imidazola uvođenjem novih supstituenata i ispitivanje djelotvornosti novih inhibitora korozije bakra i drugih metala u raznim agresivnim sredinama.
U razdoblju od 2002. do 2006. u okviru projekta objavljeno je 15 radova u CC časopisima, 1 poglavlje u knjizi, 6 radova u sekundarno citiranim časopisima, 12 radova u zbornicima radova s međunarodnih skupova, 10 radova u zbornicima radova s domaćih skupova, te 16 sažetaka radova prezentiranih na domaćim i međunarodnim znanstvenim skupovima. Obranjen je 1 doktorat, 1 magistarski rad i 5 diplomskih radova. Predložen je jedan patent. U postupku objavljivanja su 3 rada.

+385 1 4597 117 / elisac@fkit.hr
Ema Stupnišek-Lisac
Department of Electrochemistry

Principal investigator

PROJECT DESCRIPTION

Corrosion is a process of unintentional destruction of structural materials which is responsible for the loss of 1 % of the national gross product. According to this, it is of great significance to develop methods and techniques to reduce this process. Among other techniques for corrosion protection, the use of corrosion inhibitors takes a special place because of its specific protection as well as its expanded application.

The aim of this project is the development of new, efficient and ecologically acceptable corrosion inhibitors. Our previous investigations on the influence of the composition and the structure of molecules on the protective properties of a heterocyclic organic compound have shown that it is possible to design an organic molecule with good inhibiting characteristics. New synthesized imidazole derivatives with a phenyl group have shown good inhibiting properties. The synthesis procedure of these compounds, as well as their inhibiting properties, are under the procedure of getting patent rights.

KEY WORDS
corrosion of metals, non-toxic metal corrosion inhibitors, imidazoles, electrochemical methods, environmental protection

RESEARCH ASSOCIATES

Ana Dunja Mance
Rahela Gašparac
Helena Otmačić Ćurković
Katarina Marušić

CONSULTANTS

Lujo Dvoraček
(PLIVA, Zagreb)
Darko Rajhenbah
(Ministry of Agriculture, Forestry and Water Management)
Dražen Marijan
(PLIVA, Zagreb)

PROGRESS SUMMARY

Results of the research carried out on the project have shown that the imidazole derivatives are good inhibitors for atmospheric corrosion of copper as well as for copper corrosion in inorganic acid solutions and in the sea water.

For the purpose of electrochemical and spectroscopic measurements, 1-phenyl-4-methylimidazole and 1-(p-tolyl)-4-methylimidazole are synthesized again, and the new derivative 1-(o-tolyl)-4-methylimidazole is synthesized as well. On the basis of our former knowledge, the modification of imidazole molecule will be continued by introducing new substituents and testing of new corrosion inhibitors efficiency for copper and other metals. Within the framework of the project we published: 15 papers in CC journals, 1 book chapter, 6 papers in secondary cited journals, 12 papers in proceedings of international scientific meetings as well as 10 papers in Croatian scientific meetings and 16 abstracts at the congresses. In this period one Ph.D. thesis, one master thesis and 6 diploma works were finished.

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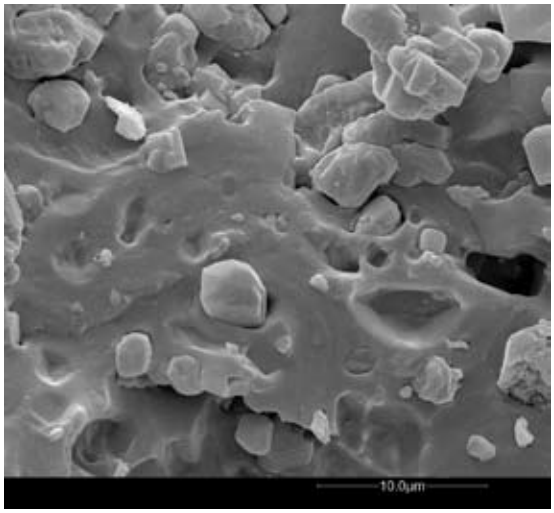
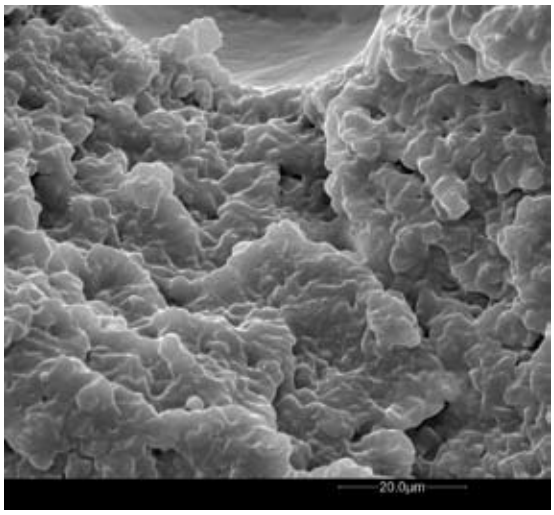


b)



Mehanizam popuštanja polimernog kompozita s a) mikro i b) nano česticama punila.
Failure mechanism of polymer composites with a) micro and b) nano filler particles.

GLAVNI ISTRAŽIVAČ

Vera Kovačević 01 4846 378 / vkovac@fkit.hr
Zavod za inženjerstvo površina polimernih materijala

SURADNICI

Jasenka Jelenčić
Zlata Hrnjak Murgić
Mirela Leskovac
Sanja Lučić-Blagojević
Ljerka Kratofil
Anita Ptiček
Domagoj Vrsaljko
Mladen Bravar
Drago Hace

VANJSKI SURADNICI

Ivan Šmit
(Institut Ruđer Bošković, Zagreb)
Dragutin Fleš
(Hrvatska akademija znanosti i umjetnosti)
Ian Sutherland
(Loughborough University)

OPIS PROJEKTA

Glavni cilj projekta bila je optimalna priprava novih polimernih materijala punjenih nanočesticama i njihova karakterizacija kao polimernih nanosustava. Hipoteza projekta je da kontrolirana modifikacija površine nanopunila predobradom može voditi do učinkovite adhezije između faza na međupovršini punjenih kompozita i polimernih mješavina i kao rezultat do novih svojstva i/ili poboljšane mješljivosti. Postizanje termodinamičkih uvjeta učinkovite adhezije između faza na međupovršini punjenih kompozita i polimernih mješavina predstavlja minimalna energija međupovršine, optimalno kvašenje i maksimalni rad adhezije. Originalna ideja bila je istražiti utjecaj nanopunila kontrolirane energije površine, dobivene kontroliranom površinskom predobradom, kao kompatibilizatora koji poboljšava mješljivost polimernih faza u odnosu na standardne dodatke kopolimera. Predviđeno je da utjecaj nanopunila u odnosu na mikropunila u odabranim polimernim kompozitima izrazito poboljšava svojstva radi ostvarenih interakcija na nanorazini i, dodatno, kada je postignuta učinkovita adhezija na međupovršini. Odabrana metodologija projekta predstavlja novi pristup istraživanja međupovršine kao centralnog mjesta u nanosustavima s ciljem postizanja odgovarajuće homogene morfologije i poboljšanja konačnih svojstava u odnosu na odgovarajuće mikrosustave.

KLJUČNE RIJEČI
nanokompoziti, mikrokompoziti, nanočesticama punjeni blendi, međupovršina, učinkovita adhezija

>> POSTIGNUTI REZULTATI

Potvrđena je glavna hipoteza projekta da se kontroliranom modifikacijom površina nanopunila kalcij karbonata stearatima i/ili silanima mogu postići termodinamički uvjeti učinkovite adhezije na međupovršini u odabranim punjenim kompozitima i polimernim mješavinama (PVAc, PU, PA, SAN/EPDM i dr.). Rezultati se mogu primijeniti u kreiranju novih nanomaterijala kao zamjena za standardne mikromaterijale, što je dijelom učinjeno u realiziranim tehnologijskim projektima. Zaključak je da polimerni nanosustavi kao novi proizvodi moraju biti pripremljeni uz homogenu raspodjelu nanočestica bez aglomerata da se ostvare interakcije na nanorazini. Ideja da se međupovršina kao centralno mjesto u kompozitima i mješavinama može kontrolirano mijenjati površinskim modifikacijama nanopunila provjerena je i potvrđena. Rezultati koji to potvrđuju objavljeni su u bazi podataka (http://bib.irb.hr), tj. u 1 poglavlju u knjizi, 5 CC radova, te 3 rada u ostalim časopisima. Kompatibilizacija nemješljivih sustava kada je postignuta efektivna adhezija na međupovršini te odgovarajuća homogena morfologija i poboljšanja konačnih svojstava potvrđena je i objavljeni su rezultati u 5 CC radova, 1 radu u ostalim časopisima, dok su 3 rada u postupku objavljivanja.

+385 1 4846 378 / vkovac@fkit.hr
Vera Kovačević
Principal investigator
Department of Surface Engineering of Polymer Materials

PROJECT DESCRIPTION

The project goal was the optimal preparation of new polymer materials filled with nanoparticles and their characterisation as the polymer nanosystems. The project hypothesis is that the controlled surface modification of nanofillers by pretreatment might lead to the effective adhesion at the interface of filled composites and/or polymer blends. The thermodynamical conditions for the effective adhesion between phases at the interface are the minimal interfacial energy, optimal wetting and maximal work of adhesion. The original idea was to investigate the effect of nanofillers with the controlled surface energy as compatibilisers that improve the miscibility in blends relative to standard copolymers. It was supposed that the effect of nanofillers vs. microfillers will significantly improve the properties of selected polymer composites due to realised interactions at nanolevel and additionally with the achieved effective adhesion. The selected project methodology represent the new approach of investigations with the interphase as the central place in order to achieve the homogeneous morphology and improved properties in nanomaterials in comparison to their micro-counterparts.

KEY WORDS
nanocomposites, microcomposites, nanoparticulate filled blends, interface, effective adhesion

PROGRESS SUMMARY

The project hypothesis is approved: the controlled surface modifications of nanofiller calcium carbonate by stearate and/or silane resulted in thermodynamical conditions of effective adhesion at the interface in selected filled composites and blends (PVAc, PU, PA, SAN/EPDM, etc.). The results might be applied in creating new nanomaterials instead of standard micromaterials which is partly done in realised technology projects. The conclusions about the necessity of homogeneous dispersion of nanoparticles without agglomerates in preparation of new nanoproducts in order to achieve the interaction at nanolevel were drawn. The idea of the interface as the central place in composites and blends to be changed by the controlled surface modification of nanofillers is checked and proved by published results (http://bib.irb.hr): 1 book chapter, 5 CC papers, and 3 papers in other journals. Compatibilisation of immiscible blends when the effective adhesion at interface and related homogeneous morphology with improved final properties is achieved and proved by published results: 5 CC papers, 1 paper in other journals, and 4 papers to be published.

RESEARCH ASSOCIATES

Jasenka Jelenčić
Zlata Hrnjak Murgić
Mirela Leskovac
Sanja Lučić-Blagojević
Ljerka Kratofil
Anita Ptiček
Domagoj Vrsaljko
Mladen Bravar
Drago Hace

CONSULTANTS

Ivan Šmit
(Ruđer Bošković Institute, Zagreb)
Dragutin Fleš
(Croatian Academy of Sciences and Arts)
Ian Sutherland
(Loughborough University)

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EKSPERIMENTALNO ISTRAŽIVANJE I MATEMATIČKI MODELI SUSTAVA ZAŠTITE OD KOROZIJE

EXPERIMENTAL INVESTIGATION AND THEORETICAL MODELS OF THE CORROSION PROTECTION SYSTEMS

Jamičasto korozijsko oštećenje ugljičnog čelika izazvano djelovanjem sulfat-reducirajućih bakterija.
Pitting corrosion damage of carbon steel developed under the influence of sulfate reducing bacteria.

EKSPERIMENTALNO ISTRAŽIVANJE I MATEMATIČKI MODELI SUSTAVA ZAŠTITE OD KOROZIJE

GLAVNI ISTRAŽIVAČ

Sanja Martinez 01 4597 116 / smartin@fkit.hr
Zavod za elektrokemiju

SURADNICI

Ivica Štern
Lidija Valek

OPIS PROJEKTA

Specifični ciljevi projekta bili su: (1) istraživanje mehanizma inhibicije korozije organskim inhibitorima, posebice prirodnim spojevima i (2) modeliranje raspodjele struje i potencijala u sustavima katodne zaštite. Eksperimentalne metode projekta bile su: linearna polarizacija, ciklička voltametrija, elektrokemijska impedancijska spektroskopija, UV-VIS spektroskopija, SEM i gravimetrijska metoda. Teoretski pristup očitovao se u primjeni adsorpcijske teorije inhibicije uz analizu rezultata kvantnog molekulskog modeliranja. Sustavi katodne zaštite modelirani su polu-analitičkom i BEM metodom.

KLJUČNE RIJEČI
korozija, inhibitor, molekulsko modeliranje, katodna zaštita

>> POSTIGNUTI REZULTATI

Kao rezultat rada na projektu objavljen je jedan rad u knjizi, 13 radova u časopisima, pet radova i sedam sažetaka u zbornicima skupova i izrađena su četiri diplomska rada. Objavljeni znanstveni radovi su do kraja 2006. godine citirani 56 puta. Primjenjivost rezultata projekta očituje se u četiri izrađena elaborata koji obrađuju korozijske probleme iz industrije i građevinarstva.

EXPERIMENTAL INVESTIGATION AND THEORETICAL MODELS OF THE CORROSION PROTECTION SYSTEMS

+385 1 4597 116 / smartin@fkit.hr
Sanja Martinez
Department of Electrochemistry

Principal investigator

RESEARCH ASSOCIATES

Ivica Štern
Lidija Valek

PROJECT DESCRIPTION

The specific objectives of the project were: (1) investigation of the mechanisms of corrosion inhibition by organic inhibitors, in particular, by nature-derived products and (2) modeling of the current and potential distributions in the cathodic protection systems. Experimental methods of the project were: linear polarization, cyclic voltammetry, electrochemical impedance spectroscopy, UV-VIS spectroscopy, SEM and gravimetric method. Theoretical approach included analysis of the inhibition mechanism in terms of the adsorption theory and results of quantum molecular modeling. Modeling of the cathodic protection systems was done by analytical, semi-analytical and the boundary element method.

KEY WORDS
corrosion, inhibitor, molecular modeling, cathodic protection

PROGRESS SUMMARY

Results of the project are summarized in one book chapter, 13 journal papers, five papers and seven abstracts in conference proceedings and four diploma works. Until the end of the year 2006, the papers published as a result of the project have been cited 56 times. Applicability of the results is demonstrated in four studies dealing with corrosion problems in industry and construction.

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0125 016

Struktura klinoptilolita.
Clinoptilolite structure.

IONSKA IZMJENA I MEMBRANSKI PROCESI U OBRADI VODA KEMIJSKE INDUSTRIJE

GLAVNI ISTRAŽIVAČ

Štefica Cerjan-Stefanović 01 4597 210 / scerjan@fkit.hr
Zavod za analitičku kemiju

SURADNICI

Emir Hodžić
Mirela Rožić
Tomislav Bolanča
Karmen Margeta
Mario Šiljeg
Sanda Stefanović
Melita Regelja
Marin Hraste

VANJSKI SURADNICI

Ivan Mijatović
(Prehrambeno-biotehnološki fakultet, Zagreb)
Stjepan Leaković
(PETROKEMIJA Tvornica gnojiva, Kutina)
Marin Matošić
(Prehrambeno-biotehnološki fakultet, Zagreb)
Branko Tripalo
(Prehrambeno-biotehnološki fakultet, Zagreb)
Ankica Krmelić
(PETROKEMIJA Tvornica gnojiva, Kutina)

OPIS PROJEKTA

U gospodarenju vodama, vodu treba kao sirovinu optimalno koristiti, a to je moguće separacijom zagađivala pomoću ionskih izmjenjivača i membranskih procesa. Izborom selektivnih ionskih izmjenjivača vezanih uz membranske procese iz vode se može ukloniti do 70 % zagađivala. Pročišćena se voda može vraćati u proizvodni proces ili ispuštati u okoliš. Koncentrirane otopine, dobivene regeneracijom ionskih izmjenjivača ili membranski koncentrati, vraćaju se kao sirovine u proces proizvodnje gnojiva, odnosno galvanizaciju. Na taj se način može rasteretiti ionski izmjenjivač koji dolazi u kontakt s agresivnim influentom. Uz sintetske smole (HP-555, HP-441, Amberlit IRA 93 SP i Lewatit S 4426), istražit će se i druge tvari, poput klinoptilolita, glina ili otpadnih troski, s obzirom na kapacitet izmjene, brzinu vezanja i krivulju prodora amonijevog iona. Istražit će se i primjenjivost reverzne osmoze, kao moderne membranske metode za obradu industrijskih otpadnih voda. Za sintetske ionske izmjenjivače te klinoptilolit, odredit će se uvjeti obrade galvanizacijskih voda, posebice otpadne kromatne vode i vode nakon pocinčavanja. Načelo ponovnog korištenja i recikliranja voda u galvanizaciji, odnosno industriji gnojiva postat će model za obradu voda u drugim industrijskim granama, posebice voda zagađenih radionuklidima.

KLJUČNE RIJEČI
ionska izmjena, membranski procesi, reverzna osmoza, nanofiltracija, vode opterećene spojevima dušika, krom, cink, zeolitski tuf, modificirana glina, troska, ionsko izmjenjivačke smole

>> POSTIGNUTI REZULTATI

Ispitan je utjecaj obrade prirodnog zeolita (granulometrijska i kemijska predobrada zeolita, vrijeme uravnoteženja, koncentracija i pH-vrijednost otopina iona, te vrsta i koncentracija liganda) na kapacitet i selektivnost uklanjanja iona. Dokazano je da navedeni parametri bitno utječu na ionsko-izmjenjivačke procese metalnih iona u zeolitu. Dobiveni rezultati modelirani su Patersonovim modelom i Langmuirovom izotermom.

Ponašanje zeolita u kontaktu s vodenim i nevodenim otopinama metalnih iona je složeni problem zbog pojavljivanja cinka i kroma u više ionskih vrsta prema kojima zeolit ima različit afinitet. Utjecaj liganda u metal-kompleksnim spojevima na uklanjanje metalnog iona može biti odlučujući, ovisno o jakosti veze metalni ion–ligand, metalni ion–zeolit i ligand–zeolit–metalni ion. Vrsta liganda utječe na ionsko izmjenjivačke procese i učinkovitost pročišćavanja vode.

Dobiveni rezultati osnova su matematičkog modela vezanja cinkovih kompleksa na klinoptilolit. Predlažu se uvjeti za postizanje dinamičke ravnoteže u koloni, što će poslužiti kao osnova za prijedlog pročišćavanja voda opterećenih metalnim ionima i amonijakom.

Ukupan broj publiciranih radova prema kategorijama navedenim u bazi podataka http://bib.irb.hr: poglavlja u knjizi (5), znanstveni radovi u CC časopisima (15), radovi u ostalim časopisima (5), radovi u postupku objavljivanja (1), pozvana predavanja na skupovima (8), radovi u zbornicima skupova s međunarodnom recenzijom (6), ostali radovi u zbornicima skupova (1), sažeci u zbornicima skupova i neobjavljeni radovi (31), disertacije i magistarski radovi (13), diplomski radovi (5).

+385 1 4597 210 / scerjan@fkit.hr **Štefica Cerjan-Stefanović**
Department of Analytical Chemistry

Principal investigator

PROJECT DESCRIPTION

Any water management process should involve optimal use of water as raw material. This may be achieved by using ion exchange and membrane processes as a tool to separate the pollutants. Water can be purified up to 70 % by using ion exchangers hyphenated to the membranes. Purified water can be returned back into the production or can be disposed into the environment. Concentrate solutions, obtained after the regeneration of ion exchangers or after the usage of membrane processes, are returned as raw materials into the fertilizer production process or galvanization process. Thus, demands for ion exchangers coming into contact with aggresive media may be significantly lowered. Besides commercial synthetic resins (HP-555, HP-441, Amberlit IRA 93 SP and Lewatit S 4426), other materials, like clinoptilolite, clays or waste slag will be examined with respect to capacity of exchange, binding rate and other parameters. The applicability of reverse osmosis as a modern membrane method for industrial wastewater treatment will be investigated. The process parameters for the treatment of galvanization wastewaters using different synthetic ion exchangers and clinoptilolite will be determined. The principle of re-use and recycling of water in galvanization as well as in fertilizer production will serve as a model for treatment of other industrial wastewaters, particularly those polluted by radionuclides.

KEY WORDS
ion exchange, membrane processes, reverse osmosis, nanofiltration, waters polluted with nitrogen compounds, chromium, zinc, zeolite, modified clay, slag, ion exchange resins

PROGRESS SUMMARY

The influence of the zeolite pretreatment (granulometric and chemical treatment, equilibrium time, concentration and pH of ion solutions, type and concentration of ligands) on the capacity and removal selectivity was investigated. It was shown that those parameters have significant influence on the processes of exchange of metal ions on zeolites. The obtained results served as a basis for modeling using Paterson's model and Langmuir isotherm.

The behavior of zeolites in contact with aqueous and non-aqueous solutions of metal ions is a complex problem due to the possibility of appearance of zinc and chromium ions in different ionic forms towards which zeolites show different affinity. The influence of ligands in metal-complex compounds on metal ion removal can be crucial, depending on bonding strength of metal ion – ligand, metal ion – zeolite, and ligand – zeolite – metal ion. The type of ligand used influences the ion exchange processes and efficiency of water treatment.

Obtained results served as a basis for the modeling of zinc ion binding on clinoptilolite. The conditions for the dynamic equilibrium in columns are proposed, which will serve as a basis for constructing the treatment procedures for waters contaminated with metal and ammonium ions.

RESEARCH ASSOCIATES

Emir Hodžić
Mirela Rožić
Tomislav Bolanča
Karmen Margeta
Mario Šiljeg
Sanda Stefanović
Melita Regelja
Marin Hraste

CONSULTANTS

Ivan Mijatović
(Faculty of Food Technology and Biotechnology, Zagreb)
Stjepan Leaković
(PETROKEMIJA Fertilizer Company, Kutina)
Marin Matošić
(Faculty of Food Technology and Biotechnology, Zagreb)
Branko Tripalo
(Faculty of Food Technology and Biotechnology, Zagreb)
Ankica Krmelić
(PETROKEMIJA Fertilizer Company, Kutina)

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0125 017

Pročišćavanje površinskih voda – pokusno postrojenje.
Surface water treatment – pilot plant.

GLAVNI ISTRAŽIVAČ

Laszlo Sipos

01 4597 290 / lsipos@fkit.hr

Zavod za opću i anorgansku kemiju

SURADNICI

Branko Kunst
Krešimir Košutić
Tamara Štembal
Nataša Pribičić
Lidija Furač
Iva Novak
Marinko Markić
Nikša Zokić
Želimir Kovačević

VANJSKI SURADNICI

Željka Filipović Kovačević
(Prehrambeno-biotehnološki fakultet, Zagreb)
Zdenko Šmit
(Zavod za javno zdravstvo grada Zagreba)

OPIS PROJEKTA

Opskrba vodom u Hrvatskoj temeljena je u prošlosti pretežno na iskorištavanju kvalitetnih izvorišta pitke vode bez složenih sustava pročišćavanja. Zahtjevi za sve većim količinama kvalitetne vode za piće, kako na kontinentalnim tako i na priobalnim turističkim područjima Hrvatske, nameću korištenje i manje kvalitetnih izvorišta vode, te primjenu kompleksnih sustava pročišćavanja. Tijekom dosadašnje realizacije projekta istraživani su temeljni kemijski i biološki procesi postupaka uklanjanja željeza, mangana, amonijaka i arsena iz karakterističnih podzemnih voda Hrvatske. Definirani su optimalni uvjeti i kinetički parametri tih procesa na biološkim filtrima. Vezano uz problematiku obrade površinskih voda razvijen je sustav za automatsko vođenje procesa koagulacije i flokulacije mjerenjem potencijala strujanja. Posebna je pozornost posvećena razvoju i primjeni suvremenih membranskih procesa i/ili njihove kombinacije s kemijskim i biološkim postupcima pročišćavanja pri uklanjanju sulfata, arsena i pesticida iz vode za piće. Ispitivana su svojstva membrana i membranskih modula, te mehanizmi membranske separacije pri uklanjanju navedenih onečišćenja iz voda.

KLJUČNE RIJEČI
membrane, membranski procesi, mikrofiltracija, reverzna osmoza, nanofiltracija, obrada voda, podzemne vode, površinske vode, željezo, mangan, arsen, amonijak, organske tvari, ultrafiltracija, voda za piće

>> REZULTATI PROJEKTA

Dosadašnje spoznaje govore o mnogim prednostima membranskih postupaka (reverzne osmoze, nanofiltracije, ultrafiltracije i mikrofiltracije) obradbe pitkih i otpadnih voda. Razvijene su i analitičke metode određivanja arsena u vodi za piće. Dosadašnji rad na projektu rezultirao je s osam (8) objavljenih radova te tri (3) rada koja se nalaze u postupku objavljivanja. Ukupno je devetnaest (19) radova objavljeno u zbornicima sa znanstvenih skupova, objavljena su tri (3) magistarska i doktorska rada, dva (2) diplomska rada, te ukupno petnaest (15) stručnih elaborata i projekata.

+385 1 4597 290 / lsipos@fkit.hr
Laszlo Sipos
Department of General and Inogranic Chemistry
Principal investigator

PROJECT DESCRIPTION

Water supply in Croatia was based in the past on high-grade drinking water sources exploited without complex purification systems. Needfulness for higher quantity of the quality drinking water, in the continental and in the coastal tourist regions in Croatia, makes demands upon exploitation of the lower quality water sources and application of advanced purification systems. In the frame of the project, research and development of efficient arsenic, ammonium, iron and manganese biological removal processes from several typical Croatian groundwaters were performed, and the kinetic parameters of these processes were determined. A sensitive analytical method for determination of arsenic was developed, as well. In the addition, investigations of the membrane process applications and/or their combination with chemical and biological treatments was performed.

KEY WORDS
membrane, membrane processes, microfiltration, reverse osmosis, nanofiltration, water treatment, groundwater, surface water, iron, manganese, arsenic, ammonium, organic matter, ultrafiltration, drinking water

RESEARCH ASSOCIATES

Branko Kunst
Krešimir Košutić
Tamara Štembal
Nataša Pribičić
Lidija Furač
Iva Novak
Marinko Markić
Nikša Zokić
Želimir Kovačević

CONSULTANTS

Željka Filipović Kovačević
(Faculty of Food Technology and Biotechnology, Zagreb)
Zdenko Šmit
(Zagreb Institute of Public Health)

PROGRESS SUMMARY

The advantages of the membrane separations (reverse osmosis, nanofiltration, ultrafiltration, microfiltration) for the treatment of potable and wastewaters for removal of natural organic matter, pesticides, arsenic and sulfates, have been proved and documented. Moreover, the results of investigations of membrane and membrane module properties, and membrane separation process mechanisms of pollutants removal from natural and industrial waters, were described. A sensitive analytical method for determination of arsenic was developed. The results of the research performed in the frame of this project are published in 8 scientific (CC) papers, in 3 manuscripts in preparation, 19 conference papers, 3 Ph.D. + M.Sc. theses, 2 diploma works, and 15 studies.

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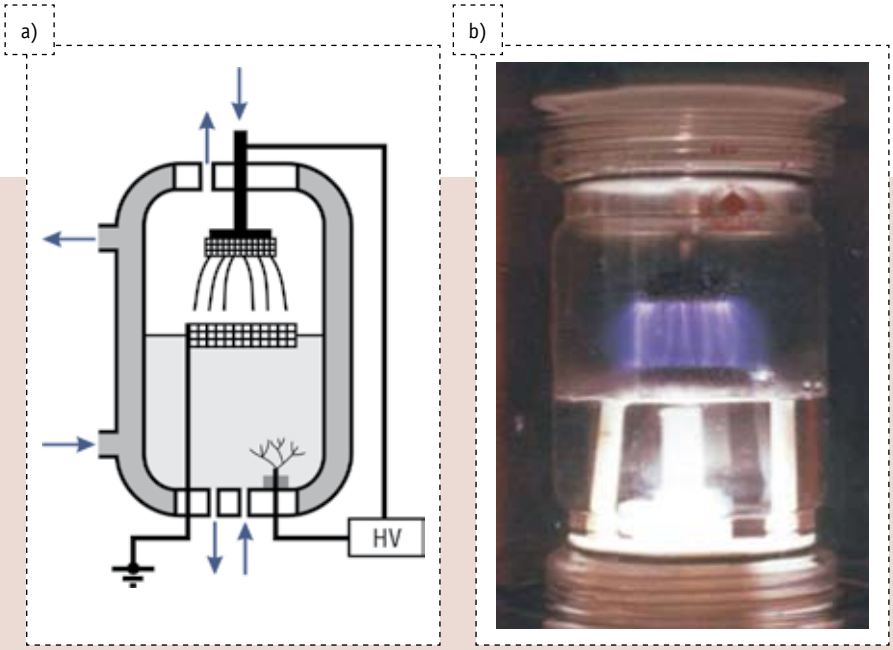

Reaktor s visokonaponskim električnim pražnjenjem za obradu otpadnih voda:
a) shematski prikaz reaktora, b) fotografija reaktora u radu.
High voltage electrical discharge reactor for wastewater treatment:
a) schematic diagram, b) photo of reactor in operating mode.

NAPREDNI OKSIDACIJSKI PROCESI ZA SMANJENJE OTPADA ORGANSKE KEMIJSKE INDUSTRIJE

GLAVNI ISTRAŽIVAČ

Natalija Koprivanac 01 4597 124 / nkopri@fkit.hr
Zavod za polimerno inženjerstvo i organsku kemijsku tehnologiju

SURADNICI

Sanja Papić
Ana Lončarić Božić
Dinko Vujević
Hrvoje Kušić
Igor Peternel

VANJSKI SURADNICI

Zvjezdana Lazarević
(PLIVA, Zagreb)
Vesna Tomić Benko
(PLIVA, Zagreb)
Jarolim Meixner
(DINA – Petrokemija, Omišalj)
Savka Kučar Dragičević
(Agencija za posebni otpad, Agencija za zaštitu okoliša)
Šefka Horvat Kurbegović
(Akademija likovnih umjetnosti, Zagreb)
Ivan Smolčić
(HERBOS, Sisak)

OPIS PROJEKTA

Vrlo zahtjevna briga o zaštiti okoliša iziskuje opsežan i cjelovit pristup rješavanju problema svih vrsta otpada. Smanjenje potrošnje energije, vode i drugih osnovnih sirovina zajedno sa smanjenjem ili uklanjanjem otpada predstavljaju najznačajnije prioritete u upravljanju okolišem. Problematika ovog projekta obuhvaća ekološke probleme vezane za industrijsku proizvodnju i primjenu organskih sintetskih bojila i pigmenata kao i pratećih intermedijara, posebno kloriranih ugljikovodika. Cilj projekta je primjena naprednih oksidacijskih procesa (AOP), samostalno i u kombinaciji s koagulacijom/flokulacijom, ne samo za potpuno obezbojenje već i za mineralizaciju organskih zagađivala u otpadnim vodama spomenutih industrija. Mjerenjem vrijednosti ekoloških parametara obrađene vode, praćenjem produkata degradacije i određivanjem brzine degradacije organskih zagađivala, te razvojem kinetičkih modela usporedit će se spomenuti procesi. Glavni cilj projekta je, prema načelu održivog razvika, primijeniti rezultate znanstvenih istraživanja kako bi se ustanovio program zaštite okoliša za procjene životnog ciklusa (LCA) boja i pigmenata koji bi se mogao primijeniti u zaštiti okoliša i drugih srodnih kemijskih industrija.

KLJUČNE RIJEČI
smanjenje otpada, obojene otpadne vode, napredni oksidacijski procesi, degradacija, bojila i pigmenti

>> POSTIGNUTI REZULTATI

Problematika ovog projekta je bila vezana uz primjenu različitih tipova naprednih oksidacijskih procesa za smanjenje organskih opterećenja u otpadnim vodama. Kao potencijalni katalizatori AOPa, primjenjivani su različiti sintetski zeoliti. Ovisno o tipu i strukturi organske tvari mijenjala se uspješnost pojedinog primijenjenog naprednog procesa. Utvrđeni su optimalni parametri pri kojima je postignuto najučinkovitije obezbojenje i uklanjanje organske tvari do razina prihvatljivih za okoliš, za svaki proučavani proces, dok je u nekim slučajevima postignuta čak i 100 %-tna mineralizacija organske tvari.

Postavljeni su odgovarajući kinetički modeli za svaki ispitivani sustav te su uspješno računalno simulirani eksperimentalni sustavi. Na temelju znanstveno-istraživačkog rada grupe istraživača na projektu ustanovljeno je da su napredni oksidacijski procesi vrlo učinkovita metoda za smanjenje organskih onečišćenja u simuliranim tehnološkim otpadnim vodama. Rezultati istraživanja očituju se brojnim objavljenim znanstvenim radovima (posebno se ističu 3 poglavlja u znanstvenim knjigama i 17 radova objavljenih u međunarodnim časopisima citiranim u tercijarnim publikacijama).

ADVANCED OXIDATION PROCESSES FOR WASTE MINIMIZATION OF ORGANIC CHEMICAL INDUSTRY

+385 1 4597 124 / nkopri@fkit.hr **Natalija Koprivanac**
Department of Polymer Engineering and Organic Chemical Technology
Principal investigator

PROJECT DESCRIPTION

Complex environmental issues demand a comprehensive integrated approach to tackle the problems of all types of waste. Reduction of energy, water and other raw materials use along with waste minimization and elimination are the highest priority in environmenatal management. The project subject matter emphasizes the ecological problems connected to the industrial production and application of synthetic dyes and pigments as well as accompanying intermediates, particulary chlorinated hydrocarbones. The main purpose of the project is application of advanced oxidation processes (AOP) separately, or in a combination with coagulation/flocculation process, not only for total decolorization but also for mineralization of organic pollutants of industrial wastewater. The AOP processes are compared on the basis of water quality parameters measurement, degradation products monitoring, determination of the degradation rate of organic pollutants and kinetic modeling. The main goal of the project is to establish environmental procedure for life cycle assessments of dyes and pigments which could be applied in environmental protection of similar chemical industries.

KEY WORDS
waste minimization, colored wastewaters, advanced oxidation processes, degradation, dyes and pigments

PROGRESS SUMMARY

The project was directed to the application of advanced oxidation processes (AOPs) as a tool for the minimization of organic loads in wastewaters. The use of zeolites as potential catalysts in combination with AOPs was also studied. The efficiency of each AOP varied concerning the structure and type of organic pollutant. The optimal parameters of each AOP, where maximal decolorization and mineralization of model wastewaters were achieved within the environmentally acceptable limits, were determined. In some cases even 100 % mineralization was achieved. For each studied system the corresponding kinetic models were established and model wastewater treatment systems were successfully simulated. On the basis of scientific work on this project it was established that the AOPs are very efficient methods for the minimization of organic content in simulated wastewaters. The results of the research are published in many scientific papers; among others 3 book chapters and 17 papers in CC/SCI/SCIex journals.

RESEARCH ASSOCIATES

Sanja Papić
Ana Lončarić Božić
Dinko Vujević
Hrvoje Kušić
Igor Peternel

CONSULTANTS

Zvjezdana Lazarević (PLIVA, Zagreb)
Vesna Tomić Benko (PLIVA, Zagreb)
Jarolim Meixner (DINA – Petrokemija, Omišalj)
Savka Kučar Dragičević (Croatian Environmental Agency; Hazardous Waste Management Agency)
Šefka Horvat Kurbegović (Academy of Fine Arts, Zagreb)
Ivan Smolčić (HERBOS, Sisak)

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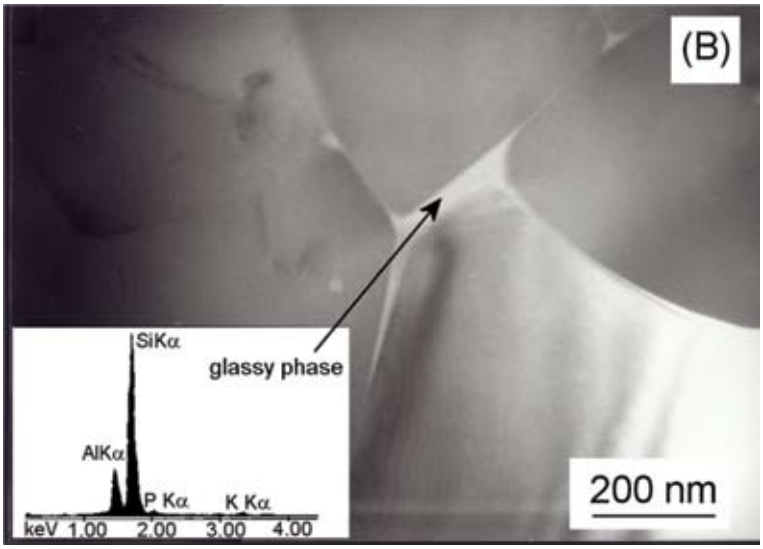

Mikrostruktura mulitne keramike.
TEM snimka mulitnih zrna s EDX analizom staklene faze.
Microstructure of mullite ceramics.
TEM micrograph of mullite grains with EDX spectrum of glassy phase.

GLAVNI ISTRAŽIVAČ

Helena Jasna Mencer 01 4597 230 / hjmencer@fkit.hr
Zavod za fizikalnu kemiju

SURADNICI

Zoran Gomzi
Marica Ivanković
Hrvoje Ivanković
Marko Rogošić
Jelena Macan
Ivan Brnardić
Petar Grošković
Vanja Kosar
Zvonimir Matusinović
Sebastian Orlić

OPIS PROJEKTA

Glavni cilj projekta bio je integracija znanstvene i inženjerske metodologije pri razvoju novih materijala i procesa. Projektni zadaci ostvarivani su u skladu s najnovijim istraživačkim smjernicama u okviru nekoliko projektnih zadataka (1) Istraživanje sol-gel postupka u svrhu priprave a) visokotemperaturne konstrukcijske keramike i tankih keramičkih prevlaka i b) organsko-anorganskih hibrida i nanokompozita; (2) Istraživanje ravnoteže kapljevina-kapljevina u niskomolekulnim sustavima te razrijeđenim i koncentriranim polimernim otopinama; (3) Istraživanje kinetike očvršćivanja i prijenosa topline u duromerima i duromernim kompozitima. Istraživanje unutar svakog zadatka bilo je organizirano prema jedinstvenoj shemi: hipoteza, model, mjerenje, karakterizacija, prilagodba modela eksperimentalnim podacima, promjena (optimiranje) procesnih parametara, željeni proces/materijal/svojstva.

KLJUČNE RIJEČI
sol-gel proces, visokotemperaturna strukturna keramika, organsko-anorganski hibridi, ravnoteža kapljevina-kapljevina, kinetički modeli

>> POSTIGNUTI REZULTATI

Uspješnim ostvarenjem ovog projekta povećana je opća razina nastavne i znanstvene osposobljenosti suradnika.
U okviru projekta suradnici su objavili tri (3) poglavlja u knjigama, dvadeset i šest (26) znanstvenih radova u CC časopisima, jedno (1) kongresno priopćenje u CC časopisu, pet (5) radova u ostalim časopisima. Šest (6) radova je u postupku objavljivanja u časopisima s međunarodnom recenzijom (od toga pet (5) u CC časopisima). U zbornicima skupova objavljeno je šesnaest (16) radova (od toga pet (5) radova u zbornicima skupova s međunarodnom recenzijom). Suradnici su prezentirali trideset i šest (36) radova na znanstvenim skupovima (sažeci). U okviru projekta izrađene su i obranjene dvije (2) doktorske disertacije, četiri (4) magistarska rada te osamnaest (18) diplomskih radova.

+385 1 4597 230 / hjmencer@fkit.hr **Helena Jasna Mencer**
Department of Physical Chemistry

Principal investigator

RESEARCH ASSOCIATES

Zoran Gomzi
Marica Ivanković
Hrvoje Ivanković
Marko Rogošić
Jelena Macan
Ivan Brnardić
Petar Grošković
Vanja Kosar
Zvonimir Matusinović
Sebastijan Orlić

PROJECT DESCRIPTION

The project was aimed at the integration of education, science and engineering by focusing the activities on novel processes and processing routes for the preparation of advanced materials. The research was subdivided into several subprojects: (1) The sol-gel process for the preparation of a) high-temperature structural ceramics and thin ceramic coatings and b) organic-inorganic hybrids/ nanocomposites (2) Liquid-liquid equilibria in low-molecular-weight systems as well as in dilute and concentrated polymer solutions (3) The curing kinetics and heat transfer in thermosets and thermoset composites. The research within every subpart of the project was organized according to the unique scheme: hypothesis, model, measurements, characterization, adjustment of the model to obtain the compatibility with experimental data, the change (optimization) of process parameters, desired process/material/properties.

KEY WORDS
sol-gel process, high-temperature structural ceramics, organic-inorganic hybrids, liquid-liquid equilibria, kinetic models

PROGRESS SUMMARY

The knowledge level of all investigators, especially young scientists, was increased.
Results of the project: 3 chapters in books, 26 articles published in international journals, another 6 accepted for publishing in international journals, 16 proceedings, 36 presentations on domestic and international scientific conferences, 2 Ph.D. theses; 4 M.Sc. theses, 18 diploma theses.

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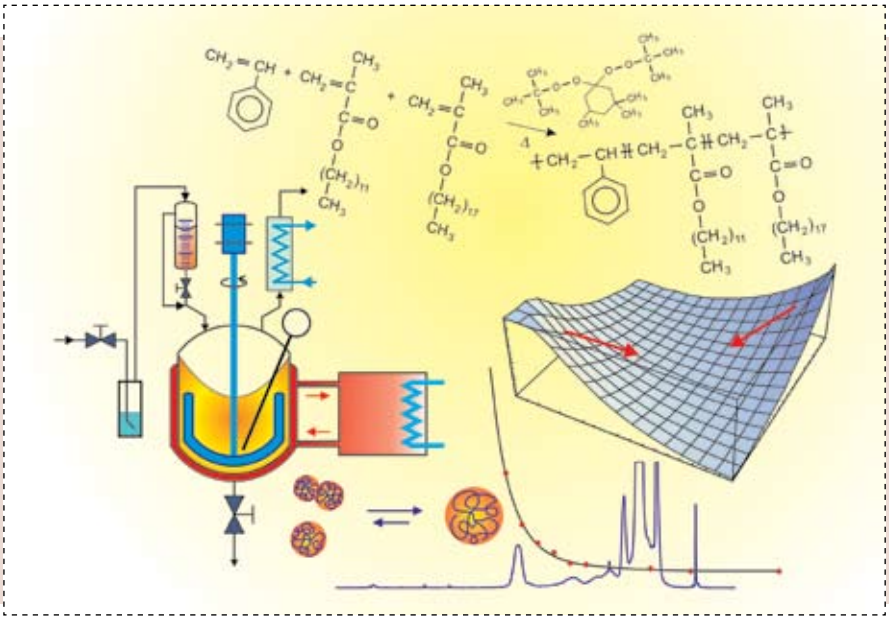
PROCESI USMJERENIH RADIKALSKIH POLIMERIZACIJA

CONTROLLED FREE RADICAL POLYMERIZATION PROCESSES



GLAVNI ISTRAŽIVAČ

Zvonimir Janović 01 4597 125 / janovic@fkit.hr
Zavod za tehnologiju nafte i petrokemiju

SURADNICI

Ante Jukić
Karla Sarić
Ljubica Tomašek
Elvira Vidović

VANJSKI SURADNICI

Ljiljana Marinić-Pajc
(INA Industrija nafte, Zagreb)
Rosana Asić
(INA Industrija nafte, Zagreb)
Otto Vogl
(University of Massachusetts, USA)

OPIS PROJEKTA

Reakcije i procesi radikalskih polimerizacija temeljni su i najviše upotrebljavani tehnologijski postupci dobivanja polimernih materijala. Izrazitih su prednosti prema ionskim i koordinativnim polimerizacijama zbog jednostavnije tehničke provedbe procesa u masi, otopini, suspenziji i emulziji. Međutim, obzirom na mehanizam i kinetiku reakcije, nije moguće istodobno postići veliku brzinu i doseg i veliku molnu masu. U zadnje vrijeme obavljaju se opsežna istraživanja usmjerenih radikalskih polimerizacija, posebice iniciranih nitroksidnim radikalima i uz prisustvo kompleksa prijelaznih metala, kao i novih diperoksidnih inicijatora. Tim inicijatorima, pri određenim procesnim uvjetima, nastaju homopolimeri, kopolimeri, terpolimeri i cijepljeni kopolimeri zahtijevanih strukturnih pravilnosti i željenih svojstava. Nalaze veliku primjenu u mnogim područjima, posebice kao poboljšavala reoloških svojstava kapljevina, najviše indeksa viskoznosti mazivih ulja.
U obavljenim istraživanjima opisane su reakcije i procesi usmjerenih radikalskih ko- i terpolimerizacija kao i cijepljenih kopolimerizacija vinilnih monomera, pretežito alkiliranih metakrilata i etilen/propilen elastomera uz monofunkcijske i difunkcijske peroksidne inicijatore. Dobivenim kopolimerima određeni su važniji strukturni čimbenici. Prema rezultatima obavljenih istraživanja modelirani su i optimirani procesi dobivanja opisanih kopolimera sa svojstvima poboljšavala indeksa viskoznosti mazivih ulja.

KLJUČNE RIJEČI
vinilni monomeri, radikalske kopolimerizacije, difunkcijski peroksisdni inicijatori, polimerni reološki modifikatori

>> POSTIGNUTI REZULTATI

Ispitani su reakcijski i procesni čimbenici dobivanja novih polimernih materijala reakcijama radikalskih kopolimerizacija sa svojstvima poboljšavala reoloških svojstava kapljevina, posebice mineralnih mazivih ulja. Provedene su reakcije kopolimerizacije i terpolimerizacije vinilnih monomera: stirena, metil-metakrilata, anhidrida maleinske kiseline i dugolančanih estera metakrilne kiseline do niskih i visokih konverzija i promjenljivog sastava smjese monomera. Ispitane su reakcije uz monofunkcijske (kao što je benzoil peroksid) i difunkcijske (1,1-di(terc-butilperoksi)-3,3,5-trimetil cikloheksan) slobodno-radikalske inicijatore u organskim otapalima i baznom mineralnom ulju.
Također su ispitane i reakcije cijepljenih kopolimerizacija navedenih monomera i poli(etilen-*ko*-propilena) (EPC) uz dvije vrste inicijatora. Strukturne značajke dobivenih polimernih vrsta utvrđene su spektroskopskim i toplinskim metodama, a molekulska masa metodom isključenja po veličini. Određena su i svojstva otopina polimera u organskim otapalima. Optimiran je proces polimerizacije pri izotermnim i adijabatskim uvjetima i primjenska svojstva kopolimera kao reoloških poboljšavala mineralnih mazivih ulja. Utvrđena je mješljivost i molekulska međudjelovanja polimernih smjesa EPC/metakrilatni homopolimeri, EPC/polilstiren kao i polistiren/metakrilatni homopolimeri. Te polimerne smjese pokazuju komplementarni učin reoloških svojstava otopina, jer EPC značajno povećava viskoznost i smičnu stabilnost, a poli(alkil-metakrilati) povećavaju indeks viskoznosti i snizuju stinište. Ukupna djelotvornost opisanih polimernih smjesa određena je njihovim sastavom, koncentracijom, temperaturom i vrstom otapala.

+385 1 4597 125 / janovic@fkit.hr
Zvonimir Janović
Principal investigator
Petroleum and Petrochemical Department

PROJECT DESCRIPTION

Reactions and processes of free radical polymerizations are the most used techniques in production of polymeric materials. This kind of polymerization has a distinct advantage over the ionic and coordination polymerization by allowing easy production by the bulk, solution, suspension or emulsion processes. However, regarding to the mechanisms and kinetics, it is not possible to achieve simultaneously the high polymerization rate, high conversion as well as very high molecular weight of the polymers obtained. Recently, the polymerization reactions with controlled initiation overcome the above shortage; complex-based and, particularly, bifunctional free radical initiators are used. In that manner, copolymers of tailored structures may be produced, that are widely used in various fields. Of particular interest is the use of copolymers as solution rheology modifiers.

In the present research, the controlled reactions and processes of production of some copolymers and terpolymers based on alkyl methacrylates and ethylene/propylene elastomers, are studied. Therein, monofunctional as well as bifunctional peroxyde initiators are investigated, and linear and grafted polymerizations are tested. The structural characteristics of obtained copolymers are established. The results are used in modeling and optimization of the polymerization processes. The properties of products to be used as rheology modifiers in lubricating oils are optimized as well.

KEY WORDS
vinyl monomers, free radical copolymerization, bifunctional peroxide initiators, polymeric rheology modifiers

PROGRESS SUMMARY

The kinetic and process parameters of various linear copolymerization, terpolymerization and graft-copolymerization reactions have been examined. The investigated monomers encompassed styrene, methyl-methacrylate, maleic anhydride and long chain methacrylic acid esters. Ethylene/propylene elastomers were used as templates for grafting. Obtained polymers possessed controlled and defined structural characteristics and were tested as solution rheology modifiers, particularly lubricating oil viscosity index improvers. The copolymerization reactions using monofunctional (benzoil peroxide) and bifunctional [1,1-di(tert-butilperoxy)-3,3,5-trimethylcyclohexane] initiators were optimized; the reactions were performed in organic solvent or base mineral oil solutions. The optimal properties of obtained copolymers to be used as lubricating oil rheology modifiers were deduced. A kinetic model was developed to account for the continous, uniform addition of initiator solution during polymerization process. Some rheological properties of mineral lubricating oils containining polyolefin and poly(alkyl methacrylate) mixtures over a wide composition range were examined. The efficiency of polymer mixtures as rheology modifiers was affected by the copolymer composition, mixture composition, total polymer concentration, temperature and solvent used.

RESEARCH ASSOCIATES

Ante Jukić
Karla Sarić
Ljubica Tomašek
Elvira Vidović

CONSULTANTS

Ljiljana Marinić-Pajc
(INA Industrija nafte, Zagreb)
Rosana Asić
(INA Industrija nafte, Zagreb)
Otto Vogl
(University of Massachusetts, USA)

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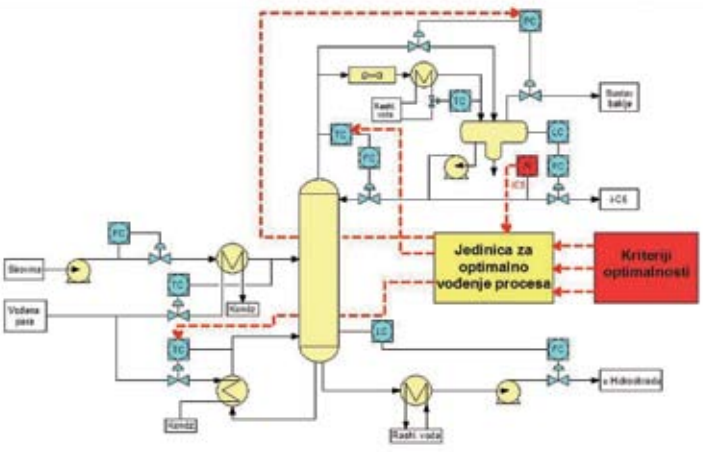
Pogon izomerizacije - INA Rijeka.
Isomerization plant - INA Rijeka.



Optimiranje izomerizacije.
Optimization of isomerization.

TEKUĆINSKA NAFTNA GORIVA POBOLJŠANIH EKOLOŠKIH ZNAČAJKI

GLAVNI ISTRAŽIVAČ

Katica Sertić-Bionda 01 4597 129 / kserti@fkit.hr
Zavod za tehnologiju nafte i petrokemiju

SURADNICI

Marko Mužic
Tamara Adžamić

VANJSKI SURADNICI

Neda Marčec-Rahelić
(INA Industrija nafte, Zagreb)
Marija Zaić-Kubatović
(INA Industrija nafte, Zagreb)
Janko Moše
(INA Industrija nafte, Zagreb)
Vlado Kuzmić
(OMV Hrvatska)
Mladen Ištuk
(INA Industrija nafte, Zagreb)
Tomislav Šarić
(INA Industrija nafte, Zagreb)

OPIS PROJEKTA

Razvoj temeljnih tehnoloških procesa proizvodnje naftnih goriva vezan je uz zahtjeve o njihovoj kakvoći, prvenstveno uz prekomjerni sadržaj sumpora i aromatskih ugljikovodika. Stoga se današnja proizvodnja motornih goriva procesima prerade nafte mora temeljiti na odgovarajućim prilagodbama postojećih procesa, ali isto tako i na razvoju novih, posebice ekološki prihvatljivih procesa. Rad na projektu provodio se s ciljem pronalaženja odgovarajućih tehnoloških rješenja što rezultiraju smanjenjem udjela spomenutih komponenata u naftnim gorivima, a istraživanja su provedena u laboratorijskom mjerilu uz primjenu modela za simulaciju i optimiranje tih procesa. U vremenu trajanja projekta istraživani su procesi katalitičkog krekiranja plinskih ulja te izomerizacije i reformiranja primarnog benzina. Također su istraženi procesi uklanjanja sumpora iz sirovina i produkata kao što su hidrodesulfurizacija i ekstrakcija. Poseban dio istraživanja bavi se ispitivanjem utjecaja procesnih parametara na fizikalne i kemijske značajke bitumena.

KLJUČNE RIJEČI
naftna goriva, hidrodesulfurizacija, katalitički kreking, katalitički reforming, izomerizacija

>> POSTIGNUTI REZULTATI

Ispitan je utjecaj hidroobrade sirovine katalitičkog krekiranja na raspodjelu produkata s obzirom na sadržaj sumpora i aromata te je postavljen kinetički model procesa. Na temelju istraživanja procesa izomerizacije C_5–C_6 ugljikovodika postavljen je matematički model korištenjem programskog sustava ChemCAD. Simulirana su tri unapređenja procesa: dodatkom kolone za izopentanizaciju, primjenom molekulskih sita te ugradnjom kolone deizoheksanizera.
Također, ispitan je proces hidrodesulfurizacije plinskih ulja u malom prokapnom reaktoru te je predložen kinetički model i provedena simulacija procesa. Utvrđeni su utjecaji najvažnijih procesnih parametara na sadržaj sumpora i ugljikovodični sastav plinskih ulja. Istražen je utjecaj procesnih parametara katalitičkog reforminga benzina na kvalitetu produkata, kao i utjecaj uvjeta regeneracije katalizatora na njegov vijek trajanja. Navedena istraživanja nalaze primjenu u naftnoj industriji sa svrhom proizvodnje naftnih goriva u skladu s europskim zahtjevima kakvoće.

+385 1 4597 129 / kserti@fkit.hr **Katica Sertić-Bionda**
Petroleum and Petrochemical department

Principal investigator

PROJECT DESCRIPTION

Development of technological processes regarding the production of petroleum fuels are tied to quality requirements, particularly to excessive sulfur compounds and aromatic hydrocarbons content restrictions. Consequently, today's production of motor fuels must relay on ability to adequately adapt current technology and to develop new environmentally friendly refining processes. The goal of the project was to find adequate technological solutions which result in reduced content of the mentioned petroleum fuels components. The experiments were performed on the laboratory scale together with the use of models for simulation and optimization of these processes. During the project, gas oil catalytic cracking processes as well as naphtha isomerization and reforming processes were examined. Processes for removing sulfur from feedstocks and products, like hydrodesulfurization and extraction were also undertaken. Separate part of the work on the project was the investigation of process parameter influence on physical and chemical properties of bitumens.

KEY WORDS
petroleum fuels, hydrodesulfrization, catalytic cracking, catalytic reforming, isomerization

RESEARCH ASSOCIATES

Marko Mužic
Tamara Adžamić

CONSULTANTS

Neda Marčec-Rahelić
(INA Industrija nafte, Zagreb)
Marija Zaić-Kubatović
(INA Industrija nafte, Zagreb)
Janko Moše
(INA Industrija nafte, Zagreb)
Vlado Kuzmić
(OMV Croatia)
Mladen Ištuk
(INA Industrija nafte, Zagreb)
Tomislav Šarić
(INA Industrija nafte, Zagreb)

PROGRESS SUMMARY

The influence of catalytic cracking feedstock hydrotreatment on product distribution with regard to sulfur compounds and aromatics content was investigated and the kinetic model of the process was developed.
Based on the exploration of the C_5–C_6 isomerization process the mathematical model was developed applying ChemCAD software. The following process improvements were simulated: by adding isopentenization column, applying molecular sieves and installing deisohexenizer column. Hydrodesulfurization of gas oils in small trickle bed reactor was investigated, the kinetic model was developed and the simulation of the process was performed. The influence of the main process parameters on the sulfur and hydrocarbon content in gas oils was established. The influence of naphtha catalytic reforming process parameters on product quality as well as the influence of catalyst regeneration conditions on their lifetime was examined. The results of the afore mentioned research are implemented in the refining industry for producing fuels that are in accordance with European quality requirements.

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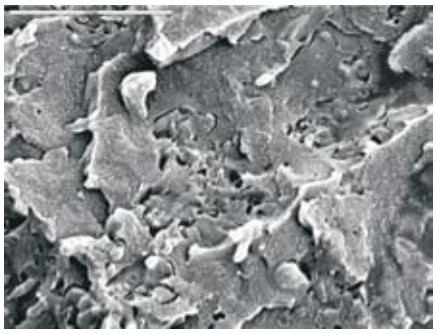
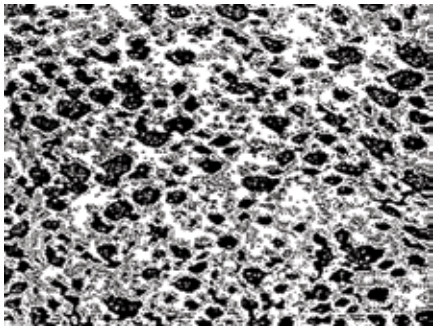


Mikrografija PS-HI/SEBS mješavine.
Micrography of PS-HI/SEBS mixture.



Mikrografija polimerne mreže u BIT/SBS.
Micrography of polymer matrix in BIT/SBS.

GLAVNI ISTRAŽIVAČ

Vesna Rek 01 4597 118 / vrek@fkit.hr
Zavod za polimerno inženjerstvo i organsku kemijsku tehnologiju

SURADNICI

Emi Govorčin Bajsić
Tamara Holjevac Grgurić
Drago Hace
Zrinka Barjaktarović
Nina Vranješ

VANJSKI SURADNICI

Želimir Jelčić
(PLIVA, Zagreb)
Marica Mišak Mlinac
(DIOKI, Zagreb)
Marijan Tuđa
(PLIVA, Zagreb)
Muhamed Sućeska
(Brodarski institut, Zagreb)
Klaus Lederer
(Leoben, Montanuniversitat)
Leopold Kranner
(Wien, Kunststoffinstitut)

OPIS PROJEKTA

Višefazni polimerni materijali, polimerne mješavine i polimer bitumeni intenzivno se studiraju s ciljem razvoja novih inženjerskih materijala željenih svojstava. Od polimernih mješavina od iznimne su važnosti mješavine termoplastičnog elastomera, TPE, i termopolasta, T, u kojima elastomerna komponenta doprinosi većoj elastičnosti i žilavosti, naročito pri niskim temperaturama, te novom reološkom ponašanju mješavina. Polimeri, termoplastični elastomeri i termoplasti su modifikatori bitumena, BIT. Mješavine BIT/polimer imaju uslijed viskoelastičnosti polimera bolja reološka svojstva pri nižim i višim temperaturama u odnosu na bitumen. Cilj projekta je sustavno istražiti utjecaj sastava i strukture (broja faza, vrste i sastava faza, te sadržaja faza) mješavina TPE/T, TPE/BIT, i T/BIT, te interakcija pojedinih faza na reološka svojstva pri preradi mješavina, na morfološku strukturu, primjenska mehanička i reološka svojstva dobivenih mješavina, te na njihovu toplinsku postojanost u cijelom području sastava. Očekuje se dobivanje novih spoznaja o utjecaju pojedinih faza i njihovih interakcija na preradbena svojstva, strukturu i primjenska svojstva mješavina. Također, očekuje se razvoj i dizajniranje novih materijala tipa TPE/T i polimer/BIT, te razvoj znanosti, odnosno unaprjeđenje nastavnog procesa.

KLJUČNE RIJEČI
mješavine termoplastičnih elastomera i termoplasta, polimer bitumeni, morfologija, reologija, toplinska stabilnost

>> POSTIGNUTI REZULTATI

U istraženim višefaznim sustavima dobivene su i utvrđene nove znanstvene spoznaje o utjecaju sastava i strukture (broja faza, vrste i sastava faza, te sadržaja faza) mješavina i interakcija pojedinih faza na reološka svojstva taline u procesiranju mješavina, kao i na morfološku strukturu, mehanička i reološka svojstva ekstrudiranih i kalupljenih uzoraka istraženih mješavina, te njihovu termičku stabilnost i stabilnost na zagrebanje. Data je procjena trajnosti mješavina, te su utvrđeni kinetički i reološki modeli. Rezultati morfoloških karakteristika, procesnih karakteristika i dinamičko mehaničkog ponašanja istraženih mješavina provjereni su kroz fraktalne veličine, Hurstov grubosni eksponent i klasičnu fraktalnu dimenziju istraženih dvokomponentnih i nekih trokomponentnih mješavina. Za mješavine bitumena i SBS-a utvrđena je modifikacija viskoelastičnog ponašanja krutih uzoraka polimer bitumena, te reološko ponašanje disperzija bitumena i SBS-a uz praćenje interakcija i morfologije polimer bitumena. Utvrđena je termooksidativna stabilnost mješavina bitumena i SBS-a, te utjecaji vrste bitumena i pojedinih faza na termooksidativnu stabilnost dispezija polimer bitumena i krutog uzorka. Prikaz postignuća dat je u ispisu iz Hrvatske znanstvene bibliografije.

+385 1 4597 118 / vrek@fkit.hr
Vesna Rek
Deparment of Polymer Engineering and Organic Chemical Technology
Principal investigator

PROJECT DESCRIPTION

The multicomponent polymer materials, polymer blends and polymer bitumens are intensively studied, with an aim to develop new engineering materials with tailored properties. Among the polymer blends of great importance are the blends of thermoplastic elastomers, TPE, and thermoplasts, T, in which the elastomeric component contributes to the greater elasticity and toughness, especially at low temperatures, as well as to the new rheological behavior of blends. Polymers, thermoplastic elastomers and thermoplasts, are used as bitumen, BIT, modifiers. BIT/polymer blends have better rheological properties at lower and higher temperatures in comparison with BIT, due to the viscoelastic properties of added polymers. The aim of the project is the sistematic research of the influence of composition and structure of the TPE/T, TPE/BIT and T/BIT blends, on their rheological properties in the processing of blends, morphological structure, mechanical and rheological application properties and their stability. The new knowledge about the influence of particular phases, their interactions on the processing properties, structure and application properties of blends is expected. New materials, TPE/T and polymer/BIT will be developed and designed. The overall scientific and educational level will be increased.

KEY WORDS
Thermoplastic elastomer and thermoplast blends, polymer bitumens, morphology, rheology, thermal stability

PROGRESS SUMMARY

The new knowledge about the influence of the number and type of the phases, phase composition, phase content and phase interactions in the new TPE/T blends and polymer bitumen is gathered, regarding the processing properties of the blends, their morphological structure, mechanical and rheological properties of extruded and moulded samples as well as their thermal stability and wear resistance. The useful life of the blends is predicted and kinetic and rheological models are established. The results of the morphological characteristics, processing parameters and dynamic mechanical behavior of investigated blends are verified by fractal parameters, Hurst roughness exponent and classic fractal dimension. The modification of viscoelastic behavior of BIT/polymer blends in processing and application is established and explained in terms of phase interactions and morphology of BIT/polymer blends. The thermooxidative stability of BIT/polymer blends is established as well as the influence of bitumen type on their stability. The overview of the achievements is given in the Croatian scientific bibliography excerpt.

RESEARCH ASSOCIATES

Emi Govorčin Bajsić
Tamara Holjevac Grgurić
Drago Hace
Zrinka Barjaktarović
Nina Vranješ

CONSULTANTS

Želimir Jelčić
(PLIVA, Zagreb)
Marica Mišak Mlinac
(DIOKI, Zagreb)
Marijan Tuđa
(PLIVA, Zagreb)
Muhamed Sućeska
(Brodarski Institute, Zagreb)
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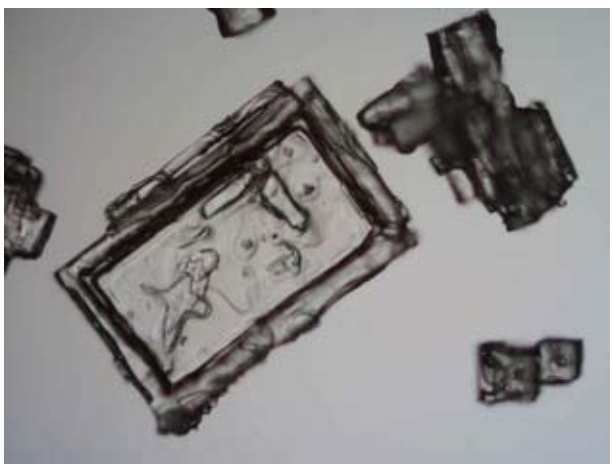
Usitnjavanje dolomita u planetarnom mlinu.
Planetary ball mill comminution of dolomite.



Kristali KCl-a dobiveni šaržnom kristalizacijom.
KCl crystals obtained in the process of batch crystalization.

GLAVNI ISTRAŽIVAČ

Antun Glasnović 01 4597 221 / aglasnov@fkit.hr
Zavod za mehaničko i toplinsko procesno inženjerstvo

SURADNICI

Marin Hraste
Aleksandra Sander
Jasna Prlić Kardum
Gordana Matijašić
Krunoslav Žižek

OPIS PROJEKTA

Kako su produkti kemijske industrije vrlo često složene tvari (heterogeni sustavi, kompoziti), suvremena istraživanja u kemijskom inženjerstvu usmjerena su na predviđanje njihovih svojstava. Proces se mora voditi na način da osigura visoku djelotvornost, nisku razinu emisija u okoliš, uštedu energije i sirovina, te posebice kvalitetu konačnog proizvoda. Za dobivanje produkta željene kvalitete, između ostalog nužno je razumijevanje interakcija na nano- i mikrorazini koje su posljedica fizikalnih svojstava disperznih sustava (raspodjela veličina čestica, oblik čestica, poroznost, specifična površina, raspodjela veličina pora, vlažnost, sastav). Predmet brojnih istraživanja jest proučavanje utjecaja karakteristika disperzne faze na procese sušenja, kristalizacije, usitnjavanja i granuliranja. Procesi se opisuju matematičkim modelima, određuju se parametri modelnih jednadžbi i povezuju s transportnim koeficijentima i granulometrijskim svojstvima. U konačnici se oblikuju funkcije svojstava, koje predviđaju svojstva proizvoda na temelju procesnih parametara i fizikalnih svojstava čvrstih čestica.

KLJUČNE RIJEČI
disperzni sustav, kinetika procesa, kristalizacija, sušenje, usitnjavanje

>> POSTIGNUTI REZULTATI

Kinetika sušenja istraživanih materijala različitim metodama u odabranom području temperatura zagrijanog zraka, tlaka ili intenziteta mikrovalnog zagrijavanja korelira se novim matematičkim modelom (modificirani Pageov model). Dobiveni rezultati ukazuju da modelni parametar *t* odgovara vremenu u kojem je difuzija (u početku prvog ili drugog perioda padajuće brzine sušenja) dominirajući mehanizam prijenosa vlage kroz unutrašnju strukturu materijala.

Istraživan je utjecaj vrste miješala i brzine hlađenja na kinetiku kristalizacije KCl, na raspodjelu veličina i oblik dobivenih kristala. Utvrđeno je da na proces kristalizacije znatnije utječe brzina hlađenja nego brzina miješanja. Gustoća populacije nukleusa kod kristalizacije povećava se s porastom intenziteta miješanja. Primjenom različitih procesnih uvjeta dobivaju se različite raspodjele veličina kristala i njihov različit oblik.

Provedena je simulacija procesa usitnjavanja polidisperznih uzoraka. Razvijen je softver koji na temelju rješenja populacijske bilance omogućuje predviđanje raspodjele veličina čestica tijekom diskontinuiranog procesa mokrog usitnjavanja. U paralelnom istraživanju, dokazano je da će usitnjavanje u visokoenergetskom mlinu nakon kratkog vremena dovesti do nastanka sustava istih granulometrijskih, a time i reoloških svojstava, bez obzira na primarna svojstva sustava prije usitnjavanja.

+385 1 4597 221 / aglasnov@fkit.hr
Antun Glasnović
Department of Mechanical and Thermal Process Engineering

Principal investigator

RESEARCH ASSOCIATES

Marin Hraste
Aleksandra Sander
Jasna Prlić Kardum
Gordana Matijašić
Krunoslav Žižek

PROJECT DESCRIPTION

Chemical industry products are usually complex substances (heterogeneous systems, composites); prediction of the final properties of such products is a fruitful topic of recent research in chemical engineering. The process must be carried out in the way that satisfies high demands of efficient production, low pollution, energy and raw material savings, and especially final product quality. In order to obtain the defined product quality, among other things, it is necessary to understand the interactions at nano- and microscale that affect physical properties of the disperse systems (particle size distribution, particle shape, porosity, specific area, pore size distribution, moisture content and composition). The important topic of the research in contemporary chemical engineering is the influence of disperse phase characteristics on processes such as comminution, drying, crystallization and granulation. Mathematical modeling, evaluation of the interactions between model equation parameters, transport coefficients and granulometric properties enhances the possibility for obtaining desired product properties. Formulation of property functions enables the prediction of product properties on the basis of process parameters and physical properties of solid particles.

KEY WORDS
comminution, crystallization, disperse system, drying, process kinetics

PROGRESS SUMMARY

Different drying methods were studied; drying kinetics of investigated materials can be successfully correlated with a newly developed mathematical model (modified Page model) in a range of hot air temperatures, pressures and/or microwave heating intensity. The results reveal the physical meaning of the model parameter *t*, which corresponds to the time at which diffusion (at the beginning of the first or second falling rate period) is the governing mechanism for moisture movement through the inner material structure.

The influence of the type of stirrer, stirrer speed and the cooling rate on crystallization kinetics of KCl, crystal size distribution and obtained crystal habit, has been investigated on a laboratory scale. Population density of crystal nuclei and overall linear growth rate are evaluated according to the procedure by Stone and Randolph. The influence of cooling rate is more pronounced than the influence of mixing rate. Higher intensity of agitation increases the population density of crystal nuclei. Different process conditions result in different crystal size distributions and shapes.

A simulation of comminution process of polydisperse samples is carried out. The solution of population balance equation is incorporated in a home-made software that enables the anticipation of particle size distribution during wet batch comminution. In a parallel investigation, it is proven that the highly energetic mill comminution will lead, in a short time, to the formation of systems possessing the same granulometric, and consequently rheological properties, regardless of the primary particle properties.

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2. **Jasna Prlić Kardum**
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3. **Aleksandra Sander**
Komparativna istraživanja kinetike sušenja čvrstih materijala: *disertacija*, Zagreb, Fakultet kemijskog inženjerstva i tehnologije, 11.07.2003., voditelj **Antun Glasnović**

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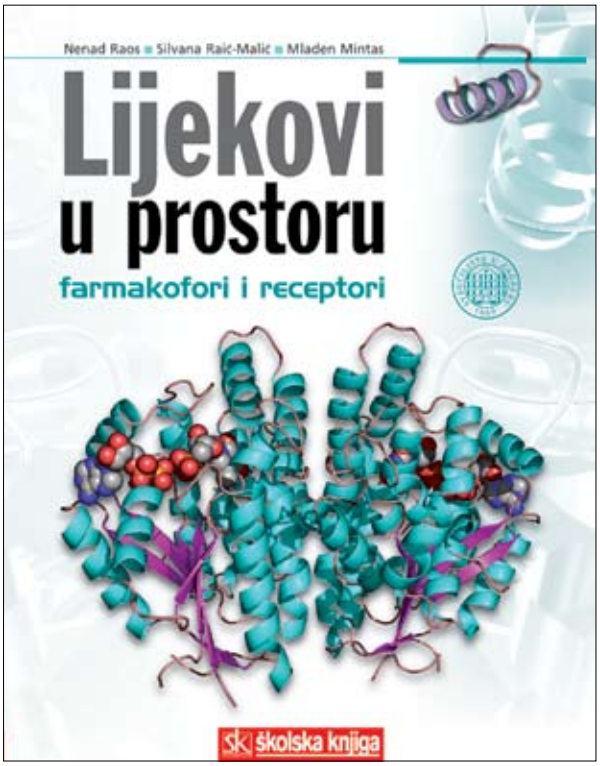
PRIRODNE ZNANOSTI
Kemija

NATURAL SCIENCES
Chemistry

0125 003

RAZVOJ NOVIH TERAPIJSKIH I DIJAGNOSTIČKIH SUPSTANCIJA
ZA GENSKU TERAPIJU RAKA

DEVELOPMENT OF NEW THERAPEUTIC & DIAGNOSTIC SUBSTANCES
FOR GENE THERAPY OF CANCER



Rendgenska struktura kompleksa homodimera timidin-kinaze (TK) virusa herpes simplex tipa 1 (HSV-1), adenozin-trifosfata (ATP) i prirodnog supstrata deoksitimidina (dT).
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N. Raos, S. Raić-Malić and M. Mintas: Stereochemistry of Drugs: Pharmacophores and Receptors, Školska knjiga, Zagreb, a book written in Croatian, 2005.

RAZVOJ NOVIH TERAPIJSKIH I DIJAGNOSTIČKIH SUPSTANCIJA ZA GENSKU TERAPIJU RAKA

GLAVNI ISTRAŽIVAČ

Mladen Mintas 01 4597 214 / mmintas@fkit.hr
Zavod za organsku kemiju

SURADNICI

Silvana Raič-Malić
Tatjana Gazivoda
Svjetlana Prekupec
Vedran Krištafor
Karlo Wittine

VANJSKI SURADNICI

Ante Nagl
(Tekstilno-tehnološki fakultet, Zagreb)
Antonija Hergold-Brundić
(Tekstilno-tehnološki fakultet, Zagreb)
Mario Cetina
(Tekstilno-tehnološki fakultet, Zagreb)
Branka Zorc
(Farmaceutsko-biokemijski fakultet, Zagreb)
Krešimir Pavelić
(Institut Ruđer Bošković, Zagreb)
Erik De Clercq
(Rega Institute for Medical Research, Leuven, Belgija)
Jan Balzarini
(Rega Institute for Medical Research, Leuven, Belgija)
Gerd Folkers
(Department Pharmazie, ETH-Zürich)

OPIS PROJEKTA

Široko rasprostranjene virusne infekcije i rak zdravstveni su problem svjetskih razmjera. Osnovni problemi u antivirusnoj i antitumorskoj kemoterapiji su rezistentnost na lijekove i njihova štetna djelovanja na normalno tkivo. Stoga je osnovni cilj naših istraživanja sintetizirati nove vrste spojeva koji bi se mogli primijeniti kao djelotvorni i selektivni agensi protiv patogenih virusa i zloćudnih tumora ljudskog porijekla.
Poseban je cilj istraživanja sintetizirati nove spojeve iz reda nukleozidnih mimetika kojima bi se prevladao problem rezistentnosti postojećih lijekova aciklovira i ganciklovira na infekcije uzrokovane virusima herpesa i koji bi se mogli primijeniti u kombinaciji s timidin-kinazom (TK) virusa herpesa kao prolijekovi za gensku terapiju raka. Cilj je istraživanja, također, razviti nove modelne spojeve za primjenu u pozitron-emisijskoj tomografiji (PET). To je metoda identifikacije tumora i mjesta nakupljanja limfocita pri odbacivanju transplantata od strane domaćina (GvHD), što je popratna (često letalna) komplikacija kod alogenske transplantacije koštane srži (allo-BMT).

KLJUČNE RIJEČI
aciklički analozi nukleozida, genska terapija raka, antitumorska ispitivanja, antivirusna ispitivanja, pozitronska emisijska tomografija.

>> POSTIGNUTI REZULTATI

Sintetizirani su novi spojevi iz reda: **A**. Purinskih i pirimidinskih derivata L-askorbinske kiseline; **B**. Derivata 1-aminociklopropan-1-karboksilne kiseline i 1-hidroksimetilciklopropana s nukleozidnim bazama; **C**. Acikličkih i epoksidnih analoga nukleozida; **D.** C-6 fluoroalkiliranih derivata pirimidina; **E.** Cikloalkil-N-aril-hidroksamskih kiselina; **F.** Aminokiselinskih derivata hidroksiuree i hidantoina; **G.** Kiralnih spiro-pirana.
Ispitano je djelovanje *in vitro* novo pripravljenih spojeva na stanične linije zloćudnih tumora porijeklom iz čovjeka i virusa. Pojedini spojevi klasa **A** i **F** pokazali su izražena i selektivna djelovanja na stanične linije pojedinih zloćudnih tumora u čovjeka, a spojevi iz reda **E** su djelovali inhibitorno i selektivno na humani citomegalovirus (HCMV). To su predvodni spojevi za optimiranje njihovih struktura kao antitumorskih i *anti*-HCMV lijekova.
Sintetiziran je, također, niz novih spojeva iz reda acikličkih analoga nukleozida kao prolijekova za gensku terapiju raka.
Provedena je, također, sinteza novih spojeva iz reda C-6 alkiliranih pirimidinskih nukleozida obilježenih radioizotopom ^{18}F, fluoriranih acikličkih analoga pirimidinskih i purinskih nukleozida i fluoriranih pirolidopirimidina kao modelnih spojeva za primjenu u pozitronsko emisijskoj tomografiji (PET).

+385 1 4597 214 / mmintas@fkit.hr
Mladen Mintas
Department of Organic Chemistry
Principal investigator

PROJECT DESCRIPTION

Widely spread viral infections and cancer represent a health problem of a world wide dimension. The main problems in antiviral and cancer chemotherapy are drug resistance and side effects on normal tissue. Therefore, the principal aim of our research is to synthesize the new types of compounds that could be used as effective and selective agents against pathogen viruses and human malignant tumors.
The specific aim is to synthesize such types of nucleoside mimetica which would overcome the problem of resistance of the existing drugs, acyclovir and ganciclovir, to herpes viral infections and which could find use in combination with herpes viral thymidine kinases as prodrugs in gene therapy of cancer. The aim of this study is also to develop the new model compounds for application in positron emission tomography (PET). PET is a method for monitoring tumor sites and lymphocytes accumulation, graft versus host disease (GvHD) which is often life threatening complication of allogeneic bone marrow transplantation (allo-BMT).

KEY WORDS
acyclic nucleoside analogues, gene therapy of cancer, antitumor evaluation, antiviral evaluation, positron-emission tomography.

PROGRESS SUMMARY

The novel classes of compounds were synthesized: **A.** Purine and pyrimidine derivatives of L-ascorbic acid; **B.** 1-aminocyclolopropane-1-carboxylic acid and 1-hydroxymethylcyclopropane derivatives of nucleoside bases; **C.** Acyclic and epoxide nucleoside analogues; **D.** C-6 fluoroalkylated derivatives of pyrimidine; **E.** Cycloalkyl-N-aryl-hydroxamic acid derivatives; **F.** Aminoacid derivatives of hydroxyurea and hydantoins; **G.** Chiral spyro-pyrans.
The newly prepared compounds were evaluated on their *in vitro* activities against malignant human tumor cell lines and viruses. Some compounds of the classes **A** and **F** showed potent and selective activities against specific human tumor cell lines while the compounds of the series **E** showed selective inhibition of the replication of human cytomegalovirus (HCMV). Those are leading compounds for synthetic structure optimization and further development as antitumoral and anti-HCMV drugs.
The series of the novel compounds of the acyclic nucleoside analogues were synthesized as prodrugs for gene therapy of cancer.
The novel C-6 alkylated pyrimidine nucleosides labeled with radioactive ^{18}F, fluorinated acyclic pyrimidine and purine nucleoside analogues as well as fluorinated pyrolidopyrimidine as model compounds for application in positron-emission tomography (PET) were synthesized.

RESEARCH ASSOCIATES

Silvana Raić-Malić
Tatjana Gazivoda
Svjetlana Prekupec
Vedran Krištafor
Karlo Wittine

CONSULTANTS

Ante Nagl (Faculty of Textile Technology, Zagreb)
Antonija Hergold-Brundić (Faculty of Textile Technology, Zagreb)
Mario Cetina (Faculty of Textile Technology, Zagreb)
Branka Zorc (Faculty of Pharmacy and Biochemistry, Zagreb)
Krešimir Pavelić (Ruđer Bošković Institute, Zagreb)
Erik De Clercq (Rega Institute for Medical Research, Leuven, Belgium)
Jan Balzarini (Rega Institute for Medical Research, Leuven, Belgium)
Gerd Folkers (Department Pharmazie, ETH-Zürich)

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SINTETSKA, FOTOKEMIJSKA I STRUKTURNA ISTRAŽIVANJA HETEROCIKLIČKIH SPOJEVA

SYNTHESIS, PHOTOCHEMISTRY AND STRUCTURE STUDIES OF HETEROCYCLIC COMPOUNDS

Fotokemijski reaktor RPR 100
Photochemical reactor RPR 100

J. Org. Chem. **2006**, *71*, 9382

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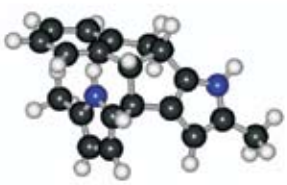

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SINTETSKA, FOTOKEMIJSKA I STRUKTURNA ISTRAŽIVANJA HETEROCIKLIČKIH SPOJEVA

GLAVNI ISTRAŽIVAČ

Marija Šindler 01 4597 246 / marija.sindler@fkit.hr
Zavod za organsku kemiju

SURADNICI

Nikola Basarić
Kristina Butković
Irena Škorić
Dragana Vidaković

OPIS PROJEKTA

Projekt uključuje sinteze i fotokemijska istraživanja novih heterocikličkih sustava. Naglasak je na fotokemijskoj metodologiji priprave heteropolicikličkih spojeva te studiju mehanizama intra- i intermolekularnih reakcija kojima ti spojevi nastaju. Studiraju se aromatski konjugirani nezasićeni sustavi s heterocikličkim jezgrama koji se pod utjecajem svjetla transformiraju u kompliciranе heteropolicikličke strukture, često vrlo teško dostupne uobičajenim reakcijama u osnovnom stanju. Koristeći svjetlo kao reagens ovim se postupkom ujedno vodi računa o očuvanju okoliša. Posebice se studiraju heterociklički derivati s furanskim, pirolskim, tiofenskim ili sidnonskim jezgrama. Tako u fotokemijskoj reakciji furanskog heksatrienskog derivata kao glavni produkt intramolekularne cikloadicije nastaje fuzionirani biciklo[3.2.1]oktadienski derivat u jednom stupnju i s visokim prinosom. U cilju proširenja metode priređuju se nezasićeni sustavi s dušikom, dušikom i kisikom, ili sumporom i istražuje se utjecaj heteroatoma na tok fotokemijske reakcije. Svi priređeni spojevi kao i njihovi fotoprodukti identificiraju se spektroskopskim metodama koristeći najmodernije tehnike. Sve studirane strukture interesantne su kao supstrati za biološka ispitivanja.

KLJUČNE RIJEČI
sintetska organska fotokemija, cikloadicije, dimerizacija, izomerizacija, heterociklički spojevi

>> POSTIGNUTI REZULTATI

U proteklom razdoblju riješene su nove strukture i mehanizmi fotokemijskih reakcija furanskih, pirolskih i sidnonskih nezasićenih sustava. Nađeno je da mono- i disupstituirani furanski derivati *o*-divinilbenzena daju u jednom stupnju u vrlo dobrom iskorištenju fuzionirane biciklo[3.2.1]oktadienske derivate. Difuranski derivati u uvjetima intermolekularnih reakcija daju ciklofanske derivate. Suprotno od ovih rezultata heksatrienski sustav, u kojem je centralna dvostruka veza dio furanske jezgre, daje fototranspozicijske produkte.

Pogodno supstituirani pirolski derivati također daju bicikličke strukture kao i fototranspozicijske produkte dok se fenilendivinilendipiroli transformiraju u fuzionirane ciklopentalenske pirolske derivate. Pronađen je i novi fotokemijski pristup sintezi indola i izoindola.

Novi sidnonski derivati fotokemijskom reakcijom prevedeni su u pirazolske derivate.

Nekoliko odabranih sintetiziranih spojeva testirani su na biološku aktivnost. Preliminarna ispitivanja (u suradnji s grupom prof. dr. sc. Pavelića) pokazala su da sidnonski derivati najbolje utječu na smanjenje rasta odabranih stanica.

U okviru projekta rezultati rada prezentirani su na brojnim domaćim i međunarodnim skupovima, izrađeno je šest diplomskih radova i dva doktorata, a objavljeno je 15 CC znanstvenih radova u istaknutim znanstvenim časopisima i jedan pregledni rad.

+385 1 4597 246 / marija.sindler@fkit.hr
Department of Organic Chemistry

Marija Šindler

Principal investigator

PROJECT DESCRIPTION

The project involves syntheses and photochemical behavior of new heterocyclic systems. The emphasis is on the photochemical metodology of the synthesis and the study of the reaction mechanisms by means of which these compounds undergo photochemical intra- or intermolecular cycloaddition reactions to heteropolycyclic compounds. What is being studied is the aromatic conjugated unsaturated system with heterocyclic rings that transform themselves under the influence of light to complicated heteropolycyclic structures, which are often hard to be obtained in a traditional synthetic approach. Moreover, photons are the environmentally most friendly reagents in chemistry. The heterocyclic derivatives that are studied include furan, pyrrole, thiophene or sydnone rings. In photochemical reaction of furan hexatriene system the fused bicyclo[3.2.1]octadiene derivative is formed in one step and with a very high yield. In order to extend the method to other heterocyclic fused bicyclo[3.2.1]octadiene derivatives the corresponding derivatives with nitrogen, nitrogen and oxygen, or sulfur are prepared and the influence of the heteroatom on the photoreaction course is investigated. Structure determination of all obtained new compounds is performed by spectroscopic methods using modern techniques. All studied structures are very interesting substrates for biological screening on the presumed pharmacological effect.

KEY WORDS
synthetic organic photochemistry, cycloadditions, dimerization, isomerization, heterocyclic compounds

PROGRESS SUMMARY

Some new structures and reaction mechanisms of photochemical reactions of furan, pyrrole and sydnone unsaturated systems have been solved in the last period of time. It has been found that mono- and disubstituted furan derivatives of *o*-divinylbenzene produce in one step and in very high yield fused bicyclo[3.2.1]octadiene derivatives. Under the intermolecular reaction conditions difuran derivatives give cyclophanes. Contrary to these results, the hexatriene system with the central double bond incorporated into the furan ring gives phototransposition products.

Correspondingly, substituted pyrrole derivatives also produce bicyclic structures as well as the phototransposition products. Phenylendivinylendipyrroles are transformed into fused cyclopentalene pyrrole derivatives. A new photochemical way to the synthesis of indole and isoindole has been found.

In the presence of alkenes new sydnone derivatives are transformed by photochemical reaction into the pyrazole derivatives.

Some selected compounds are tested for biological activity. Preliminary screening (group of prof. dr. sc. Pavelić) showed that sydnone derivates have the best effect on selected cell growth.

The results of the project have been presented at numerous domestic and international symposia, there were six graduation works and two PhDs completed and 15 CC papers have been published in outstanding scientific journals as well as one review.

RESEARCH ASSOCIATES

Nikola Basarić
Kristina Butković
Irena Škorić
Dragana Vidaković

ZNANSTVENI RADOVI U CC ČASOPISIMA ..... SCIENTIFIC PAPERS IN CC JOURNALS

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Synthesis of the novel conjugated omega, omega'-diaryl/heteroaryl hexatriene system with the central double bond in a heteroaromatic ring: Photochemical transformation of 2, 3-divinylfuran derivatives, *Tetrahedron* **62** (2006) 7396-7407

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Characterization of acetylated *o*-glucofuranosides: Direct glucosylation of volatile alcohols from unprotected glucose, *Croatica Chemica Acta* **78** (2005) 313-318

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Identifiability of the model of the excited-state proton exchange reaction in the presence of pH buffer, *Journal of Physical Chemistry* **A108** (2004) (40) 8180-8189

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On the photochemical dimerization of some 5-substituted 2-styryl-4-pyrones. The effect of 5-hydroxy-/5-methoxy- substitution, *Journal of Heterocyclic Chemistry* **39** (2002) (1) 37-44

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E-5-methyl-2-(2-methylstyryl)pyrrole, *Acta Crystallographica* **E58** (2002) 909-910.

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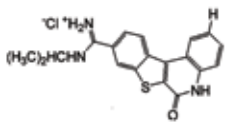
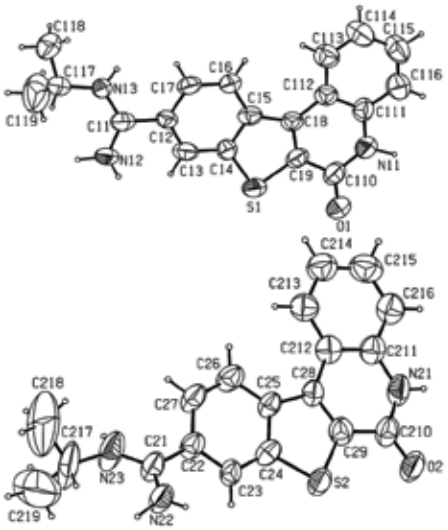
0125 005

J. Med. Chem. **2005**, *48*, 2346–2360

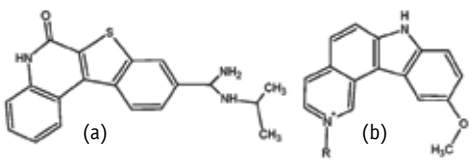
9a



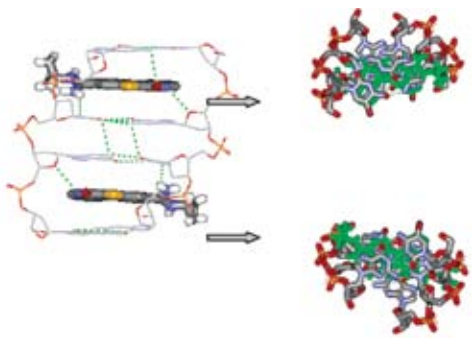
Benzotieno[2,3-c]kinolinhidroklorid.
Benzothieno[2,3-c]quinolin hydrochloride.



Kristalna struktura **9a**. / Crystal structure of **9a**.



Molekula **9a** (a) u usporedbi s 7H-piridokarbazolonom (b).
Molecule of **9a** (a) in comparison with 7H-pyridocarbazole (b).



Modeliranje molekule **9a** kao interkalatora u isječak DNA.
Molecular modeling of **9a** as intercalator in segment of DNA.

GLAVNI ISTRAŽIVAČ

Grace Karminski-Zamola 01 4597 297 / gzamola@fkit.hr
Zavod za organsku kemiju

SURADNICI

Kristina Starčević
Ivana Jarak
Marijana Hranjec
Irena Ćaleta

VANJSKI SURADNICI

Vesna Tralić-Kulenović (Tekstilno-tehnološki fakultet, Zagreb)
Livio Racanè (Tekstilno-tehnološki fakultet, Zagreb)
Jasna Dogan (PLIVA, Zagreb)
Vesna Lesko-Kelović (Klinika za onkologiju KBC Zagreb)

OPIS PROJEKTA

Tumorske bolesti su, uz kardiovaskularne, najraširenije bolesti današnjice; dok se kardiovaskularne uspješno liječe, tumorske bolesti i dalje predstavljaju veliki problem. Istraživanja se usmjeravaju kako na promjene u biološkom sustavu (molekularna medicina) tako i na pripravu novih sintetskih supstancija (razvoj kemoterapeutskih sredstava).
Cilj ovog projekta bio je sinteza novih ciljanih i specifično odabranih heterocikličkih sustava sa svrhom ispitivanja njihovog biološkog djelovanja, naročito na tumorske stanice kao i na stanice HIV-a. Na taj način članovi Zavoda za organsku kemiju nastavljaju tradiciju slavnog prethodnika nobelovca Preloga.
U tu svrhu bilo je potrebno prirediti nove heterocikličke spojeve, koji bi u odnosu na svoju strukturu mogli interagirati s DNA stvarajući komplekse i tako sprječavati replikaciju tumorskih stanica. Molekule su ciljano odabrane iz reda amidino supstituiranih benzotiazola, benzimidazola, piridopirimidobenzimidazola, benzimidazokinolina te njihovih heterocikličkih analoga. Svim novo priređenim spojevima određivano je antitumorsko djelovanje *in vitro*.

KLJUČNE RIJEČI
sinteza, DNA-kompleksiranje, antitumorsko djelovanje

>> POSTIGNUTI REZULTATI

Priređeni su novi supstituirani benzo-tieno-kinoloni kao i tieno-tienil-kinoloni iz odgovarajućih amidnih prekursora. Također su sintetizirani novi spojevi iz grupe naftofurana i naftotiofena, te benzotienofurana i benzoditiofena. Ispitano je njihovo kompleksiranje na isječku prirodne i sintetičke DNA u smislu sprječavanja replikacije tumorske DNA kao i antitumorsko djelovanje *in vitro* Neki spojevi pokazali su dobru antitumorsku aktivnost. Najznačajniji radovi iz tog područja objavljeni su u J. Med. Chem 2003 (IF 4,86), J. Med. Chem 2005 (IF 4,926), Bioorganic & Medicinal Chemistry 2006 (IF 2,28) i Eur. J. Med. Chem. 2006 (IF 2.02.). Rezultati koji opisuju fotodinamičku terapiju liječenja tumorskih bolesti pomoću UV zračenja, *in situ* priređenom supstancijom iz reda amidino supstituiranih naftofurana zaštićeni su patentom u Hrvatskoj. Nakon isteka zaštite, objavljen je rad u J. Am. Chem. Soc. 2005 (IF 7.419). Kemijskom i fotokemijskom sintezom priređen je čitav niz amidino supstituiranih 2-stiril-benzimidazola i benzimidazo-kinolina. Ispitana je njihova antitumorska aktivnost i nađeno je da je nekoliko spojeva iz te grupe vrlo antitumorski aktivno te su rezultati patentirani u Državnom zavodu za intelektualno vlasništvo u Hrvatskoj. Patent istječe sredinom 2007., a nakon eventualnog prihvaćanja novog projekta, kao nastavka prethodnog, supstancija će se pokušati zaštititi u europskim zemljama; provest će se ispitivanje primjene najaktivnijih spojeva *in vivo*, sve do eventualnih kliničkih ispitivanja. Na tim spojevima obranjena su dva doktorata iz područja molekularne medicine. Novi ciklobutanski derivati supstituirani amidino-benzimidazolnom jegrom i benzenskom, odnosno furanskom ili tiofenskom jezgrom priređeni su fotokemijskom [2+2] ciklizacijom u vodi, što je doprinos tzv. „zelenoj fotokemiji". Spojevi su dobri inhibitori metalopeptidaze DPP III. Rad je dostupan u časopisu Bioorg. Chemistry (IF 1.56) doi:10.1016/j.boorg.2006.11.002 i dio je izrađene doktorske disertacije. Također, u okviru druge disertacije priređen je niz novih benzotiazola koji su ispitani na antitumorsko djelovanje te kompleksiranje s DNA. Od priređenih spojeva, nekoliko pokazuje izrazito antiumorsko djelovanje.

+385 1 4597 297 / gzamola@fkit.hr **Grace Karminski-Zamola**
Department of Organic Chemistry
Principal investigator

PROJECT DESCRIPTION

Since cancer still remains a major public health issue, there is a great medical need for new anticancer small molecule therapeutics.
The goal of this project was the synthesis of new specifically selected heterocyclic systems and the examination on their biological activity, especially on the human tumor cells as well as on the HIV cells. In this way the members of the Department of Organic Chemistry are continuing the tradition of the famous predecessor, Nobel prize winner Vladimir Prelog.
For this purpose, new heterocyclic compounds were aimed to be synthesized, which could interact with DNA relevant to their structure. In this case, the compounds could be able to form chemical complexes with DNA and prevent the replication of tumor cells. We selected and synthesized new heterocyclic compoundes from the series of amidino-substituted-benzothiazoles, benzimidazoles, pyridopyrimidobenzimidazoless, benzimidazoquinolines. All new compounds were tested on their anitumor activity *in vitro*.

KEY WORDS
Synthesis, DNA complexation, antitumor action

RESEARCH ASSOCIATES
Kristina Starčević
Ivana Jarak
Marijana Hranjec
Irena Ćaleta

CONSULTANTS
Vesna Tralić-Kulenović (Faculty of Textile Technology, Zagreb)
Livio Racanè (Faculty of Textile Technology, Zagreb)
Jasna Dogan (PLIVA, Zagreb)
Vesna Lesko-Kelović (Oncology Clinic KBC Zagreb)

PROGRESS SUMMARY

New amino or amidino substituted benzothienoquinolones, thieno-thienyl-quinolones as their hydrochloride salts were synthesized. New compounds from the naphthofuran, naphthothiophene, benzothienofuran and benzodithiophene series were synthesized, too. Their antiproliferative action was examined, where cyclic compounds showed much more active antitumor action than their acyclic precursors. Antiproliferative activity is very likely caused by intercalation into DNA. The most important papers in this field are reported in the following journals; J. Med. Chem 2003 (IF 4,86), J. Med. Chem 2005 (IF 4,926), Bioorganic & Medicinal Chemistry 2006 (IF 2,28) and Eur. J. Med. Chem. 2006 (IF 2.02.)
The paper which describes the application of photodynamic therapy in the cancer diseases by the *in situ* action of UV light with photochemically prepared amidino-substituted naphthofuran was reported in J. Am. Chem. Soc. 2005 (IF 7.419). The active substance was earlier patent protected in Croatia.
A series of amidino-substituted 2-styrylbenzimidazoles and benzimidazoquinolines is chemically and photochemically synthesized, and their antitumor action is examined. Some of the compounds have shown very strong antitumor activity and they are patent protected in Croatia before reporting. The further examination *in vivo* follows. Two Ph.D. theses in the field of molecular medicine dealing with prepared compounds were defended.
Novel cyclobutane derivatives of benzimidazoles were photochemically prepared and their inhibitory action on dipeptidyl peptidaze III was examined. Photochemical [2+2] cyclization was performed in water solution; this is the contribution belonging to the field of so-called "green photochemistry". The paper is reported in Bioorg. Chemistry 2007 (IF 1.56), doi:10.1016/j.boorg.2006.11.002. The article is the part of a defended Ph.D. thesis.
New compounds from the benzothiazole series were synthesized and their antitumor activity was evaluated.

ZNANSTVENI RADOVI U CC ČASOPISIMA ..... SCIENTIFIC PAPERS IN CC JOURNALS

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Novel cyano- and amidino-substituted derivatives of thieno[2, 3-b]- and thieno[3, 2-b]thiophene-2-carboxanilides and thieno[3', 2' 4, 5]thieno- and thieno[2', 3' 4, 5]thieno [2, 3-c]quinolones: Synthesis, photochemical synthesis, DNA binding and antitumor evaluation, *Bioorganic & Medicinal Chemistry* **14** (2006) (8) 2859-2868

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Synthesis, photochemical synthesis, DNA binding and antitumor evaluation of novel cyano- and amidino-substituted derivatives of naphtho-furans, naphtho-thiophenes, benzo-thieno-furans, benzo-dithiophenes and their acyclic precursors, *European Journal of Medicinal Chemistry* **41** (2006) 925-939

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Antitumour efficiency of novel fluoro substituted 6-amino-2-phenylbenzothiazole hydrochloride salts in vitro and in vivo, *Methods and Findings in Experimental and Clinical Pharmacology* **28** (2006) (6) 347-354

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Chemical and photochemical synthesis of substituted dihydro-thieno[2', 3':4, 5]thieno[2, 3-c]quinolin-6-ones and tetrahydro-dithieno[2, 3-b:2', 3'-d]thieno[2", 3"-c:2", 3"-c']diquinolin-6, 14-dione, *Molecules* **10** (2005) 279-288

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Novel cyano- and N-isopropylamidino-substituted derivatives of benzo[b]thiophene-2-carboxanilides and benzo[b]thieno[2,3-c]quinolones: Synthesis, photochemical synthesis, crystal structure determination and antitumor evaluation, Part 2, *Journal of Medicinal Chemistry* **48** (2005) 2346-2360

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Photoinduced switch of a DNA/RNA inactive molecule into a classical intercalator, *Journal of American Chemical Society* **127** (2005) 1074-1075

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2-Furancarboxanilide, *Acta Crystallographica* **E60** (2004) o631-o633

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Synthesis and crystal structure determination of 6-(N-isopropyl)amidino-2-methylbenzothiazole hydrochloride monohydrate and 2-(amino-6-(N-isopropyl)amidinobenzothiazole hydrochloride, *Structural Chemistry* **14** (2003) (6) 585-592

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Novel derivatives of benzo((b)thieno(2, 3-c)quinolones: Synthesis, photochemical synthesis, and antitumor evaluation, *Journal of Medicinal Chemistry* **46** (2003) (21) 4516-4524

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Synthesis and antitumor evaluation of some new substituted amidino-benzimidazolyl-furyl-phenyl-acrylates and naphtho[2, 1-b]furan-carboxylates, *Il Farmaco* **58** (2003) (12) 1319-1324

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1,3-Benzothiazole-6-carboxamidinium chloride dihydrate, *Acta Crystallographica* **C59** (2003) (4) o190-o191

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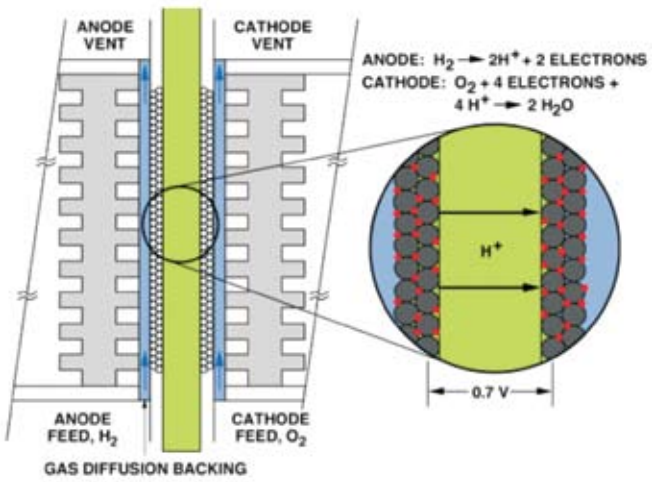
Hip joint implant.



Gorivni članak s polimernom membranom.
Polymer membrane fuel cell.

GLAVNI ISTRAŽIVAČ

Mirjana Metikoš-Huković 01 4597 140 / mmetik@fkit.hr
Zavod za elektrokemiju

SURADNICI

Ana Kwokal
Željka Petrović
Rajka Pavković

VANJSKI SURADNICI

Ranko Babić
(Sveučilište u Zagrebu)
Zoran Grubač
(Kemijsko-tehnološki fakultet, Split)
Saša Omanović
(Department of Chemical Engineering, Montreal, Quebec, Canada)
Ingrid Milošev
(Institut Jožef Štefan, Ljubljana, Slovenija)
Nikola Radić
(Institut Ruđer Bošković, Zagreb)
Jasenka Piljac
(Institut Ruđer Bošković, Zagreb)

OPIS PROJEKTA

Osnovni cilj predloženog projekta je utvrđivanje odnosa između elektronskih, strukturnih, električkih i dielektričkih svojstava kovinskih, poluvodičkih, izolatorskih funkcionalnih materijala i strukture međufazne granice čvrsto/elektrolit. Da bi se ostvarili ciljevi projekta razvojem pogodnih teorijskih modela i novih eksperimentalnih metoda, predložene su tri skupine specifičnih istraživanja: nanostrukturirani i bifunkcionalni katalizatori za gorivne članke i vodikove generatore; novi kovinski biokompatibilni materijali; dizajniranje funkcionalnih inženjerskih materijala tankim filmovima nanometarske debljine.
Predloženi zadaci predstavljaju izbor sustava značajnih s fundamentalnog stajališta i važnih za primjenu u konverziji energije, biomedicini i zaštiti materijala od korozije.
U istraživanjima su korištene visokosofisticirane *in-situ* tehnike (elektrokemijske i optičke metode, EIS) i *ex-situ* tehnike (XPS, AES, Mössbauer, Raman, SEM, X-ray) s ciljem da se koreliraju površinska i intrinzička svojstva istraživanih materijala.
Značaj predloženog istraživanja je, kako u intenziviranju povezanosti između kemije, fizike i inženjerstva materijala, tako i u edukaciji mladih znanstvenika za ovo perspektivno područje. Projekt pokreće inicijativu interdisciplinarnog pristupa materijalima – katalizatorima, korozijski otpornim i biokompatibilnim kovinskim materijalima da bi se ostvarilo razumijevanje elektrokatalize i korozije na molekulskom nivou.

KLJUČNE RIJEČI:
nano-strukturirani i kompozitni hipo-hiper-*d*-intermetalni katalizatori, gorivni članci, vodikova energija, titanijeve biokompatibilne slitine, dizajniranje korozijski stabilnih površina materijala

>> POSTIGNUTI REZULTATI

Ostvareni su planirani rezultati u fundamentalnim i aplikativnim kategorijama istraživanja. Naša istraživanja izravno su primjenjiva u znanstvenoj edukaciji studenata i mladih suradnika.
Elektrokemijski procesi su temelj za razumijevanje tehnološke prikladnosti materijala, posebice njihovih elektrokatalitičkih, fotokatalitičkih, fotoelektrokemijskih i korozijskih svojstava.
Prijedlog dijela projekta odnosi se na razvoj i optimizaciju elektrokatalizatora koji su najskuplji i najbitniji dio membranskih gorivnih članaka i generatora za proizvodnju vodika. Vodik je najčišće, nepresušno i idealno gorivo čiji je izvor voda. Električna energija i voda (vraća se nepromijenjena u prirodu) su jedini produkti pri sagorijevanju u gorivnim člancima.
Očekuje se da će se u budućnosti energija vodika kombinirano s fotovoltaičkim izvorima energije, najviše koristiti u gorivnim člancima za decentraliziranu proizvodnju energije. Mnogobrojni su industrijski procesi u kojima je nužan elektrolitski vodik (primjerice, hidrogenacija u proizvodnji hrane).
Dio korozijskih istraživanja odnosi se na zaštitu realnog okoliša ljudskog organizma od toksičnih kovinskih iona kod primjene kovinskih implantata, koji se ugrađuju u ljudski organizam. Dizajnirani su i istraživani novi biokompatibilni materijali (zamjena vanadija u titanijevim slitinama niobijem) s primjenom u biomedicini za izradu implantata.
Publicirani radovi: poglavlja u knjizi, 1; znanstveni radovi u CC časopisima, 35; radovi u ostalim časopisima, 1; pozvana predavanja na skupovima, 6; radovi u zbornicima skupova s međunarodnom recenzijom, 8; ostali radovi u zbornicima skupova, 5; sažeci u zbornicima skupova i neobjavljeni radovi, 24; disertacije i magistarski radovi, 3; diplomski radovi, 11; ostale vrste radova, 2.

+385 1 4597 140 / mmetik@fkit.hr **Mirjana Metikoš-Huković**
Department of Electrochemistry

Principal investigator

PROJECT DESCRIPTION

The main goal of the project is determination of relationships between the electronic structure, electric and dielectric properties of the material and the structure of the interphase boundary solid/electrolyte. In order to accomplish the goals of this project through the development of suitable theoretical model and novel experimental methods, we suggest three specific fields of research: nano-structured and bifunctional catalysts for fuel cells and hydrogen generators; new metallic biocompatible materials; designing of functional engineering materials by modifying their surface with thin films of nanometer thickness.
The proposed tasks, from the fundamental point of view, encompass the significant systems important in energy conversion, biomedicine and corrosion protection.
The research was conducted using highly sophisticated *in-situ* techniques (electrochemical and optical methods, EIS) as well as *ex-situ* techniques (XPS, AES, Mössbauer, Raman, SEM, X-ray) with a goal of correlating surface and intrinsic properties of investigated materials.
The significance of research lies in interconnection between chemistry, physics and materials engineering as well as in education of young scientists for this perspective area of science. The project compliments the initiative for an interdisciplinary approach to materials – catalysts, corrosion resistant and biocompatible alloy materials, in order to achieve an understanding of electrocatalysis and corrosion at a molecular level.

KEY WORDS
nano-structured and composite hypo-hyper-*d*-intermetallic catalysts, fuel cells, hydrogen energy, titanium biocompatible alloys, designing of corrosion resistant surface materials

RESEARCH ASSOCIATES

Ana Kwokal
Željka Petrović
Rajka Pavković

CONSULTANTS

Ranko Babić
(University of Zagreb)
Zoran Grubač
(Faculty of Chemistry and Technology, Split)
Saša Omanović
(Department of Chemical Engineering, Montreal, Quebec, Canada)
Ingrid Milošev
(Institute Jožef Štefan, Ljubljana, Slovenia)
Nikola Radić
(Ruđer Bošković Institute, Zagreb)
Jasenka Piljac
(Ruđer Bošković Institute, Zagreb)

PROGRESS SUMMARY

Proposed tasks in fundamental and applicable categories of investigation are realized. Our research is directly applied in scientific education of students and young collaborators. Electrochemical processes are the key factors for understanding the technological applicability of materials, especially their electrocatalytic, photocatalytic, photoelectrochemical, and corrosive properties. A part of the project proposal is related to development and optimization of electrocatalysts which are the most expensive and most significant parts of the membrane fuel cells and hydrogen generators. Hydrogen is the cleanest, inexhaustible and at the same time ideal fuel, because its main source is water and, by burning it in fuel cells, energy and water are the only products. It is expected that hydrogen energy will be used in the future in combination with photovoltaic sources of energy in fuel cells for decentralized production of energy. There exist numerous industrial processes, requiring hydrogen from water.
Part of the corrosion investigation is related to the protection of human bodies from toxic metallic ions as a result of application of metallic implants. New biocompatible materials (vanadium replacement with niobium in titanium alloys) are designed and investigated with regard to the application in biomedicine for production of implants.

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Korozijska svojstva Ni katalizatora u alkalnom elektrolizeru: sunčev vodik energetski sustav, *Zbirka referata Korozija, antikorozijski postupci i zaštita okoliša,* Zagreb 17.-18. travanj 2002 / Franjo Kroneisl (ur.), Zagreb, Hrvatsko društvo za zaštitu materijala, 2002, pp. 32-40

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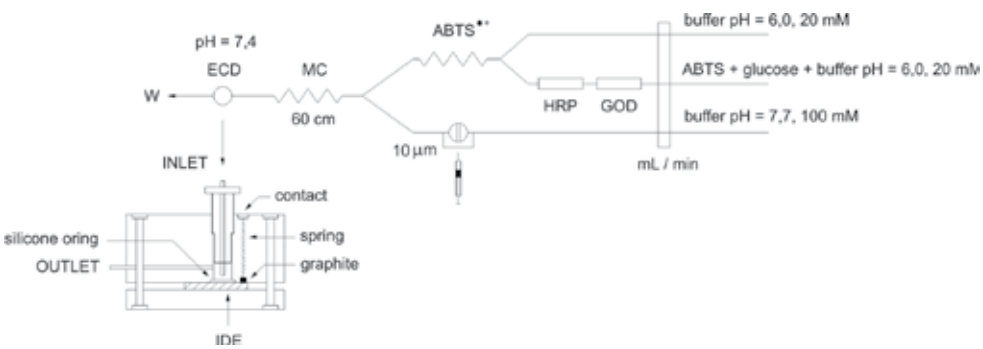
Hrvatska solarna kuća - Studija izvodljivosti, 2002. (*elaborat*).

RAZVOJ BIOSENZORA I METODE MJERENJA ANTIOKSIDATIVNOG STATUSA KRVI

DEVELOPMENT OF AN AMPEROMETRIC BIOSENSOR FOR DETERMINATION OF TOTAL PLASMA ANTIOXIDANTS



Protočni mjerni sustav za mjerenje antioksidativnog kapaciteta s interdigitaliziranom elektrodom.
Flow injection analysis of antioxidant capacity using interdigitated electrode.

RAZVOJ BIOSENZORA I METODE MJERENJA ANTIOKSIDATIVNOG STATUSA KRVI

GLAVNI ISTRAŽIVAČ

Stjepan Milardović 01 4597 289 / stjepan.milardovic@fkit.hr
Zavod za opću i anorgansku kemiju

SURADNICI

Biserka Tkalčec
Ivana Steinberg Murković
Lili Plenković

VANJSKI SURADNICI

Vlatko Rumenjak
(Opća bolnica "Sveti duh", Zagreb)
Predrag Hercog
(KBC Zagreb, Zagreb)

OPIS PROJEKTA

Kemijski sastav ljudske krvi je puno proučavan, međutim stvarna priroda antioksidansa prisutnih u plazmi trenutno je predmet velikih rasprava. Studija antioksidanasa prisutnih u ljudskoj plazmi je posebno stimulirana zadnjih godina, posebice radi novorazvijenih metoda mjerenja. Uporabljene metode mjerenja se baziraju na generiranju slobodnih radikala, a količina generiranih radikala se kvantificira na pogodan način. Dodatkom antioksidansa dolazi do inhibicije organske boje koja je bila razvijena u kontaktu sa slobodnim radikalom. Dakle, metode mjerenja zasnivaju se većinom na optičkim metodama detekcije. Uređaji koji se koriste u mjerenju antioksidativnog statusa krvi baziraju se na fosforescenciji ili fluoroescenciji. Kemijski kitovi koji se temelje na mjerenju absorbancije još uvijek nisu za komercijalnu, već samo znanstvenu uporabu. Prevladava mišljenje da je većina današnjih modernih bolesti posljedica utjecaja slobodnih radikala, te bi mjerenje ukupnog antioksidativnog statusa krvi imalo značajan utjecaj na razumijevanje mehanizma nastanka sljedećih bolesti: ateroskleroze, raka, dijabetesa, respiratornih bolesti, oštećenja bubrega, reumatoidnog artritisa, AIDS-a, Parkinsonove bolesti i mnogih drugih.
Grupa istraživača predložena ovim projektom bavi se niz godina razvojem i primjenom amperometrijskih biosenzora za prepoznavanje metabolita. Tako su razvijeni biosenzori za mjerenje glukoze i ureje u krvi, oksalata u urinu, a radi se i na istraživanju biosenzora za određivanje laktata u krvi.
Cilj ovog projekta je razvoj amperometrijskog biosenzora, te pogodne metode mjerenja ukupnog antioksidativnog statusa krvi. Mjerenje je potrebno izvesti u klasičnoj neprotočnoj kao i u protočnoj elektrokemijskoj ćeliji. Potrebno je provesti usporedbu rezultata postignutim biosenzorom sa zasad jedino postojećom kemijskom metodom mjerenja. Biosenzor treba ispitati u vodenim otopinama, kao i u uzorcima pune krvi ili krvnog seruma. Treba ispitati i predložiti najpogodnije sredstvo za baždarenje. Isto tako treba provesti procjenu (evaluaciju) metode. Planira se i izvedba kombinirane metode mjerenja koja bi uključivala spektroelektrokemijski biosenzor, te mjerenja u protoku.

KLJUČNE RIJEČI
ABTS, amperometrijska detekcija, antioksidant, biamperometrijska detekcija, DPPH, interdigitalizirana elektroda, Trolox ekvivalent

>> POSTIGNUTI REZULTATI

Tijekom navedenog razdoblja istraživanja voditelj projekta i ostali istraživači na projektu publicirali su 8 radova u časopisima koji pripadaju bazi Current Contents s prosječnom vrijednosti faktora značaja 2,499. Također je bilo 13 sudjelovanja na kongresima i to 2 međunarodna i 11 domaćih kongresa s međunarodnim sudjelovanjem, 1 diplomski rad i jedan rad koji je nagrađen Rektorovom nagradom, te 3 patenta.
Ostvarena je i suradnja s International Society of Electrochemistry i to posjetom podpredsjednika ISE prof. Luisa Alberta Avace koji je izrazio želju da se upozna s radom grupe koja je izvodila projekt. Prilikom posjeta profesor Avaca održao je predavanje pod naslovom "Chronoamperometric determination of the antioxidant capacity. The Cerium Reducing Antioxidant Capacity (CRAC) assay on Boron-doped Diamond electrodes".

DEVELOPMENT OF AN AMPEROMETRIC BIOSENSOR FOR DETERMINATION OF TOTAL PLASMA ANTIOXIDANTS

+385 1 4597 289 / stjepan.milardovic@fkit.hr **Stjepan Milardović**
Department of General and Inorganic Chemistry

Principal investigator

RESEARCH ASSOCIATES

Biserka Tkalčec
Ivana Steinberg Murković
Lili Plenković

CONSULTANTS

Vlatko Rumenjak
(General Hospital "Sveti duh", Zagreb)
Predrag Hercog
(KBC Zagreb, Zagreb)

PROJECT DESCRIPTION

The chemical composition of human blood is widely studied and well-known. However, the exact nature of antioxidants of plasma is very much open to dispute. The study of plasma antioxidants has been highly stimulated in recent years by development of new methods for measurement of hydrogen-donating antioxidant activity. Addition of antioxidants inhibits the development of organic redox dye which can react with previously generated free radical. Therefore, the intensity of absorption or intensity of chemiluminiscence is proportional to the concentration of free radical present in sample. The simple measurement of absorbance of developed color (intensity of phenolic dye is proportional to the quantity of free radical) by using of chemical kit is nowadays the mainly used method for determination of total blood antioxidants activity. The producer of chemical kit suggested the described method only for scientific use.
Free radicals are highly reactive molecules generated by biochemical redox reaction that occur as part of normal cell metabolism and are generated by exposure to environmental influence such as cigarette smoke, UV light and some other pollutance. Therefore, as results of radical attack to cell structure, numerous diseases have been implicated: atherosclerosis, cancer, diabetes, respiratory diseases, liver damage, AIDS, Parkinson's disease and many others. The group of scientists proposed by this project has been involved in development and construction of many different types of biosensors which can be used in recognition of electrolytes and metabolites. In the past few years the biosensors for determination of blood sugar and for determination of urea content in blood were developed as well as the method for determination of oxalate content in urine. The main goal of this project is the development of useful amperometric biosensor and the reliable method for measuring of total blood antioxidant status. All measurements will be done in classical electrochemical cell and in flow-through cell. Biosensor will be tested in water solution of known concentration of antioxidants as well as in blood samples and serums. The results will be compared with the reference method. Some calibrating solutions also can be tested.

KEY WORDS
ABTS, amperometric detection, antioxidant, biamperometric detection, DPPH, interdigitated electrode, Trolox equivalent

PROGRESS SUMMARY

The results obtained during three years of working on project are as follows:
8 articles published in CC journals (average impact factor 2.499), 13 participatings on congresses: 2 international and 11 domestic congresses, 1 diploma work, 1 student work awarded by Rector's award and 3 patents.

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A novel amperometric method for antioxidant activity determination using DPPH free radical, *Bioelectrochemistry* **68** (2005) 180-185

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Use of DPPH· DPPH redox couple for biamperometric determination of antioxidant activity, *Electroanalysis* **17** (2005) 273-278

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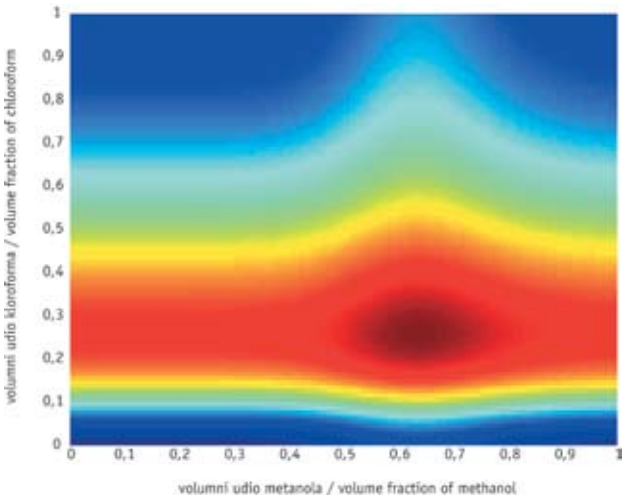
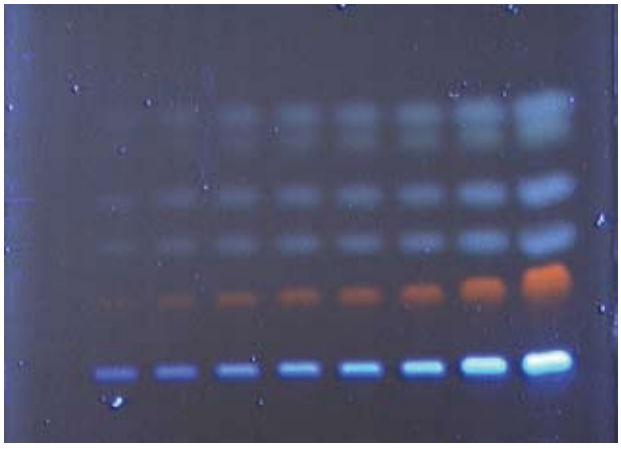


Optimizacija dvodimenzijske tankoslojne kromatografije.
Optimization of two-dimensional thin-layer chromatography.



Kromatogram smjese farmaceutika.
Chromatogram of a pharmaceutical mixture.

GLAVNI ISTRAŽIVAČ

Marija Kaštelan-Macan 01 4597 211 / mmacan@fkit.hr
Zavod za analitičku kemiju

SURADNICI

Alka Horvat
Sandra Babić
Danijela Ašperger
Dragana Mutavdžić

VANJSKI SURADNICI

Goran Srečnik
(Krka, Jastrebarsko)
Lidija Pozaić-Frketić
(PLIVA, Zagreb)

OPIS PROJEKTA

Cilj je projekta razviti i primijeniti moderne kemometrijske postupke pri predviđanju, optimizaciji i procjeni separacijskih parametara. Težište istraživanja je na modernim kemometrijskim postupcima koji se u kemijskoj analizi nedovoljno primjenjuju. Istraživanja su usmjerena na novije ektrakcijske tehnike: mikrovalnu ekstrakciju, ultrazvučnu ekstrakciju i ekstrakciju čvrstom fazom koje omogućuju izolaciju i koncentriranje analita iz složenih ekoloških uzoraka i manje zagađuju okoliš. Modernim kromatografskim tehnikama uz vezanje sustava tekućinske kromatografije visoke djelotvornosti s različitim detektorima (DAD, Fl, MS) postići će se optimalna razlučivost i točnost određivanja u višekomponentnoj analizi organskih zagađivala u vodi i tlu. Validiranjem i standardiziranjem postupaka te optimizacijom separacijskih parametara smanjuje se mjerna nesigurnost i sustavna pogreška.

KLJUČNE RIJEČI
moderne separacijske tehnike, validacija, optimizacija, kemometrija

>> POSTIGNUTI REZULTATI

Razvijene su kromatografske metode izolacije i određivanja organskih zagađivala (pesticidi, antibiotici) iz složenih uzoraka iz okoliša. Metode su optimirane modernim kemometrijskim tehnikama.
U razdoblju 2002.- 2006. objavljeno je ukupno 64 znanstvena rada, od toga 25 radova u CC časopisima (18 objavljenih, 4 prihvaćena za objavljivanje i 3 u postupku recenzije), 3 rada u ostalim časopisima, 14 objavljenih radova u zbornicima (10 u međunarodnim, 4 u domaćim), 2 pozvana predavanja na skupovima i 20 sažetaka, pretežito na međunarodnim skupovima. Iz područja projekta objavljeno je i 1 poglavlje u uglednom međunarodnom kromatografskom priručniku, 3 poglavlja u znanstvenoj knjizi, 1 znanstvena knjiga i 1 sveučilišni udžbenik. Obranjeno je 7 disertacija i magistarskih radova te 7 diplomskih radova.

+385 1 4597 211 / mmacan@fkit.hr **Marija Kaštelan-Macan**
Department of Analytical Chemistry

Principal investigator

PROJECT DESCRIPTION

Project objective is to develop and implement the latest chemometric procedures for the prediction, optimization and evaluation of separation parameters. The focus will be on the up-to-date chemometric procedures. The research will also focus on the latest extraction techiques: microwave, ultrasound and solid phase extraction which enable analyte isolation and preconcentration from the complex sample matrix and are less environmentally unfriendly. Using modern hypenathed chromatographic techniqes with various detectors (DAD, Fl, MS), an optimal resolution and accuracy in multicomponent analysis of the organic pollutants in water and soil will be achieved. Validated and standardized procedures along with the optimized separation parameters are expected to minimize the measurement uncertainty and systematic error.

KEY WORDS
latest separation techniques, validation, optimization, chemometrics

RESEARCH ASSOCIATES

Alka Horvat
Sandra Babić
Danijela Ašperger
Dragana Mutavdžić

CONSULTANTS

Goran Srečnik
(Krka, Jastrebarsko)
Lidija Pozaić-Frketić
(PLIVA, Zagreb)

PROGRESS SUMMARY

Modern chromatographic methods for isolation and determination of organic pollutants from complex environmental matrix are developed. Methods are optimized using latest chemometric procedures.
In period 2002-2006. 64 scientific papers were published (25 cited in CC base, 3 in other journals, 14 papers in conference proceedings, 2 invited lectures and 20 abstracts).
From the field of project, 1 chapter in the international chromatographic handbook is published, as well as 3 chapters in scientific book, 1 scientific book and 1 textbook. Seven doctoral and master theses, as well as seven graduation theses are defended.

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Determination of the veterinary antibiotics pollution in soil from agricultural sources, *Agriculture and the Environment VI - Managing Rural Diffuse Pollution, Edinburgh 5.-6. travanj 2006* / Lynda Gairns, Karen Crighton, Bill Jeffrey (ur.), Edinburgh SAC/SEPA, 2006, pp. 218-223

2. **Danijela Ašperger**, **Sandra Babić, Dragana Mutavdžić, Alka Horvat, Marija Kaštelan-Macan**
TLC determination of sulfonamides and trimethoprim, *Planar Chromatography 2005 "Milestones in Instrumental TLC"*, *Siofok 29.-31. svibanj 2005* / Sz. Nyiredy (ur.), Budakalasz, Hungary, Research Institute for Medical Plants, 2005, pp. 217-225

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4. Tanja Tomić
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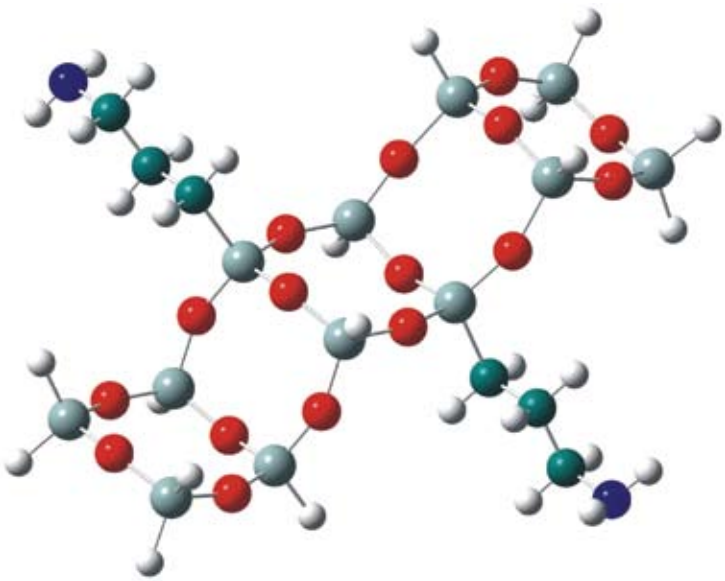
PRIRODNE ZNANOSTI
Fizika

NATURAL SCIENCES
Physics

0125 007



Si-O-Si ljestvasta struktura sa dva aminopropilna lančića.
Si-O-Si ladder structure with two aminopropyl chains.

GLAVNI ISTRAŽIVAČ

Vesna Volovšek 01 4597 135 / volovsek@fkit.hr
Zavod za fiziku

SURADNICI

Vladimir Dananić
Iva Movre Šapić

VANJSKI SURADNICI

Lahorija Bistričić
(Fakultet elektrotehnike i računarstva, Zagreb)

OPIS PROJEKTA

Suvremena istraživanja u fizici čvrstog stanja velikim su dijelom usmjerena na proučavanje svojstava neuređenih i djelomično uređenih sustava. Rješenja za mnoge zahtjevne tehnološke probleme temelje se na poznavanju fizikalnih svojstava materijala, kao što su polimeri, tekući kristali i različite vrste stakla. Napredak u primjeni navedenih materijala posljedica je boljeg razumijevanja povezanosti njihovog makroskopskog ponašanja s mikroskopskim molekulskim svojstvima. U našim smo istraživanjima određivali strukturu i dinamiku polimernih materijala kombinirajući eksperimentalni i teorijski pristup. Eksperimentalnu osnovu činile su vibracijske spektroskopije, Ramanova i infracrvena. Vibracijske spektre analizirali smo računanjem dinamike slobodne molekule. Taj nam je račun omogućio određivanje karakterističnih vrpci i transferabilnog polja sila pojedinih podjedinica. Analizom utjecaja vanjskih parametara kao što su temperatura i udio aditiva na vibracijske spektre kompozita određena su međudjelovanja koja su na molekulskoj razini odgovorna za opažena makroskopska svojstva.

KLJUČNE RIJEČI
molekulska dinamika, karakteristične vibracije, polimeri, temperaturna ovisnost.

>> POSTIGNUTI REZULTATI

1. Određeno je potencijalno polje i asignirani su vibracijski spektri kristala 4,4´-dibromobenzofenona. Neobično temperaturno ponašanje nekih niskofrekventnih vibracija objašnjeno je "*dephasing*" relaksacijskim procesima.
2. Napravljena je interpretacija unutarmolekulskih vibracija 2-adamantanona analizom normalnih koordinata DFT metodom, korištenjem 6-31G(d,p) skupa funkcija.
3. Ramanskim raspršenjem istraživan je tanki film molekula adamantana. Temperaturno ponašanje Boseove vrpce ukazuje na postepeni prijelaz iz amorfne u uređenu fazu.
4. Proučavao se utjecaj nanopunila na promjenu strukture i svojstava kompozita punjenih netretiranim kalcij karbonatom u polivinilacetatnoj i poliuretanskoj matrici. Također je istraživan utjecaj površinske obrade nanopunila na mehanička svojstva kompozita.
5. Ispitivanjem konformacijske stabilnosti aminopropilsilantriola utvrđeno je postojanje dvaju enantiomera. Interpretacija unutarmolekulskog vibracijskog gibanja provedena je analizom normalnih koordinata na osnovi DFT potencijalnog polja izračunatog sa B3LYP funkcionalom i 6-31G(d,p) baznim setom funkcija.
6. Vibracijskim metodama istraživan je utjecaj vanjskih uvjeta (temperatura, UV zračenje, podloga) na konačnu strukturu polimeriziranog aminopropilsilantriola.
7. Istraživano je temperaturno ponašanje niskofrekventnih, polariziranih Ramanovih spektara tankog sloja poli-aminopropilsilantriola na PVC podlozi. Analizom Boseove vrpce zaključeno je da tanki sloj ima ljestvastu strukturu s uređenjem srednjeg dosega koja ne ovisi o temperaturi.
8. Ispitivana je konformacijska stabilnost gama-aminopropiltrietoksisilana i njegova vibracijska dinamika. Dobiveni rezultati ukazuju na postojanje sedam stabilnih konformacija promatranog spoja.
9. DFT metodom i vibracijskim spektroskopijama istraživana je polimerna struktura aminopropilsiloksana. Komparativna analiza ukazuje na stvaranje ljestvaste, slojevite strukture s uređenjem srednjeg dosega. Također je istraživan utjecaj molekula vode na stabilnost promatranog spoja.

+385 1 4597 135 / volovsek@fkit.hr
Vesna Volovšek
Department of Physics

Principal investigator

PROJECT DESCRIPTION

Solid state physics is in the last two decades greately interested in exploring disordered and partially ordered systems and their properties. Solutions for many demanding technological problems are based on our knowledge of physical properties of materials like polymers, liquid crystals and different kinds of glasses. Progress in application of mentioned materials is a consequence of a better understanding of relationships between their macroscopic behavior and microscopic molecular properties. In our investigations we determine the structure and dynamics of polymer materials by combining experimental and theoretical approaches. The experimental basis consists of vibrational spectroscopy, Raman's and IR. The vibrational spectra are analyzed by dynamic calculation of a free molecule. Vibrational spectroscopy is a suitable method for these investigations since each band in the spectra represents an intrinsic probe of a particular region of a molecule. Vibrational dynamics calculations would enable us to determine the characteristic bands for individual subunits. Since the physical properties of complex molecular systems change under the influence of external parameters (temperature, pressure, ageing, additive content), the knowledge of characteristic bands would make possible the microscopic desription of the observed behavior.

KEY WORDS
molecular dynamics, characteristic vibrations, polymer, temperature dependence

PROGRESS SUMMARY

1. The valence force field and vibrational spectra of 4,4'-dibromobenzophenone were determined. Unusual temperature behavior of some low-frequency bands was explained by dephasing relaxation processes.
2. The interpretation of intermolecular vibrations of 2-adamantanone has been made by DFT calculation using 6-31G(d,p) basis set.
3. Thin film of adamantane molecules has been investigated. Temperature behaviour of Bose band indicates a gradual transition from amorphous to crystal phase.
4. The influence of nanofiller on the structure and properties of composites filled with untreated $CaCO_3$ in PVAc and PU matrix was investigated. The influence of the surface pretreatment of nanoparticles on the mechanical properties of composites was also studied.
5. Examination of the conformational stability of aminopropylsilanetriol confirmed the existence of two enantiomers. The interpretation of the intermolecular vibrations was realized by normal coordinate analysis based on DFT potentional, calculated by B3LYP functional and 6-31G(d,p) basis set.
6. Vibrational methods were used to investigate the influence of the external parameters (temperature, UV radiation, surface) in the final structure of polymerized aminopropylsilanetriol.
7. Temperature behaviour of the low-frequency polarized Raman spectra of thin poly-aminopropylsilanetriol layer was studied. Bose band analysis revealed the ladder structure of middle range order which does not depend on the temperature.
8. The conformational stability and vibrational dynamics of gamma-aminopropyl triethoxysilane was investigated. The results show the existence of seven stable conformations of this compound.
9. DFT method along with the vibrational analysis was used to investigate the polymer structure of aminopropylsiloxane. Comparative study suggests the forming of the layered ladder structure of a middle-range order.

RESEARCH ASSOCIATES

Vladimir Dananić
Iva Movre Šapić

CONSULTANTS

Lahorija Bistričić
(Faculty of Electrical Engineering and Computing, Zagreb)

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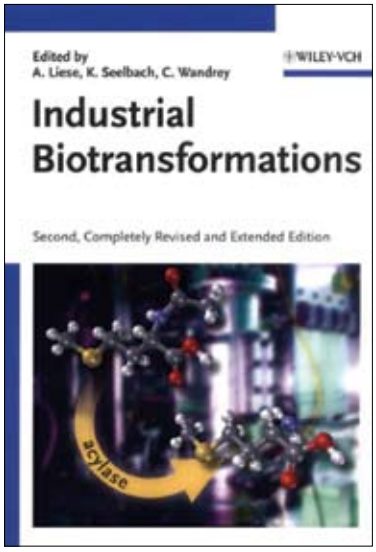
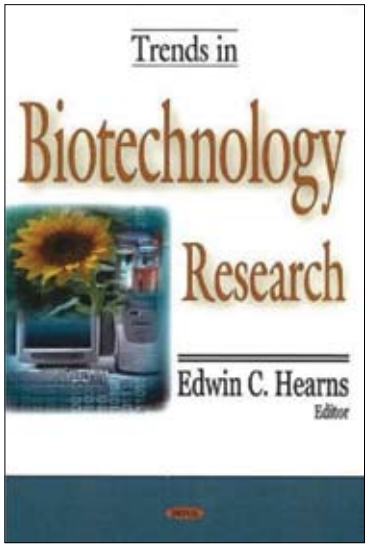
BIOTEHNIČKE ZNANOSTI
Biotehnologija

BIOTECHNICAL SCIENCES
Biotechnology

0125 021



Knjiga / Book
Industrial Biotransformations



Knjiga / Book
Trends in Biotechnology Research

Enzimski membranski reaktor.
Membrane enzyme reactor.

GLAVNI ISTRAŽIVAČ

Đurđa Vasić-Rački 01 4597 104 / dvracki@fkit.hr
Zavod za reakcijsko inženjerstvo i katalizu

SURADNICI

Bruno Zelić
Ana Vrsalović Presečki
Zvjezdana Findrik

OPIS PROJEKTA

Cilj istraživanja na projektu je bio razvoj industrijski zanimljivih biotransformacija koje kataliziraju stereospecifični biokatalizatori, koji za svoje katalitičko djelovanje trebaju koenzim, uz: a) primjenu jeftinijih enzima za regeneraciju koenzima pri provedbi oksido-redukcija kataliziranih s pročišćenim enzimima kao biokatalizatorima; b) primjenu enzimskog sustava za regeneraciju koenzima u cijelim stanicama pekarskog kvasca za provedbu industrijski zanimljivih oksido-redukcija kataliziranih enzimima u cijelim stanicama.
Svrha istraživanja je bila, pri steroselektivnim oksido-redukcijama (redukcija 2-keto-kiselina, redukcija ketona) koje su temelj potencijalno industrijski zanimljivih biotransformacija, pronaći optimalan oblik biokatalizatora, sustav za regeneraciju koenzima, reakcijski medij, te način i uvjete provedbe procesa, zbog toga što su dosadašnja istraživanja pokazala da su biotransformacije pri blagim uvjetima s netoksičnim i obnovljivim biokatalizatorima, uz uporabu jeftinijih i obnovljivih sirovina, te stereoselektivne i potpune konverzije, alternativa u kemijskoj, farmaceutskoj i industriji agrokemikalija s obzirom na ekonomičnost i zaštitu okoliša.

KLJUČNE RIJEČI
biokatalizatori, biotransformacije, enzimi, koenzimi, metodologija kemijskog inženjerstva

>> POSTIGNUTI REZULTATI

Razvijen je integralni bioproces oksidacije glukoze u pirogrožđanu kiselinu u cijelim stanicama genetski modificirane *E. coli*. Rezultati istraživanja objavljeni su kao poglavlje u knjizi, te u pet radova. Metodologija kemijskog inženjerstva koja je korištena pri razvoju mikrobioloških procesa prikazana je u stručnom radu objavljenom u domaćem časopisu i time je popularizirano ovo veoma zanimljivo područje u nas. Metodologija kemijskog inženjerstva, upotrijebljena pri razvoju mikrobioloških procesa, primijenjena je na izolaciju prirodnih spojeva pirogrožđane i ružmarinske kiseline. Modelirani su bio-separacijski i bio-transformacijski procesi.
Razvijen je proces dobivanja alkohol dehidrogenaze u cijelim stanicama kvasca. S pročišćenim enzimom alkohol dehidrogenaze iz *Thermoanaerobacter* sp. razvijen je proces dobivanja enantio-selektivnog alkohola (S-feniletanola) iz ketona.
Optimirani su početni uvjeti redukcije 3,4-dihidroksifenil pirogrožđane kiseline.
Istraživane su reakcije oksidacije optički čistih aminokiselina s enantioselektivnim oksidazama aminokiselina. Ispitana je mogućnost sinteze enantiomerno čistih aminokiselina u reakciji kataliziranoj s novom oksidazom D-aminokiselina iz *Arthrobacter protophormiae*. Optimirana je reakcija hidratacije fumarne kiseline s pročišćenom fumarazom i fumarazom u cijelim permeabiliziranim stanicama kvasca. Provedena su istraživanja liaza u suradnji s Institutom za biotehnologiju Istraživačkog centra u Jülichu u kojima je primijenjena metodologija kemijskog inženjerstva. Ova metodologija je prikazana u još nekoliko radova. Metode regeneracije koenzima u enzimskim reakcijama oksido-redukcija su prikazane u monografskoj seriji koju izdaje Springer: "Advances in Bioengineering and Biotechnology". Napisano je jedno potpuno prerađeno poglavlje u drugom izdanju knjige o biotransformacijama pri blagim uvjetima s regio- i enantioselektivnim biokatalizatorima koje su ekološka i ekonomska alternativa u kemijskoj, farmaceutskoj i agrokemijskoj industriji, jer mogu pojednostavniti proizvodne procese i učiniti ih ekonomski atraktivnijim i prihvatljivim za okoliš. Održano je nekoliko pozvanih predavanja na domaćim i međunarodnim skupovima.
Rezultati istraživanja su predloženi kao podloga za razvojni projekt proizvodnje kiralnih alkohola, pročićenog enzima alkohol dehidrogenaze i optički čiste jabučne kiseline, koji se može ponuditi malim poduzetnicima. Ovaj je prijedlog nagrađen 2004. od Srednjeeuropske inicijative.

+385 1 4597 104 / dvracki@fkit.hr **Đurđa Vasić-Rački**
Department of Chemical Reaction Engineering and Catalysis

Principal investigator

RESEARCH ASSOCIATES

Bruno Zelić
Ana Vrsalović Presečki
Zvjezdana Findrik

PROJECT DESCRIPTION

The goal of the project "Biocatalysts and biotransformations" was to demonstrate two main technologies for industrially interesting biotransformations using sterospecific biocatalysts: oxidoreductases – dehydrogenases. These enzymes need coenzyme regeneration: a) first, a technology based on the use of isolated enzymes with coenzyme regeneration. b) second, a technology based on the use of enzymes in the whole cells of baker's yeast.
The purpose of the project was to find the optimal form of biocatalyst, suitable system of coenzyme regeneration, suitable reaction media and optimal process conditions in industrially interesting biotransformations. The biotransformations at mild conditions with highly regio- and enantioselective biocatalysts are a green and economical alternative in chemical, pharmaceutical and agrochemical industry.

KEY WORDS
biocatalysts, biotransformations, enzymes, coenzymes, methodology of chemical engineering

PROGRESS SUMMARY

The integrated bioprocess for *Escherichia coli* based pyruvate production from glucose was developed. The results were published in a book chapter and five papers. The methodology of chemical engineering used in the development of microbiological process was published in the professional paper.
The methodology of chemical engineering used in the development of microbial process was applied in the processes of isolation of natural compounds, like pyruvic acid and rosmarinic acid. Bio-separation processes as well as biotransformations were modelled.
The alcohol dehydrogenase production in baker's yeast was developed. The acetophenone reduction catalyzed by isolated alcohol dehydrogenase from *Thermoanaerobacter sp*. was developed.
The optimization of the initial conditions in (R)-(+)-3,4-dihydroxyphenyllactic acid production catalyzed with D-lactate dehydrogenase from *Lactobacillus leishmannii* using genetic algorithm was performed.
The oxidation of amino acid by enantioselective amino acid oxidases was investigated.
The hydratation of fumaric acid catalysed by isolated fumarase and fumarase in the permeabilized cells of commercial *Saccharomyces* sp. strain was optimized.
In the cooperation with the Institute of biotechnology, Research Centre Jüelich, the reaction catalyzed by lyase was investigated. The methodology of chemical engineering was applied. This methodology was published in some other papers.
The methods of coenzyme regeneration were described and published in Springer series: "Advances in Bioengineering and Biotechnology".
Biotransformations at mild conditions with regio- and enantioselective biocatalysts are an ecological and economical alternative in chemical, pharmaceutical, and agro-chemical industry. They can simplify the production process and make it economically attractive and environmentally friendly. A chapter in the book "Industrial biotransformation" on this subject was published. Some invited lectures at national as well as international meetings were also delivered.
Some results of the investigations were proposed for the project of production of chiral alcohols, isolated enzyme alcohol dehydrogenase and L-malic acid. The project proposal was awarded by the Central European Initiative.

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2. **Bruno Zelić, Đurđa Vasić-Rački**
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3. **Ana Vrsalović Presečki**, **Zvjezdana Findrik**, **Bruno Zelić**
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4. **Zvjezdana Findrik**, **Đurđa Vasić-Rački**, Birgit Geueke, Mutlu Kuzu, Werner Hummel
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8. **Đurđa Vasić-Rački**, Udo Kragl, Andreas Liese
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5. **Bruno Zelić, Đurđa Vasić-Rački**
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2. **Ana Vrsalović Presečki**
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6. **Bruno Zelić**
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PRILOZI APPENDICES

NAGRADE I PRIZNANJA DJELATNICIMA (2002. - 2006.)

1. **Mr. sc. BRUNO ZELIĆ**
   Nagrada Hrvatskog društva kemijskih inženjera i tehnologa mladom kemijskom inženjeru za 2002.

2. **Prof. dr. sc. RAJKA BUDIN** i
   prof. dr. sc. ALKA MIHELIĆ-BOGDANIĆ
   Godišnja nagrada "Josip Juraj Strossmayer" za 2002.

3. **Prof. dr. sc. ĐURĐA VASIĆ-RAČKI**
   Zlatna plaketa Senata Univerziteta u Mariboru, 2003.

4. **Prof. dr. sc. NATALIJA KOPRIVANAC**
   Nagrada EMAT-a – 1. međunarodnog sajma zaštite okoliša, ekotehnologije i komunalne opreme za organizaciju I. međunarodnog simpozija za upravljanje okolišom, SEM-2003.

5. **Prof. dr. sc. LJERKA DUIĆ**
   Nagrada "Franjo Hanaman" za 2004.

6. **Prof. dr. sc. MARIJA KAŠTELAN-MACAN**
   Nagrada "Fran Bošnjaković" za 2004.

7. **Prof. dr. sc. ĐURĐA VASIĆ-RAČKI**
   Nagrada Central Europen Initiative (CEI) za projekt "Production of bioproducts with high purity including biocatalysis and downstream processing", 2004.

8. **Mr. sc. HELENA OTMAČIĆ**
   Nagrada Hrvatskog društva kemijskih inženjera i tehnologa mladom kemijskom inženjeru za 2004.

9. **Dr. sc. NIKOLA BASARIĆ**
   Nagrada "Vladimir Prelog" za organsku kemiju za 2004.

10. **Prof. dr. sc. ŠTEFICA CERJAN STEFANOVIĆ** i
    prof. dr. sc. MARIJA KAŠTELAN-MACAN
    Nagrada "Franjo Hanaman" djelatnicama Fakulteta kemijskog inženjerstva i tehnologije, 2005.

11. **Prof. dr. sc. NATALIJA KOPRIVANAC**
    Posebno priznanje rektorice prigodom proslave Dana Sveučilišta, 2005.

12. **Prof. dr. sc. ĐURĐA VASIĆ-RAČKI**
    Državna nagrada za znanost za 2005. u području biotehničkih znanosti

13. **Prof. dr. sc. ĐURĐA VASIĆ-RAČKI**
    Godišnje priznanje za poticanje međunarodne suradnje Sveučilišta u Zagrebu u ak. god. 2005./2006.

14. **Prof. dr. sc. MARIN HRASTE**
    izabran za redovitog člana Hrvatske akademije znanosti i umjetnosti u 2006.

15. **Prof. dr. sc. ZORAN GOMZI**
    Nagrada "Fran Bošnjaković" za 2006.

16. **Prof. dr. sc. NATALIJA KOPRIVANAC**
    Državna nagrada za znanost za 2006. u području tehničkih znanosti

17. **Dr. sc. JELENA MACAN**
    Državna nagrada za znanost za 2006. – mladim mladim znanstvenicima u području tehničkih znanosti

18. **Dr. sc. ZVJEZDANA FINDRIK**
    Državna nagrada za znanost za 2006. – mladim znanstvenicima u području biotehničkih znanosti

19. **DRAGANA VIDAKOVIĆ, dipl. inž.**
    Nagrada Hrvatskog kulturnog društva Napredak u povodu 100. obljetnice rođenja nobelovca dr. Vladimira Preloga, 2006.

LIST OF HONORS AND AWARDS (2002 - 2006)

1. **BRUNO ZELIĆ, M.Sc.**
   Annual Award of the Croatian Society of Chemical Engineers for junior chemical engineers – 2002

2. **Prof. RAJKA BUDIN, Ph.D.** and
   Prof. ALKA MIHELIĆ-BOGDANIĆ, Ph.D.
   Annual Award "Josip Juraj Strossmayer" of the Zagreb Fair and Croatian Academy of Sciences and Arts for the best scientific publications in Croatian language – 2002

3. **Prof. ĐURĐA VASIĆ-RAČKI, Ph.D.**
   Golden Medal of the Senate of University of Maribor, Slovenia – 2003

4. **Prof. NATALIJA KOPRIVANAC, Ph.D.**
   Award of the International Environment Protection, Eco-Technology and Municipal Equipment Fair – for the organization of the 1st International Symposium on Environmental Management – 2003

5. **Prof. LJERKA DUIĆ, Ph.D.**
   "Franjo Hanaman" Award of the Faculty of Chemical Engineering and Technology of the University of Zagreb – for the promotion of Alma Mater – 2004

6. **Prof. MARIJA KAŠTELAN-MACAN, Ph.D.**
   "Fran Bošnjaković" Award of the University of Zagreb for the scientific achievements, promotion of the profession and education of junior scientists in the field of technical sciences – 2004

7. **Prof. ĐURĐA VASIĆ-RAČKI, Ph.D.**
   Award of the Central European Initiative for the project "Production of bioproducts with high purity including biocatalysis and downstream processing" – 2004

8. **HELENA OTMAČIĆ, M.Sc.**
   Annual Award of the Croatian Society of Chemical Engineers for junior chemical engineers – 2004

9. **NIKOLA BASARIĆ, Ph.D.**
   Annual Award "Vladimir Prelog" of the Croatian Chemical Society and Pliva pharmaceuticals for the scientific achievements in organic chemistry – 2004

10. **Prof. ŠTEFICA CERJAN STEFANOVIĆ, Ph.D.**
    and
    Prof. MARIJA KAŠTELAN-MACAN, Ph.D.
    "Franjo Hanaman" Award of the Faculty of Chemical Engineering and Technology of the University of Zagreb – for the promotion of Alma Mater – 2005

11. **Prof. NATALIJA KOPRIVANAC, Ph.D.**
    Special Award of the Rector of University of Zagreb given on the University Day Celebration – 2005

12. **Prof. ĐURĐA VASIĆ-RAČKI, Ph.D.**
    Annual State Award for Science in the field of biotechnical sciences – 2005

13. **Prof. ĐURĐA VASIĆ-RAČKI, Ph.D.**
    Annual University Award for the promotion of international cooperation of the University of Zagreb – 2005/6

14. **Prof. MARIN HRASTE, Ph.D.**
    Elected the Full Member of the Croatian Academy of Sciences and Arts – 2006

15. **Prof. ZORAN GOMZI, Ph.D.**
    "Fran Bošnjaković" Award of the University of Zagreb for the scientific achievements, promotion of the profession and education of junior scientists in the field of technical sciences – 2006

16. **Prof. NATALIJA KOPRIVANAC, Ph.D.**
    Annual State Award for Science in the field of technical sciences – 2006

17. **JELENA MACAN, Ph.D.**
    Annual State Award for Science (junior scientists) in the field of technical sciences – 2006

18. **ZVJEZDANA FINDRIK, Ph.D.**
    Annual State Award for Science (junior scientists) in the field of biotechnical sciences – 2006

19. **DRAGANA VIDAKOVIĆ, B.Sc.**
    Award of the Croatian Cultural Society "Napredak" – given on the 100th birth anniversary of the Croatian Nobel Prize winner Vladimir Prelog – 2006

POPIS UMIROVLJENIH ISTRAŽIVAČA / LIST OF RETIRED RESEARCHERS

Prof. dr. sc. EMIR HODŽIĆ	30.09.2002.
Prof. dr. sc. BRANKO KUNST	30.09.2002.
Prof. dr. sc. MATE STRUNJE	30.09.2002.
Dr. sc. BOŽICA PINTARIĆ	30.12.2002.
Dr. sc. ALOJZ CAHARIJA	30.12.2003.
Mr. sc. PETAR GORAN	30.09.2004.
Prof. dr. sc. ZVONIMIR JANOVIĆ	30.09.2004.
Prof. dr. sc. ŽELJKO BAJZA	22.02.2005.
Prof. dr. sc. LJERKA DUIĆ	30.09.2005.
Prof. dr. sc. ZVONIMIR ŠOLJIĆ	30.09.2005.
Prof. dr. sc. JURAJ BOŽIČEVIĆ	30.09.2006.

POPIS TRENUTNIH PROJEKATA, 2007. / LIST OF CURRENT PROJECTS, 2007

Šifra projekta / **Project code**	**Glavni istraživač** / **Principal Investigator**	**Naziv projekta** / **Project Title**
125-0000000-1970	**Lucija Foglar**	Primjena biološke imobilizacije za uklanjanje nitrata iz površinskih voda / Application of biological immobilization for nitrate removal from surface water
125-0821504-1976	**Zlata Hrnjak-Murgić**	Istraživanje, razvoj i ocjena polimernih kompozita za primjenu u građevinarstvu / Research, development and evaluation of polym. composites for use in civil engineering
125-0822161-2982	**Sanja Martinez**	Inhibicija korozije prirodnim spojevima: od molekulskih modela do primjene / Inhibiting corrosion by nature derived compunds: from molecular scale models to application
125-1251936-1964	**Nenad Bolf**	Softverski senzori i analizatori za motrenje i vođenje procesa / Soft sensors and analyzers for process monitoring and control
125-1251963-1968	**Felicita Briški**	Aerobno kompostiranje čvrstog otpada u reaktorskom sustavu /Aerobic composting of solid waste in reactor system
125-1251963-1972	**Antun Glasnović**	Procesna svojstva disperznih sustava / Process characteristics of disperse systems
125-1251963-1974	**Zoran Gomzi**	Analiza i modeliranje kemijskih reaktora / Chemical reactor analysis and modelling
125-1251963-1980	**Ante Jukić**	Optimiranje svojstava kopolimera u procesima usmjerenih radikalskih polimerizacija / Optimization of copolymer properties using controlled radical polymerizations
125-1251963-2573	**Stanka Zrnčević**	Primjena katalize u zaštiti okoliša / Application of catalysis in environmental protection
125-1251963-2580	**Katica Sertić-Bionda**	Napredni procesi odsumporavanja ugljikovodičnih goriva / Advanced processes of hydrocarbon fuels desulfurization
125-1252970-2981	**Stanislav Kurajica**	Keramički nanokompoziti dobiveni sol-gel postupkom / Sol-gel derived ceramic nanocomposites

125-1252970-2983	**Tomislav Matusinović**	Razvoj modela procesa hidratacije / Development of hydration process model
125-1252970-3005	**Hrvoje Ivanković**	Biokeramički, polimerni i kompozitni nanostrukturirani materijali / Bioceramic, polymer and composite nanostructured materials
125-1252971-2575	**Mirela Leskovac**	Inženjerstvo površina i međupovršina nanočestica u adhezijskim nanomaterijalima / Surface and interface engineering of nanoparticles in adhesive nanomaterials
125-1252971-2578	**Vesna Rek**	Modifikacija i stabilnost višefaznih polimernih sustava / Modification and stability of multiphases polymer systems
125-1252971-3033	**Jasenka Jelenčić**	Razvoj inovativnih višefunkcionalnih polimernih mješavina / Development of innovative multifunctional polymer blends
125-1252973-2572	**Ema Lisac**	Novi netoksični inhibitori korozije metala / New non-toxic metal corrosion inhibitors
125-1252973-2576	**Zoran Mandić**	Temeljna i primijenjena istraživanja vodljivih polimera / Fundamental and applied research of conducting
125-1253008-2571	**Laszlo Sipos**	Pročišćavanje i stabilizacija vode u velikim vodoopskrbnim sustavima / Water purification and stabilization in large water supply systems
125-1253008-3009	**Krešimir Košutić**	Membranski i adsorpcijski postupci otklanjanja organskih tvari pri obradbi voda / Membrane and adsorption processes for organics removal in water treatment
125-1253092-1981	**Natalija Koprivanac**	Obrada otpadnih voda naprednim oksidacijskim tehnologijama / Wastewater treatment by advanced oxidation technologies
125-1253092-3004	**Štefica Cerjan-Stefanović**	Procesi ionske izmjene u sustavu kvalitete industrijskih voda / Ion exchange processes in industrial water quality system
125-1951390-3000	**Rajka Budin**	Sniženje specifične potrošnje energije u industrijskim procesima / Reducing specific energy consumption in industrial processes
125-0982464-1356	**Grace Karminski-Zamola**	Novi heterocikli kao antitumorski i antivirusni (“pametni”) lijekovi / New heterocycles as antitumor and antiviral (“smart”) drugs
125-0982464-2922	**Mladen Mintas**	Razvoj novih prolijekova i lijekova protiv virusa i raka / Development of new prodrugs and drugs against viruses and cancer
125-0982464-2925	**Silvana Raić-Malić**	Razvoj i primjena novih molekula u positron emisijskoj tomografiji (PET) / Development of new tracer molecules for positron emission tomography (PET)
125-0982904-2923	**Mirjana Metikoš-Huković**	Novi materijali i katalizatori za održive tehnologije / New materials and catalysts for sustainable technologies
125-0982933-2926	**Marija Šindler**	Heteropolicikli, strukturne osnove za bioaktivne spojeve. Sinteza i fotokemija / Heteropolycycles, scaffolds to bioactive compounds. Synthesis and photochemistry
125-1253008-1350	**Sandra Babić**	Razvoj naprednih analitičkih metoda za određivanje farmaceutika u okolišu / Advanced analytical methods for pharmaceuticals determination in the environment
125-2120898-3148	**Marija Kaštelan-Macan**	Hrvatsko nazivlje u analitičkoj kemiji / Croatian nomenclature of analytical chemistry
125-1252971-2868	**Vesna Volovšek**	Vibracijska dinamika i struktura multifunkcionalnih polimernih sustava / Vibration dynamics and structure of multifunctional polymeric systems
125-1252086-2793	**Đurđa Vasić-Rački**	Biokatalizatori i biotransformacije / Biocatalysts and biotransformations