



ICACCHE

3rd International Conference on Applications
in Chemistry and Chemical Engineering

BOOKS OF PROCEEDINGS

11 - 15 September 2019 **Skopje**

www.icacche.com



ICACChE

3rd International Conference on Applications
in Chemistry and Chemical Engineering

11 - 15 September 2019 **Skopje**

Organized by



Partners



**INTERNATIONAL CONFERENCE ON APPLICATION IN CHEMISTRY AND
CHEMICAL ENGINEERING (ICACChE)**

ISBN 978-605-67917-4-1



ICACChE

3rd International Conference on Applications
in Chemistry and Chemical Engineering

11 - 15 September 2019 **Skopje**

**BOOK OF PROCEEDINGS OF THE
INTERNATIONAL CONFERENCE ON APPLICATION IN
CHEMISTRY AND CHEMICAL ENGINEERING (ICACCHE)
11-15 SEPTEMBER 2019, SKOPJE**

Edited by
Prof. Dr. Ömer Şahin

Published, 2019

info@icacche.com
www.icacche.com

This work is subject to copyright. All rights are reserved, whether the whole or part of the material is concerned. Nothing from this publication may be translated, reproduced, stored in a computerized system or published in any form or in any manner, including, but not limited to electronic, mechanical, reprographic or photographic, without prior written permission from the publisher.

The individual contributions in this publication and any liabilities arising from them remain the responsibility of the authors. The publisher is not responsible for possible damages, which could be a result of content derived from this publication.



SCIENTIFIC COMMITTEE

1. Prof. Dr. İbrahim DİNÇER-University of Ontario
2. Prof. Dr. Gülhayat NASÜN SAYGILI - İstanbul Technical University
3. Prof. Dr. İnci EROĞLU- Middle East Technical University
4. Prof. Dr. Baki ÇİÇEK- Balıkesir University
5. Prof. Dr. Akın AZİZOĞLU- Balıkesir University
6. Prof. Dr. Mustafa BÖYÜKATA - Bozok University
7. Prof. Dr. Ferdinand Bego - University of Tirana, Albania
8. Prof. Dr. M. Salih AĞIRTAŞ - Yüzüncü Yıl University
9. Prof. Dr. Spiro Drushku - University of Tirana, Albania
10. Prof. Dr. Mahmut DOĞRU - Fırat University
11. Prof. Dr. Ahmet ÖZER - Fırat University
12. Prof. Dr. Muhtar KOCAKERİM - Çankırı University
13. Prof. Dr. Sinan YAPICI - İnönü University
14. Prof. Dr. Tahir Arbnesi - University of Pristina
15. Prof. Dr. İbrahim DİNÇER - Yıldız Teknik Üniversitesi
16. Prof. Dr. İsmail ÇAKMAK - Kafkas University
17. Prof. Dr. Ahmet KILIÇ - Harran University
18. Prof. Dr. Ahmet Duran ŞAHİN - İstanbul Technical University
19. Prof. Dr. Mustafa DEĞİRMENCİ - Harran University
20. Prof. Dr. Kozeta Vaso - University of Tirana, Albania
21. Prof. Dr. Zübeyde BAYSAL - Dicle University
22. Prof. Dr. Hasan TOĞRUL - Eskişehir Osmangazi University
23. Prof. Dr. Filiz KARAOSMANOĞLU - İstanbul Technical University
24. Prof. Dr. Fikret AKDENİZ - Kafkas University
25. Prof. Dr. Sermet KABASAKAL - Eskişehir Osmangazi University
26. Prof. Dr. Handan KAMIŞ - Selçuk University
27. Prof. Dr. Ülker BEKER - Yıldız Teknik Üniversitesi
28. Prof. Dr. Mahmut KUŞ - Selçuk University
29. Prof. Dr. Hafız ALİSOY - Namık Kemal University
30. Prof. Dr. Ömer YAVUZ - Dicle University
31. Prof. Dr. Mesut AKGÜN - Yıldız Teknik Üniversitesi
32. Prof. Dr. Birsen Şengül OKSAL - Giresun University
33. Assoc. Prof. Dr. Koray KÖKSAL - Bitlis Eren University
34. Assoc. Prof. Dr. Naser Troni - University of Pristina
35. Assoc. Prof. Dr. Nasrettin GENLİ - Dicle University
36. Assoc. Prof. Dr. M. Zafer KÖYLÜ - Dicle University
37. Assoc. Prof. Dr. Cafer SAKA - Siirt University
38. Assoc. Prof. Dr. Abdurrahman ASAN - Hitit University
39. Assoc. Prof. Dr. Halil DEMİR - Siirt University
40. Assoc. Prof. Dr. A. Abdullah CEYHAN - Selçuk University
41. Assist. Prof. Dr. Yunus ÖNAL - İnönü University
42. Assist. Prof. Dr. Vedat ADIGÜZEL - Kafkas University
43. Assist. Prof. Dr. Mustafa ÖZDEMİR - Süleyman Demirel University



ORGANIZATION COMMITTEE

Honorary Chairs

Prof. Dr. Murat ERMAN – Rector – Siirt University

Conference Chairman

Prof. Dr. Ömer ŞAHİN – Vice Rector– Siirt University

Members of the Committee

- Assoc. Prof. Dr. Mehmet Sait İZGİ - Siirt University
- Assoc. Prof. Dr. Sabit HOROZ - Siirt University
- Assoc. Prof. Dr. Orhan BAYTAR - Siirt University
- Assoc. Prof. Dr. Dilek KILINÇ - Siirt University
- Assist. Prof. Dr. Arzu EKİNCİ - Siirt University
- Assist. Prof. Dr. Sinan KUTLUAY - Siirt University
- Assist. Prof. Dr. Mehmet Şakir ECE – Mardin Artuklu University

Secretariat of the Committee

- Research assistant Tülin Avcı HANSU - Siirt University
Tel: +90 539 666 00 69 - tulinn_avci@hotmail.com



WELCOME TO ICACCHE 2019

On behalf of the organizing committee, we are pleased to announce that the International Conference on Application in Chemistry and Chemical Engineering (ICACCHE-2019) is held from September 11 to 15, 2019 in Skopje/Republic of North Macedonia. ICACCHE 2019 provides an ideal academic platform to present the latest research finding on design, manufacture and operation of plants and machinery, the development of new materials or substances, developing novel materials and processes, analyzing substances, measuring the physical properties of substances and testing theories. This event gives a chance for all the professionals to gain and share information on Chemistry and Chemical Engineering and other related science branches issues and research.

Chemistry and Chemical engineering are multidisciplinary branches of applied engineering and science consisting of the application of physical science (Chemistry & Physics), life sciences including biochemistry with applied mathematics and economics to produce transform and use of chemicals, molecules materials, energy to make the whole production process successful with economic benefits.

Over the last 50 years, the discoveries in the basic sciences and the engineering of these inventions have been targeted at the development of applied technology and the prosperity of mankind and the distant and high quality of life away from environmental destructions for a sustainable future. Mathematics, physics, chemistry, and biology, which are accepted as basic sciences, and their engineering applications are now accepted in the scientific circles that have been intertwined and one of which is not worthless. It is foreseen by sectoral and academic stakeholders that these interdisciplinary relationships will continue to increase over the next several years.

The ability to identify, model, and solve engineering problems, and the ability to apply engineering knowledge develops with the knowledge of basic sciences. So, in terms of engineering education and the application of the engineering profession, the basic sciences have an important place and the necessary importance should be given.

Our goal is to transform this conference into an exchange of views on future vision and scenarios in chemistry, chemical engineering and related sciences, and to make science a tool of peace and justice.

Best regards,

Prof. Dr. Ömer ŞAHİN



CONTENT	PAGE
SYNTHESIS AND CHARACTERISATION OF SOME IMPORTANT PYRAZOLO[1,5-C]PYRIMIDINE DERIVATIVES	1
SYNTHESIS, DFT, MOLECULAR DYNAMICS SIMULATION, MOLECULAR DOCKING OF CAPROLACTAM-ZINC CHLORIDE IONIC LIQUID (IL)	2
CATALYTIC ACTIVITY OF EUPERGIT C SUPPORTED-CO-COMPLEX CATALYST IN NABH₄ HYDROLYSIS	3
AN OPTIMIZATION STUDY ON GAS ADSORPTION APPLICATION OF TOLUENE BY USING FORMALDEHYDE-TREATED PISTACHIO SHELLS	4
APPLICATION OF RESPONSE SURFACE METHODOLOGY FOR MODELING OF GAS-PHASE ADSORPTION PROCESS OF BENZENE	5
BOX-BEHNKEN RESPONSE SURFACE METHODOLOGY FOR OPTIMIZATION OF PROCESS PARAMETERS FOR GAS ADSORPTION OF TOLUENE ONTO Fe₃O₄ NANO-ADSORBENT	6
SYNTHESIS OF SILICA-COATED MAGNETIC Fe₃O₄@SiO₂ NANOPARTICLES AS A NEW ADSORBENT AND ITS USE IN GAS-PHASE ADSORPTION OF BENZENE	7
ACTIVATED CARBON SUPPORTED Fe₃O₄ NANOPARTICLES: A NOVEL ADSORBENT FOR GAS-PHASE ADSORPTION OF TOLUENE	8
APPLICATION FOR GAS ADSORPTION OF BENZENE BY USING MAGNETIC Fe₃O₄/AC@SiO₂@EDTA NANO-ADSORBENT	9
APPLICATION FOR GAS ADSORPTION OF BENZENE BY USING MAGNETIC Fe₃O₄/AC@SiO₂@EDTA NANO-ADSORBENT	10
APPLICATION FOR GAS ADSORPTION OF BENZENE BY USING MAGNETIC Fe₃O₄/AC@SiO₂@EDTA NANO-ADSORBENT	11
HYDROLYSIS OF AMMONIA BORANE IN THE PRESENCE OF RU BASED MAGNETIC NANO CATALYST	12
INVESTIGATION OF MALACHITE GREEN ADSORPTION WITH RESPONSE SURFACE METHOD	13
INVESTIGATION OF THE EFFECTS OF VARIOUS IMPURITIES ON NUCLEIC FORMATION AND GROWTH OF BORIC ACID IN STATIONARY MEDIUM OF SINGLE CRYSTAL SYSTEM	14
INVESTIGATION OF THE EFFECTS OF VARIOUS IMPURITIES ON NUCLEIC FORMATION AND GROWTH OF BORAX PENTAHYDRATE IN STATIONARY MEDIUM OF SINGLE CRYSTAL SYSTEM	15
CONDUCTIVE POLYMERIC FILM PRODUCTION FOR CONTROLLED DRUG RELEASE APPLICATIONS	16
THE ADSORPTION OF METHYLENE BLUE BY RESPONSE SURFACE METHOD	17
ANALYSES ON ELECTROCHEMICAL PROPERTIES OF NICO2O4 SUPERCAPACITOR ELECTRODES	18
PHOTOELECTROCHEMICAL ACTIVITY OF ELECTRODEPOSITED CDXZN1-XS PHOTOELECTRODES UNDER SOLAR LIGHT IRRADIATION	19
DFT STUDY ON THE RING-OPENING OF CYCLOPROPYLIDENOID TO ALLENE INCORPORATED INTO Seven-MEMBERED RING	20
DFT INVESTIGATION OF HALOGENATED SUMANENES	21
AMMONIA FOR THE HYDROLYSIS REACTION OF BORANE EFFECT OF YTTRIUM BASED RU-CO-Y ALLOY CATALYST ON HYDROGEN PRODUCTION	22



SYNTHESIS OF BENZO-AZA CROWN ETHERS BY MICROWAVE METHOD AND CHARACTERIZATIONS	23
MINERAL ANALYSIS OF CANCEROUS AND NON-CANCEROUS PROSTATE TISSUE SAMPLES	24
SINGLE CELL PEM FUEL CELL DESIGN AND APPLICATION	25
INVESTIGATION OF PROPERTIES CDSE QUANTUM DOTS SYNTHESIZED BY LASER ABLATION	26
EFFECT OF CO-CR-B CATALYST AMMONIA BORANE HYDROLYSIS	27
SYNTHESIS AND PROPERTIES OF LIQUID CRYSTALS COMPOUND	28
ELECTROCHEMICAL DETERMINATION OF DOPAMINE USING A GRAPHENE SCREEN-PRINTED CARBON ELECTRODE COUPLED WITH MAGNETIC SOLID-PHASE MICROEXTRACTION	29
FATTY ACID ETHYL ESTER SYNTHESIS FROM BEEF TALLOW USING SUPERCRITICAL ETHANOL	30
AN EASY PROCEDURE FOR IDENTIFYING FAME, FAEE AND FAEF OBTAINED WITH SUPERCRITICAL ALCOHOLS AND BEEF TALLOW	31
QUANTITATIVE DETERMINATION OF ACTIVE COMPONENTS IN A TABLET BY RATIO SPECTRA-DERIVATIVE METHOD	32
FUEL GAS PRODUCTION FROM GUAVA BY GASIFICATION WITH SUPERCRITICAL WATER	33
CERIUM OXIDE SUPPORTED NICKEL SCHIFF BASE COMPLEX AS A CATALYST FOR HYDROGEN PRODUCTION	34



SYNTHESIS AND CHARACTERISATION OF SOME IMPORTANT PYRAZOLO[1,5-C]PYRIMIDINE DERIVATIVES

ELIF KORKUSUZ^{a*}, ŞERIFE GELİR^b, SEHER ARSLAN^c, ISMAIL YILDIRIM^d

^aKAYSERİ UNIVERSITY, VOCATIONAL COLLEGE

*elifdus@hotmail.com

Abstract

Pyrazolo[1,5-c]pyrimidines are biologically active, synthetically useful and important heterocyclic compounds. The synthesis of novel pyrazolo-pyrimidine derivatives and investigation of their chemical and biological behavior have gained more importance in recent decades for biological, medicinal and agricultural reasons. Different classes of pyrazolo-pyrimidine compounds possess an extensive spectrum of pharmacological activities. Differently substituted pyrazolo[1,5-c]pyrimidine moiety has also been found to have other important activities such as antibacterial, antifungal, anti-inflammatory, antifungal, anticonvulsant, analgesic, antimicrobial, antitumor, cytotoxic and herbicidal [1,2].

It should be noted that pyrazolo[1,5-c]pyrimidines are least studied among various types of pyrazolo-pyrimidines. Due to our interest in pyrazolo[1,5-c]pyrimidines, we have investigated the reactivity and synthetic applications of these compounds. Herein, we report the first synthesis of pyrazolo[1,5-c] pyrimidines by reactions of 1-amino-5-(aroyl)-4-(aryl)pyrimidin-2(1H)-one and its pyrimidine-2(1H)-thione are synthesized in two steps from 4-(aroyl)-5-(aryl)furan-2,3-dione [2-4] using DMAD, DEAD, ethyl-2-chloroacetate, 3-chloroacetylacetone as electrophiles. The result of these experiments is discussed in this study. The chemical structure of synthesized derivatives will be elucidated by elementary analysis, FT-IR and NMR spectroscopic techniques after the pureness control of them done by TLC and melting point analyses.

Keywords: Pyrazolo[1,5-C]Pyrimidine, Condensation, Recyclization

**This study was financially supported by Research Foundation of Erciyes University (FBA-2013-4215)*

References

1. Cheng C. C., Prog. Med. Chem., 6, 67-134, 1969.
2. Önal Z., Yıldırım İ., Kandemirli F., Struct. Chem., 21, 809-8016, 2010.
3. Yıldırım İ., Tezcan M., Güzel Y., Sarıpınar E., Akçamur Y., Turk. J. Chem., 20, 27-32, 1996.
4. Önal, Z., Korkusuz, E., İlhan İ. Ö. Heterocycl Commun., 16, 79-84, 2010.



SYNTHESIS, DFT, MOLECULAR DYNAMICS SIMULATION, MOLECULAR DOCKING OF CAPROLACTAM-ZINC CHLORIDE IONIC LIQUID (IL)

SEFA ÇELİK^a, ALİ TUĞRUL ALBAYRAK^{b*}, SEVİM AKYÜZ^c, AYŞEN E. ÖZEL^d

^aISTANBUL UNIVERSITY - CERRAHPASA

^bISTANBUL UNIVERSITY - CERRAHPASA

^cISTANBUL KULTUR UNIVERSITY

^dISTANBUL UNIVERSITY

*albayrak@istanbul.edu.tr

Abstract:

Introduction: Ionic liquids are generally eutectic mixtures of organic salts and inorganic salts or organic salts consisting of anions and cations, whose melting points are frequently below 100 °C. They have unusual properties such as high thermal and chemical stability, low volatility, high conductivity and the ability to dissolve inorganic compounds. Room-temperature ionic liquids have the potential to be used in electrical batteries because of their high thermal and electrical conductivity. Furthermore, the H-bonds formed by the interaction of the ionic liquids with DNA increase the stability of the DNA by playing an important role in the stability of the DNA.

Methods: Caprolactam-zinc chloride ionic liquid was synthesized and characterized by spectroscopic and DSC analyses. The optimized geometry and electrostatic potential map of the new synthesized ionic liquid were calculated by the DFT method wb97xd functional, which is the quantum chemical calculation method, using the 6-31++G(d,p) basis set. Conformational analysis of the ionic liquid was also carried out by Molecular Dynamic Simulation. As a result of the interaction of this ionic liquid with DNA, the possible binding modes were found by molecular docking analysis. Besides, ADMET (Absorption, distribution, metabolism, excretion, and toxicity) calculation was made to predict the pharmacokinetics and toxicity profile of the synthesized ionic liquid.

Results: The structure of this ionic liquid, which was synthesized for the first time, was elucidated theoretically (with Quantum Chemical and Molecular Dynamic Methods) and experimentally (IR, Raman). It was determined theoretically that which nucleotides in DNA constitutes hydrogen bond/bonds with the ionic liquid. In addition, pharmacokinetic and toxicity profile were calculated theoretically, and drug availability was evaluated.

Discussion: In this study, the potential of caprolactam-zinc chloride ionic liquid to be a pioneering molecule, which has many advantages such as low toxicity, low cost and simple preparation process, has been uncovered.

Conclusion: Molecular modeling of the synthesized ionic liquid and determination of the ligand-receptor interaction site by docking analysis of this ionic liquid with DNA can be guiding, especially in the synthesis of anticancer drugs and enhancing their activity.

Keywords: Ionic Liquid, Dft, Molecular Dynamics, Molecular Docking



CATALYTIC ACTIVITY OF EUPERGIT C SUPPORTED-CO-COMPLEX CATALYST IN NaBH_4 HYDROLYSIS

DILEK KILINÇ^{a*}, ÖMER ŞAHİN^b

^aFACULTY OF SCIENCE AND LETTERS, DEPARTMENT OF CHEMISTRY, SIIRT
UNIVERSITY, 56100 SIIRT

^bFACULTY OF ENGINEERING, DEPARTMENT OF CHEMICAL ENGINEERING,
SIIRT UNIVERSITY, 56100 SIIRT

*dkilinc@siirt.edu.tr

Abstract:

The increasing energy demands, the depletion of fossil fuels and the related environmental problems are prompting scientists to search for various types of clean, low-cost, high efficiency and sustainable energy production, storage, transportation and utilization technologies [1].

H_2 is difficult to store in liquefied and compressed forms due to its low boiling point, which is one of the major obstacles in establishing a hydrogen economy [2].

A great deal of metal-hydride complexes are able to be used for hydrogen storage, but their hydrogen capacities are relatively low [3]. Alternatively, boron-hydrides (NaBH_4 , NH_3BH_3 , LiBH_4 , etc.) are deemed to be one of the best potential candidates for chemical hydrogen storage materials, and possess advantages as a low molecular weight and a high hydrogen content (10–20 wt%), non-toxicity and high solubility in water and stability in air at room temperature [4].

Here, we report to synthesize Eupergit C supported 4,4-methylenebis(2,6-diethyl)aniline-3,5-di-tert-butylsalicylaldehyde-Co complex as a catalyst for NaBH_4 Hydrolysis to H_2 generation. Eupergit C polymer supported Co complex catalyzed NaBH_4 hydrolysis reaction was researched based on different parameters and the kinetic data were studied. All results were shown that Eupergit C supported Co complex was highly active catalyst in NaBH_4 hydrolysis to H_2 generation.

Keywords: NaBH_4 , Co-Complex, Eupergit C, H_2 Production.

References

- [1] J. Graetz, Chem. Soc. Rev., 2009, 38, 73–82.
- [2] S. Niaz, T. Manzoor and A. H. Pandith, Renewable Sustainable Energy Rev., 2015, 50, 457–469.
- [3] W. Li, C. Li, H. Ma and J. Chen, J. Am. Chem. Soc., 2007, 129, 6710–6711.
- [4] B. Peng and J. Chen, Energy Environ. Sci., 2008, 1, 479–483.



AN OPTIMIZATION STUDY ON GAS ADSORPTION APPLICATION OF TOLUENE BY USING FORMALDEHYDE-TREATED PISTACHIO SHELLS

SİNAN KUTLUAY^a
^aSIIRT UNIVERSITY

kutluays2012@gmail.com

Abstract:

In this study, the use of formaldehyde-treated pistachio shells as a bioadsorbent for the adsorption of toluene in gas phase was investigated. In this context, parameters such as adsorption time, concentration of toluene in gas phase at the inlet and the adsorption temperature, which play a key role in the adsorption process, were optimized using Response Surface Method (RSM) based on Box-Behnken design. RSM is a combination of statistical and mathematical techniques used to model the relationships between output variables and several input variables. One of the major advantages of RSM based on Box-Behnken design is the ability to optimize multiple experimental parameters that have an impact on the process response by performing a small number of experimental studies. Adsorption time, concentration of toluene in gas phase at the inlet and the adsorption temperature were selected as independent variables and adsorption capacity was chosen as the dependent variable which was the response of the process. In the experimental design, RSM based on Box-Behnken design was successfully applied using ANOVA with > 95% confidence level ($p < 0.05$) to develop an approach to better understand the relationship between adsorption conditions and adsorption capacity in order to determine optimal process parameters. An empirical model was developed by RSM to estimate the output response. The maximum adsorption capacity was found to be as 59.99 mg/g, under the optimum process parameters such as adsorption time of 69.97 min, initial concentration of 9.10 ppm and temperature of 25.10°C

Keywords: Adsorption; Box-Behnken Experimental Design, RSM; Optimization; Pistachio Shells; Toluene.



APPLICATION OF RESPONSE SURFACE METHODOLOGY FOR MODELING OF GAS-PHASE ADSORPTION PROCESS OF BENZENE

SİNAN KUTLUAY^{a*}, ÖMER ŞAHİN^b, ORHAN BAYTAR^c

^aSIIRT UNIVERSITY

^bSIIRT UNIVERSITY

^cSIIRT UNIVERSITY

*kutluays2012@gmail.com

Abstract:

In recent years, volatile organic compounds have become a group of major pollutants that endanger human health and the ecological environment. This study presents the utilization of formaldehyde-treated pistachio shells as a bioadsorbent for the gas-phase adsorption of benzene which is one of the most important volatile organic compounds. In the study, the central composite design (CCD) approach-based response surface methodology (RSM) was applied to analyze, modeling and optimize the process parameters that play an important role in gas adsorption of benzene. In the study, adsorption time, gas-phase benzene initial concentration and temperature were selected as independent variables, adsorption capacity was selected as dependent variables that are the response of the process. One of the biggest advantages of the CCD approach-based RSM is that by performing a small number of experimental studies, it provides optimization of several experimental parameters that have an effect on the process response. The adsorption process carried out under atmospheric pressure was investigated using a continuous flow fixed-bed reactor system. In the experimental design, the CCD approach-based RSM was successfully applied using ANOVA with >95% confidence level ($p < 0.05$) to develop an approach to better understand the relationship between adsorption conditions and adsorption capacity in order to determine optimal process parameters. An empirical model was developed by RSM to estimate the output response. The maximum adsorption capacity was found to be as 82.19 mg/g, under the optimum process parameters such as adsorption time of 59.98 min, initial concentration of 11.99 ppm and temperature of 25.19°C

Keywords: Adsorption; Central composite design; Response surface methodology; Benzene; Modeling.



BOX-BEHNKEN RESPONSE SURFACE METHODOLOGY FOR OPTIMIZATION OF PROCESS PARAMETERS FOR GAS ADSORPTION OF TOLUENE ONTO Fe₃O₄ NANO-ADSORBENT

ÖMER ŞAHİN^{a*}, SİNAN KUTLUAY^b, MEHMET ŞAKİR ECE^c

^aSIIRT UNIVERSITY

^bSIIRT UNIVERSITY

^cMARDIN ARTUKLU UNIVERSITY

*omersahin@siirt.edu.tr

Abstract:

In the present study, we report the first use of magnetic Fe₃O₄ to be used as a new nano-adsorbent for gas-phase adsorption of toluene, one of the most important volatile organic compounds (VOCs). In recent years, VOCs have become a group of major pollutants that endanger human health and the ecological environment. The magnetic nano-adsorbent to be used in gas-phase adsorption of toluene was synthesized by co-precipitation and sol-gel method. The effects of adsorption time, concentration of toluene in gas phase at the inlet and the adsorption temperature on the adsorption capacity of toluene were optimized using the Box-Behnken experimental design approach-based Response Surface Method (RSM). RSM is a combination of statistical and mathematical techniques used to model the relationships between output variables and several input variables. Adsorption time, concentration of toluene in gas phase at the inlet and the adsorption temperature were selected as independent variables and adsorption capacity was chosen as the dependent variable which was the response of the process. In the experimental design, Box-Behnken experimental design approach-based RSM was successfully applied using ANOVA with > 95% confidence level (p<0.05) to develop an approach to better understand the relationship between adsorption conditions and adsorption capacity in order to determine optimal process parameters. An empirical model was developed by RSM to estimate the output response. The maximum adsorption capacity was found to be as 188.01 mg/g, under the optimum process parameters such as adsorption time of 49.28 min, initial concentration of 17.63 ppm and temperature of 25.47°C

Keywords: Adsorption; Box-Behnken Experimental Design, RSM; Magnetic Fe₃O₄ Nanoparticles; Optimization; Toluene.



SYNTHESIS OF SILICA-COATED MAGNETIC $\text{Fe}_3\text{O}_4@\text{SiO}_2$ NANOPARTICLES AS A NEW ADSORBENT AND ITS USE IN GAS-PHASE ADSORPTION OF BENZENE

ÖMER ŞAHİN^{a*}, MEHMET ŞAKİR ECE^b, SİNAN KUTLUAY^c

^aSIIRT UNIVERSITY

^bMARDIN ARTUKLU UNIVERSITY

^cSIIRT UNIVERSITY

*omersahin@siirt.edu.tr

Abstract:

In this study, silica-coated magnetic $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanoparticles were successfully synthesized and applied for the first time as a new high-efficiency nano-adsorbent for gas-phase adsorption of benzene which is one of the most important volatile organic compounds (VOCs). The magnetic nano-adsorbent used in gas-phase adsorption application of benzene was synthesized by co-precipitation and sol-gel method. Then, the effects of adsorption time, concentration of benzene in gas phase at the inlet and the adsorption temperature on adsorption capacity of benzene were studied by using the Box-Behnken experimental design approach-based Response Surface Method (RSM). The value of response variable, adsorption capacity, was determined from the experiments performed under design conditions. In the experimental design, the Box-Behnken experimental design approach-based RSM was successfully applied using ANOVA with > 95% confidence level ($p < 0.05$) to develop an approach to better understand the relationship between adsorption conditions and adsorption capacity in order to determine optimal process parameters. An empirical model was developed by RSM to estimate the output response. It was seen that the obtained quadratic model successfully represent the response variable. The results of analysis of variance (ANOVA) and response surface curves revealed that adsorption parameters were significantly effective on response variables. It has been shown that the response surface method can be successfully applied in the adsorption of gas-phase benzene. The maximum adsorption capacity was found to be as 197.50 mg/g, under the optimum process parameters such as adsorption time of 39.48 min, initial concentration of 14.21 ppm and temperature of 26.51°C. The results showed that magnetic $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanoparticles could be applied as a low cost adsorbent for gas-phase adsorption of benzene, one of the most important VOCs.

Keywords: Benzene; Box-Behnken experimental design, Gas-Phase Adsorption; RSM; Nanotechnology.



ACTIVATED CARBON SUPPORTED Fe₃O₄ NANOPARTICLES: A NOVEL ADSORBENT FOR GAS-PHASE ADSORPTION OF TOLUENE

MEHMET ŞAKİR ECE^{a*}, SİNAN KUTLUAY^b, ÖMER ŞAHİN^c

^aMARDIN ARTUKLU UNIVERSITY

^bSIIRT UNIVERSITY

^cSIIRT UNIVERSITY

*sakirece@gmail.com

Abstract:

In this study, we report the first application of activated carbon functionalized Fe₃O₄/AC to be used as a new nano-adsorbent for the gas-phase adsorption of toluene which is one of the most important volatile organic compounds (VOCs). In recent years, VOCs have become a group of major pollutants that endanger human health and the ecological environment. Magnetic nano-adsorbent used in gas-phase adsorption applications of toluene was synthesized by co-precipitation and sol-gel method. In this context, parameters such as adsorption time, concentration of toluene in gas phase at the inlet and the adsorption temperature, which play a key role in the adsorption process, were optimized using the central composite design (CCD) approach-based response surface methodology (RSM). RSM is a combination of statistical and mathematical techniques used to model the relationships between output variables and several input variables. Adsorption time, concentration of toluene in gas phase at the inlet and the adsorption temperature were selected as independent variables and adsorption capacity was chosen as the dependent variable which was the response of the process. In the experimental design, the CCD approach-based RSM was successfully applied using ANOVA with > 95% confidence level (p<0.05) to develop an approach to better understand the relationship between adsorption conditions and adsorption capacity in order to determine optimal process parameters.

Keywords: Adsorption; Central composite design, Nanotechnology; RSM; Fe₃O₄/AC; Toluene.



APPLICATION FOR GAS ADSORPTION OF BENZENE BY USING MAGNETIC $\text{Fe}_3\text{O}_4/\text{AC}@\text{SiO}_2@\text{EDTA}$ NANO-ADSORBENT

MEHMET ŞAKİR ECE^a

^aMARDIN ARTUKLU UNIVERSITY

sakirece@gmail.com

Abstract:

In recent years, nanotechnology has been the most effective technology that improves the core challenges of environmental researchers, improves/changes processes, and offers safer, cheaper and more convenient approaches to remove contaminants. This environmental study contributes to the existing benzene adsorption technology by providing a deeper perspective. In this study, nanotechnology was used for the adsorption of benzene which constitutes a vital risk. Although ethylenediamine tetraacetic acid (EDTA) was previously directly bound to Fe_3O_4 , this study also covered Fe_3O_4 , first with activated carbon, then with SiO_2 , then with EDTA, so that synthesis for benzene adsorption was very simple, adsorbent was synthesized, this synthesized nano magnetic adsorbent was applied successfully and efficiently in benzene adsorption. Magnetic nano-adsorbent used in gas-phase adsorption applications of benzene was synthesized by co-precipitation and sol-gel method. In this context, parameters such as adsorption time, concentration of benzene in gas phase at the inlet and the adsorption temperature, which play a key role in the adsorption process, were optimized using the central composite design (CCD) approach-based response surface methodology (RSM). In the experimental design, CCD approach-based RSM was successfully applied using ANOVA with >95% confidence level ($p < 0.05$) to develop an approach to better understand the relationship between adsorption conditions and adsorption capacity in order to determine optimal process parameters.

Keywords: Central composite design; Nanotechnology; Gas Adsorption; RSM; $\text{Fe}_3\text{O}_4/\text{AC}@\text{SiO}_2@\text{EDTA}$; Benzene.



WATER AND SEDIMENT QUALITY ASSESSMENT OF MERIÇ RIVER BASIN: PSYCOCHEMICALS AND TOXIC METALS

CEM TOKATLI^a, İPEK ATILGAN HELVACIOĞLU^{b*},

^aTRAKYA UNIVERCITY, IPSALA VOCATIONAL SCHOOL, DEPARTMENT OF
LABORATORY TECHNOLOGY, TURKEY

^bTRAKYA UNIVERCITY, IPSALA VOCATIONAL SCHOOL, DEPARTMENT OF
LABORATORY TECHNOLOGY, TURKEY

*ipekhelvacioğlu@gmail.com

Abstract:

Meriç River is the longest river of Balkans and has a vital importance for Thrace Region, where is located on north – west side of Marmara Region of Turkey. But as many aquatic ecosystems, it is known to be exposed to an intensive organic – inorganic pollution by means of agricultural and industrial applications conducted on its watershed. The aim of this investigation was to evaluate the water – sediment quality of Meriç River Basin by investigating some psychochemicals and toxic metals. Water and sediment samples were collected in spring season of 2017 from 14 stations (7 stations on the Meriç River, 3 stations on the Ergene River, 2 stations on the Tunca River and 2 stations on the Sazlıdere Stream) selected on the basin. Total of 19 water quality parameters including temperature, dissolved oxygen, % oxygen saturation, pH, EC, TDS, salinity, turbidity, nitrate, nitrite, ammonium, phosphate, sulphate, fluoride, chloride, ORP, COD, BOD and fecal coliform were investigated in water samples and also total of 9 inorganic pollution parameters including Cd, Pb, As, B, Cu, Zn, Cr, Ni and Se were investigated in water and sediment samples. According to detected data, contamination levels of the investigated aquatic habitats as follows; Ergene River >Meriç River >Tunca River in general. It was also determined that phosphate, biological oxygen demand and fecal coliform parameters were recorded as the most critical parameters on the water quality of the basin, and chromium and nickel were recorded as the most critical parameters on the sediment quality of the basin.

Keywords: Meriç River Basin, Water quality, Sediment quality, Psychochemicals, Toxic Metals

Acknowledgement

This investigation has been supported by the project numbered as 2016/247 accepted by Trakya University, Commission of Scientific Research Projects.



WATER AND SEDIMENT QUALITY ASSESSMENT OF MERIÇ RIVER BASIN: PESTICIDES

CEM TOKATLI^a, İPEK ATILGAN HELVACIOGLU^{b*},

^aTRAKYA UNIVERCITY, IPSALA VOCATIONAL SCHOOL, DEPARTMENT OF
LABORATORY TECHNOLOGY, TURKEY

^bTRAKYA UNIVERCITY, IPSALA VOCATIONAL SCHOOL, DEPARTMENT OF
LABORATORY TECHNOLOGY, TURKEY

*ipekhelvacioğlu@gmail.com

Abstract:

Rapid growth of world population, development of industry and unconscious agricultural activities are significant pressure factors on the environment. Pesticides can be accumulated in water and sediments and can be reached to the fishes, birds and human by means of bio – magnification. Therefore pesticide contamination especially around the rural areas threatens not only the aquatic life but also the health of local people. Meriç River Basin is the most important aquatic habitat of Thrace Region of Turkey and exposed to an intensive pollution by means of especially agricultural applications conducted around its watershed. The aim of this study was to evaluate the pesticide contamination in water and sediment of Meriç River Basin by determining a total of 174 different pesticide varieties in water and sediment samples. For this purpose, water – sediment samples were collected in spring season of 2017 from 14 stations (7 stations on the Meriç River, 3 stations on the Ergene River, 2 stations on the Tunca River and 2 stations on the Sazlıdere Stream) selected on the basin and pesticide contents were investigated. According to data observed, pesticide concentrations detected in the Meriç River Basin were found to be in quite high levels and the system has III. – IV. Class water quality in terms of total pesticide accumulations in general. It was also determined that Ergene River was found to be the most polluted ecosystem among the investigated components of Meriç River Basin and carbendazim was found to be the most widely used pesticide variety in the region.

Keywords: Meriç River Basin, Water quality, Sediment quality, Pesticides

Acknowledgement

This investigation has been supported by the project numbered as 2016/247 accepted by Trakya University, Commission of Scientific Research Projects.



HYDROLYSIS OF AMMONIA BORANE IN THE PRESENCE OF RU BASED MAGNETIC NANO CATALYST

MEHMET SAIT IZGI^{a*}, ERHAN ONAT^b, ŞAKIR ECE^c

^aSIIRT UNIVERSITY

^bSIIRT UNIVERSITY

^cMARDIN ARTUKLU UNIVERSITY

*saitizgi@gmail.com

Abstract:

In this work; Ru-based Magnetic Nano catalyst complex catalyst synthesized and was tested for hydrogen production from alkaline ammonia borane (AB) via hydrolysis process. A high-density and low-cost hydrogen generation technology is required for the energy system. Catalytic activity of the Fe₃O₄/AC@SiO₂@/Ru catalyst were investigated on the basis NaOH concentration, amount of catalyst, NH₃BH₃ concentration (1mmol-2mmol) and temperature effect 30 oC-60oC). Hydrogen generation rate (HGR) and Ea were obtained 30 oC as 8794 mLmin⁻¹g⁻¹(30 oC, %1 NaOH, 1 mmol NH₃BH₃, 5 mg catalyst).

In this work; Ru-based Magnetic Nano catalyst complex catalyst synthesized and was tested for hydrogen production from alkaline ammonia borane (AB) via hydrolysis process. A high-density and low-cost hydrogen generation technology is required for the energy system. Catalytic activity of the Fe₃O₄/AC@SiO₂@/Ru catalyst were investigated on the basis NaOH concentration, amount of catalyst, NH₃BH₃ concentration (1mmol-2mmol) and temperature effect 30 oC-60oC). Hydrogen generation rate (HGR) and Ea were obtained 30 oC as 8794 mLmin⁻¹g⁻¹(30 oC, %1 NaOH, 1 mmol NH₃BH₃, 5 mg catalyst).

In this work; Ru-based Magnetic Nano catalyst complex catalyst synthesized and was tested for hydrogen production from alkaline ammonia borane (AB) via hydrolysis process. A high-density and low-cost hydrogen generation technology is required for the energy system. Catalytic activity of the Fe₃O₄/AC@SiO₂@/Ru catalyst were investigated on the basis NaOH concentration, amount of catalyst, NH₃BH₃ concentration (1mmol-2mmol) and temperature effect 30 oC-60oC). Hydrogen generation rate (HGR) and Ea were obtained 30 oC as 8794 mLmin⁻¹g⁻¹(30 oC, %1 NaOH, 1 mmol NH₃BH₃, 5 mg catalyst).

Keywords: Magnetic Nano Catalyst, NH₃BH₃, Hydrolysis, Ru



INVESTIGATION OF MALACHITE GREEN ADSORPTION WITH RESPONSE SURFACE METHOD

ORHANBAYTAR^{a*}, ÖMER ŞAHİN^b, SİNAN KUTLUAY^c

^aSIIRT UNIVERSITY

^bSIIRT UNIVERSITY

^cSIIRT UNIVERSITY

*baytarorhan@gmail.com

Abstract:

In this study; adsorption of malachite green was investigated by using color immobilized walnut shell with formaldehyde. Adsorption of malachite green was investigated by experimental design method. Experimental design was carried out with Box-Behnken model in Response Surface Method. Adsorption capacity (q_e) was chosen as the response parameter. In the experimental design, the effect of solution initial concentration, temperature and time parameters were investigated. In the analysis of malachite green adsorption with experimental design, ANOVA table and regression equation were determined. Adsorption of malachite green is represented by a quadratic model. According to ANOVA table created with quadratic model, the value of the model was found to be less than 0.05 and F value was greater than 4 and the selected model was found to be suitable. It was determined from the ANOVA table that the p value of the solution initial concentration and temperature parameters were very small and hence the most effective parameters. According to ANOVA table, it was determined that single parameters were more effective than binary parameters. According to the ANOVA table, the p value of Lack of Fit was found to be high and this model shows that the selected model is suitable. According to the quadratic model, R^2 adjusted = 0,9713 and R^2 prediction = 0,8493, and this result shows that the experiments performed are consistent with the predicted experiments. Two- and three-dimensional graphs of Malachite green adsorption were drawn. Malachite green adsorption was optimized with experimental design and conditions were determined

Keywords: Malachite Green, Adsorption, Experimental Design, ANOVA



INVESTIGATION OF THE EFFECTS OF VARIOUS IMPURITIES ON NUCLEIC FORMATION AND GROWTH OF BORIC ACID IN STATIONARY MEDIUM OF SINGLE CRYSTAL SYSTEM

HALIL DEMIR^{a*}, ÖMER ŞAHİN^b, FESİH ATKU^c

^aSIIRT UNIVERSITY

^bSIIRT UNIVERSITY

^cSIIRT UNIVERSITY

*halildemir@siirt.edu.tr

Abstract:

The production of boron salts is generally carried out in two stages. The first of step is nuaculation and the second is crystal growth. In this study, the effects of various impurities on the crystal habit and particle size distribution of boric acid were investigated to determine optimum conditions during the production of boron compounds from raw materials.

MSMPR (mixed suspension mixed product removal) type crystallizers are the most widely used in the industry. However, in the case of many parameters to be examined from such systems, some of these parameters can be eliminated in the single crystal system (the effect of various factors on habit change) and some in the fluidized bed system (such as the effect of hydrodynamic conditions and various impurities).

In this study, it has been tried to determine the change of habit structures of the crystals formed in the supersaturated solution of boric acid solutions prepared at different temperatures by using pure boric acid crystals under microscope and in the presence of various impurities.

As a result, boric acid crystals in pure solutions and in the presence of various impurities such as Ca, sulfuric acid and Mg, the growth of single crystals put in the solution medium before nuclei formation was found to be dendritic structure and dentrites were weaker than those formed with nuclei. When a certain supersaturation value is exceeded it is determined that new nuclei are formed in the solution instead of collapsing on the single crystal in the supersaturated medium. Another result obtained in the quiescent single crystal system is that the dendrites formed in the presence of magnesium impurity are less and weaker than those formed in the presence of calcium and sulfuric acid impurities.

Keywords: Boric Acid, Crystallization, Supersaturation, Single Crystal, Impurities

**This work was supported by ETI MADEN with the project number 400.02.(TGD.2014/3)*



INVESTIGATION OF THE EFFECTS OF VARIOUS IMPURITIES ON NUCLEIC FORMATION AND GROWTH OF BORAX PENTAHYDRATE IN STATIONARY MEDIUM OF SINGLE CRYSTAL SYSTEM

HALIL DEMIR^{a*}, ÖMER ŞAHİN^b, FESİH ATKU^c

^aSIIRT UNIVERSITY

^bSIIRT UNIV.

^cSIIRT UNIVERSITY

*halildemir@siirt.edu.tr

Abstract:

Technical properties expected from a product obtained by crystallization technique in chemical technology; is the production of highly pure, suitable sized, homogeneous and smooth outer appearance crystals. The production of crystals of suitable size and homogeneous structure is possible by knowing the growth kinetics and the conditions under which the nucleation of the crystallized material will occur.

In this study, it has been tried to determine the change of habit structures of the crystals formed in the supersaturated solution of borax pentahydrate solutions prepared at different temperatures by using pure borax pentahydrate crystals under microscope and in the presence of various impurities. The growing single crystals of borax pentahydrate is observed in the presence of different supersaturation solution in a stationary medium single crystal system; It was observed that the crystals were grown in uniform structure, no dendritic structures were formed, but a large number of nuclei formed into the solution medium with increasing saturation. In the presence of various impurities, dendritic structures were formed and they are weaker and when a certain supersaturation value is exceeded it is determined that new nuclei are formed in the solution instead of collapsing on the single crystal in the supersaturated medium. Another result obtained in the quiescent single crystal system is that the dendrites formed in the presence of magnesium impurity are less and weaker than those formed in the presence of calcium and sulfuric acid impurities.

When the linear growth rates of single crystals placed in different supersaturated solution media in constant medium single crystal system were examined due to the variation of the supersaturation, borax pentahydrate crystals showed dispersion at growth rates.

Keywords: Borax, Crystallization, Supersaturation, Single Crystal, Impurities

**This work was supported by ETI MADEN with the project number 400.02.(TGD.2014/3).*



CONDUCTIVE POLYMERIC FILM PRODUCTION FOR CONTROLLED DRUG RELEASE APPLICATIONS

DİDEM AYCAN^{a*}, NESLİHAN ALEMDAR^b

^aMARMARA UNIVERSITY

^bMARMARA UNIVERSITY

*didem.aycan@marmara.edu.tr

Abstract:

Electrically conductive polymers are promising class of multifunctional materials. Therefore, researchers have been showing increasing interest them in the field of electrochromic devices, organic photovoltaics, biomedical and tissue engineering applications. Moreover, the conductive nature of these type of polymers can regulate cellular activities including promoting cell adhesion, proliferation, migration and differentiation of electrically stimulated cells. Poly (3, 4-ethyleendioxythiophene) (PEDOT) is one of the best candidate especially for biomedical applications owing to its enhanced biocompatibility, good electrical conductivity and long-term oxidative and chemical stability.

This study aims to fabricate polymeric films by using different amount of gelatin (Gel), sodium alginate (SA), and hyaluronic acid (HyA) with conductive properties for controlled drug release applications. The conductive nature was provided to polymeric films through incorporation of PEDOT: PSS (Poly (3, 4-ethyleendioxythiophene) poly (styrene sulfonate)). Fourier transform infrared spectroscopy (FT-IR) was used to identify chemical structure of the composite films. Swelling capacity of the films were tested via water uptake measurements gravimetrically. The electrical conductivity of the composite films were measured using the four-point probe technique. The conductive polymeric films were loaded with an antibiotic drug and in vitro drug release of the composite films was investigated to observe the potentially applicability of the films as drug carrier.

All results demonstrated that conductive polymeric films were fabricated successfully. Furthermore, results of in vitro drug release studies showed that obtained PEDOT: PSS-based composite films are very promising materials to be employed as drug carriers for controlled release applications.

Keywords: Biopolymer, Conductive Film, PEDOT:PSS, Controlled Release



THE ADSORPTION OF METHYLENE BLUE BY RESPONSE SURFACE METHOD

ORHANBAYTAR^{a*}, SINAN KUTLUAY^b

^aSIIRT UNIVERSITY

^bSIIRT UNIVERSITY

*baytarorhan@gmail.com

Abstract:

Water pollution increases with increasing technology. Water pollution is cleaned by many methods. These include advantages of easy and convenient photocatalytic application. In this study; adsorption of methylene blue was investigated by using color immobilized walnut shell with formaldehyde. Adsorption of methylene blue was investigated by experimental design method. Experimental design was carried out with Box-Behnken model in Response Surface Method. Adsorption capacity (q_e) was chosen as the response parameter. In the experimental design, the effect of solution initial concentration, temperature and time parameters were investigated. In the analysis of methylene blue adsorption with experimental design, ANOVA table and regression equation were determined. Adsorption of methylene blue is represented by a quadratic model. According to ANOVA table created with quadratic model, the value of the model was found to be less than 0.05 and F value was greater than 4 and the selected model was found to be suitable. It was determined from the ANOVA table that the p value of the solution initial concentration and temperature parameters were very small and hence the most effective parameters. According to ANOVA table, it was determined that single parameters were more effective than binary parameters. According to the ANOVA table, the p value of Lack of Fit was found to be high and this model shows that the selected model is suitable. According to the quadratic model, R^2 adjusted = 0,9790 and R^2 prediction = 0,8877, and this result shows that the experiments performed are consistent with the predicted experiments. Two- and three-dimensional graphs of methylene blue adsorption were drawn. Adsorption of methylene blue was optimized with experimental design and conditions were determined.

Keywords: Methylene Blue, Adsorption, Experimental Design, ANOVA



ANALYSES ON ELECTROCHEMICAL PROPERTIES OF NiO₂ SUPERCAPACITOR ELECTRODES

ÖZLEM BUDAK^{a*}, ATIF KOCA^b

^aCHEMICAL ENGINEERING PROGRAM, CHEMICAL ENGINEERING DEPARTMENT, ENGINEERING FACULTY, MARMARA UNIVERSITY

^bCHEMICAL ENGINEERING PROGRAM, CHEMICAL ENGINEERING DEPARTMENT, ENGINEERING FACULTY, MARMARA UNIVERSITY

*ozlem.budak@marmara.edu.tr

Abstract:

In recent years, energy need generally is met from the fossil fuels. But, when these fossil fuels are used, the biggest problem is global warming which is harmful for environment and living life due to the gas emissions such as carbon dioxide (CO₂) and carbon monoxide (CO). Accordingly to solve this problem, scientists attach importance to both reversible and sustainable energy and also energy conversion and storage applications all around the world. Batteries and supercapacitors are the devices for storage the electrical energy. Electrical energy storage mechanism is based on the electrochemical processes for both of these storage devices. Supercapacitors which are known as electrochemical capacitors have advantages when there is a need for urgent power and fast charge. With high power density, fast charge/discharge periods and high specific capacitances and long life service, supercapacitors are superior than the batteries for the energy storage applications. Here, supercapacitor working electrodes which were composed of the transition metal oxides, synthesised by using hydrothermal method, such as Ni and Co, were prepared. As working electrodes, the prepared electrodes were tested in a three-electrode system (counter electrode: Pt wire, reference electrode: standard calomel electrode) to get information about their electrochemical properties. CV (Cyclic Voltammetry), EIS (Electrochemical Impedance Spectroscopy) ve CDC (Charge/Discharge Capacity) measurements were examined and all the results which were obtained from the mentioned tests showed that the prepared electrodes could be used for production of a supercapacitor successfully.

Keywords: Hydrothermal Method, Supercapacitor, Transition Metal Oxides



PHOTOELECTROCHEMICAL ACTIVITY OF ELECTRODEPOSITED CDXZN1-XS PHOTOELECTRODES UNDER SOLAR LIGHT IRRADIATION

ÖZLEM UĞUZ^{a*}, ATIF KOCA^b

^aCHEMICAL ENGINEERING PROGRAMME, DEPARTMENT OF CHEMICAL ENGINEERING, ENGINEERING FACULTY, MARMARA UNIVERSITY

^bCHEMICAL ENGINEERING PROGRAMME, DEPARTMENT OF CHEMICAL ENGINEERING, ENGINEERING FACULTY, MARMARA UNIVERSITY

*ozlem.uguz@marmara.edu.tr

Abstract:

Due to the exponentially increasing population and the need for rising standards of living, scientists have been seeking for the alternative ways of clean and reliable energy resources [1]. In this concern, photoelectrochemical hydrogen production method is one of the most promising approaches and there have been many efforts to make it a more applicable and cost-effective energy production method. Using metal chalcogenides to construct photoanodes to be utilized in photoelectrochemical hydrogen production studies are one of the good options to increase the photoelectrochemical performance of photoanodes.

In this study, $Cd_xZn_{1-x}S$ ($x=0.0, 0.5, 1.0$) photoanodes were prepared by electrodeposition method using repetitive cyclic voltammetry. To do this, a three-electrode system was prepared (Counter electrode: Pt wire, reference electrode: Ag/AgCl electrode, working electrode: ITO) after adding the required amounts of Cd, Zn and S precursor solutions, which were $CdSO_4$, $ZnSO_4$ and $Na_2S_2O_3 \cdot 5H_2O$ solutions, respectively. After applying appropriate voltage interval for coating of $Cd_xZn_{1-x}S$ composites onto ITO, constructed photoanodes were cleaned with distilled water and left to dry in ambient atmosphere. Subsequently, photoelectrochemical performance studies of the photoanodes were carried out in the presence of sacrificial agent (Na_2S/Na_2SO_3 solution) under the illumination of the sunlight (intensity: 1000 W/cm^2) which was supplied by Solar Simulator AM1.5G. Photoelectrochemical activity analysis results by using open circuit potential (OCP), linear sweep voltammetry (LSV), and chronoamperometry (CA) techniques revealed the effect of the adjusted ratios of CdS and ZnS in the composites on the photoelectrochemical performance of constructed electrodes.

References

[1] Acar, C. and Dincer, I. (2019). Investigation of a novel photoelectrochemical hydrogen production system, *Chem.Eng.Sci.*, vol.197, pp.74-86.

Keywords: Photoelectrochemical Performance; Electrodeposition; Repetitive Cyclic Voltammetry.



DFT STUDY ON THE RING-OPENING OF CYCLOPROPYLIDENOID TO ALLENE INCORPORATED INTO SEVEN-MEMBERED RING

AKIN AZIZOGLU^a

^aBALIKESIR UNIVERSITY

azizoglu@balikesir.edu.tr

Abstract

The ring-opening of lithiumbromo bicyclo[4.1.0]hept-7-ylidenoid to the related allene structure was examined with the density functional methods. The activation barrier energies for intramolecular CH-insertions to yield highly strained molecules, tricyclo[4.1.0.02,7]-heptane and tricyclo[4.1.0.03,7]heptane, were also calculated at the B3LYP/6-31+(d,p) level.

Keywords: carbene, cyclopropylidene, allene, DFT

1. INTRODUCTION

Allenes are the simplest class of cumulenes, with two contiguous C=C bonds, and show unique physical and chemical properties. For the past decades, the synthesis of allenes has attracted increasing interest because of allowing chemists to access a variety of structurally interesting and biologically active products [1-8]. From among the numerous synthetic approaches to the allenes, Doering-Moore-Skattebol method and β -elimination method are most widely studied in the literature. β -elimination method includes an **HX** (**X=F, Cl, Br**) elimination step from an organic molecule with help of a strong base in order to synthesize an allene unit. There are many scientific work related with β -elimination in the literature [9-11]. First step of the Doering-Moore-Skattebol reaction, dihalocarbene unit, which is produced by α -elimination method, added to double bond to obtain *gem*-dihalocyclopropane. In the second step, *gem*-dihalocyclopropane is treated with alkyllithium in order to produce desired allene unit. Before the formation of allene, the lithium-halogen exchange reaction of 1,1-dibromocyclopropane with methyl lithium affords 1-halo-1-lithiocyclopropane. The question is that how the elimination of LiX occurs or what happens in the second step of the reaction. Now we wish to present our preliminary results of theoretical calculations about the effects of ring size and substituents (**X: -CH₃ and -OCH₃**) on the ring-opening of cyclopropylidene *via* concerted or stepwise mechanism (Figure 1).

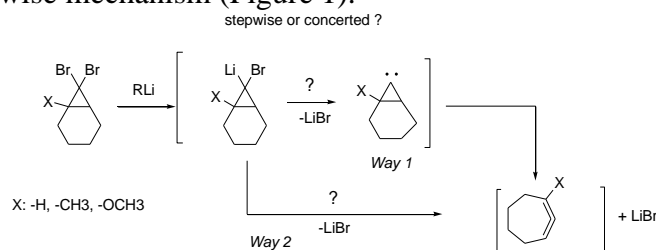


Figure 1. Purpose of work



2. COMPUTATIONAL METHODOLOGY

The GAUSSIAN 03 program was used for density functional theory calculations, employing Becke's three-hybrid method and the exchange functional of Lee, Yang, Parr (B3LYP) [12]. The geometry optimizations of all the structures were achieved at the B3LYP/6-31+G(d) level. Energies were refined by using B3LYP/6-31+G(d) single-point evaluations. Stationary points were characterized as minima or transition structures by way of an analytic evaluation of harmonic vibrational frequencies at the level of geometry optimization.

3. RESULTS AND DISCUSSION

The Doering-Moore-Skattebol reaction is the most efficient for the generation of 1,2-cyclohexadiene [1], but this method was not successful for the synthesis of 1,2-cycloheptadiene [2,3]. Hence, Schleyer et al. investigated the ring opening of bicyclo[4.1.0]hept-7-ylidene by using density functional theory computations at the B3LYP/DZP and TZP levels [4]. The half-chair conformation of the cyclohexane moiety in bicyclo[4.1.0]hept-7-ylidene must change to a chair conformation during the ring-opening reaction.

The activation barrier energies for intramolecular CH-insertions to yield highly strained molecules, tricyclo[4.1.0.02,7]-heptane and tricyclo[4.1.0.03,7]heptane, were also calculated at the B3LYP/6-31+(d,p) level. For the ring-opening reactions of lithium bromocyclopropylidenoids to allenes, two pathways can also be considered: the reaction may either proceed stepwise with the intermediacy of a free cyclopropylidene or in a concerted fashion.

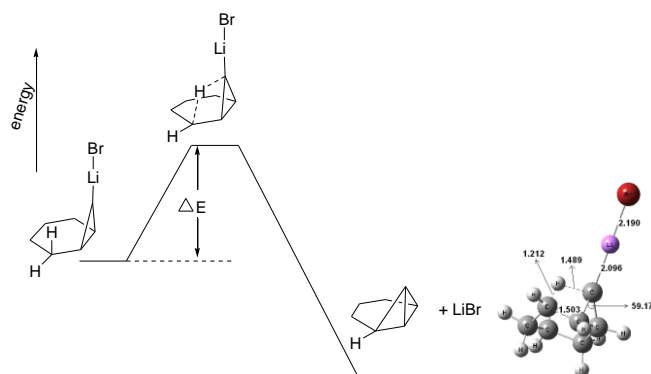


Figure 2. CH-insertion for X: H

The computed activation energy barriers of stepwise mechanism for CH-insertion is found to be 13.3 kcal/mol (Figure 2). The ring-openings of bicyclo[4.1.0]hept-7-ylidene can proceed in a stepwise fashion, and its energy barrier is calculated to be 21.9 kcal/mol.

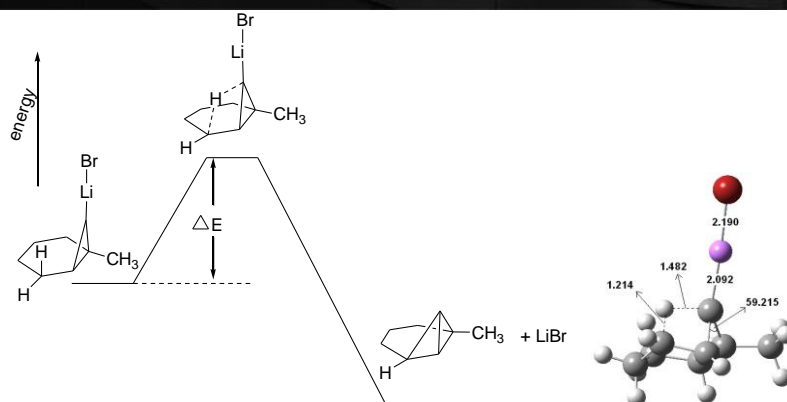


Figure 3. CH-insertion for X: CH₃

The computed activation energy barriers of *stepwise mechanism* for CH-insertion is found to be 11.6 kcal/mol (Figure 3). The ring-openings of methyl substituted bicyclo[4.1.0]hept-7-ylidene can proceed in a *stepwise fashion*, and its energy barrier is calculated to be 13.9 kcal/mol.

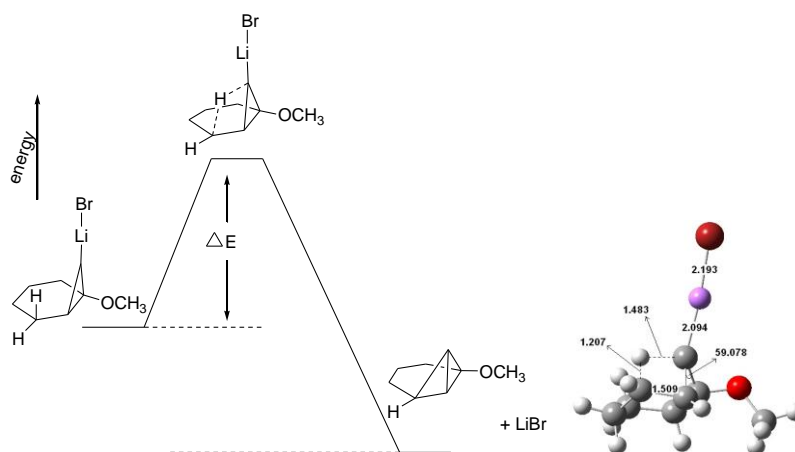


Figure 4. CH-insertion for X: OCH₃

The computed activation energy barriers of *stepwise mechanism* for CH-insertion is found to be 17.7 kcal/mol (Figure 4). The ring-openings of methyl substituted bicyclo[4.1.0]hept-7-ylidene can proceed in a *concerted fashion*, and its energy barrier is calculated to be 13.7 kcal/mol. In other words, the ring-opening of for X: -OCH₃ substituted cyclopropylidene can be proceed in stepwise mechanism with low activation energy (13.9 kcal/mol).

In conclusion, the stepwise process does not play obviously a role in the Doering-Moore-Skattebøl allene rearrangement for X: -OCH₃.

ACKNOWLEDGMENT

This work was supported by Balikesir University Research Grant No.: 2018-175.



REFERENCES

- [1]. W. R. Moore and W.R. Moser, *J. Am. Chem. Soc.*, Vol. 92, pp. 5469- 5474, 1970.
- [2]. W. R. Moore and H. R. Ward,; Merritt, R. F. *J. Am. Chem. Soc.*, vol. 83, pp. 2019-2020, 1961.
- [3]. L. A. Paquette and R. T. Taylor, *J. Am. Chem. Soc.*, vol. 99, pp. 5708- 5715, 1977.
- [4]. H. F. Bettinger; P. v. R Schleyer and P.R. Schreiner.; Schaefer, H. F, III *J. Org. Chem.*, vol. 62, pp. 9267-9275, 1997.
- [5]. F. Algi, R. Ozen, and M. Balci, *Tetrahedron Lett.*, vol. 43, pp. 3129-3131, 2002.
- [6]. M. Christl., G. Stefan, and K. Günther, *Angew. Chem. Int. Ed.*, vol. 39, pp. 3261-3263, 2000.
- [7]. A. Azizoglu,, M. Balci, J. L. Mieusset, U.H. Brinker, *J. Org. Chem.* vol. 73, pp. 8182–8188, 2008.
- [8]. T. Mahlokozera,, J.B. Goods, A.M. Childs, D.M. Thamattoor,, *Org. Lett.* vol. 11, pp. 5095–5097, 2009.
- [9]. A. E. Favorskii, *J. Gen. Chem. USSR* (Eng. Transl.) vol 6, pp. 720, 1936.
- [10]. B. Kılbaş, A. Azizoglu ve M. Balcı*, *Helvetica Chimica Acta*, vol: 89, pp. 1449-1456, 2006.
- [11]. M. Christl, S. Groetsch, *Eur. J. Org. Chem.* vol. 2000, pp. 1871, 2000.
- [12]. M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03. Revision C02, Gaussian, Inc., Pittsburgh, PA. 2003.



DFT INVESTIGATION OF HALOGENATED SUMANENES

AKIN AZIZOGLU^{a*}, DUYGU EMIR^b

^aBALIKESIR UNIVERSITY

^bBALIKESIR UNIVERSITY

*azizoglu@balikesir.edu.tr

Abstract

Sumanene structures were prepared by replacing H atoms of sumanene with F, Cl and Br atoms. Trigermasumanene structure was also formed by replacing three benzylic carbon atoms with three Ge atoms. The geometry optimizations of these new compounds were performed with density frnctional methods and ab-initio methods. The lowest bowl-to-bowl inversion energy value for sumanene was calculated as 16.4 kcal/mol at the B3LYP/6-31G(d,p), and the highest one was 18.9 kcal/mol at the HF/6-31+G(d,p)..

Keywords: sumanene, DFT, ab-initio

1. INTRODUCTION

Chemistry of nonplanar π -conjugated carbon molecules has received considerable attention in recent years due to their unique physical, chemical and assembling features [1,2]. They display unique properties such as bowl-to-bowl inversion, bowl chirality, electron conductivity, columnar packing structure in the solid state [3].

Sumanene ($C_{22}H_{12}$, C_{3v}) is mainly derived from fullerene (C_{60}), consisting of alternating benzene rings and cyclopentadiene rings around the central benzene rings [4]. It can be defined as a piece of buckminsterfullerene with 21 carbon atoms and it poses both concave and convex π -surfaces with all vacant valences terminated by hydrogen [5].

The bowl-to-bowl inversion is the character of some π -bowls. Reported value of bowl-to-bowl inversion barrier for the sumanene is 16.9 kcal/mol employing B3LYP/cc-pVTZ//B3LYP/ccpVDZ level of theory [6]. And the experimental value of bowl-to-bowl inversion barrier is 20 kcal/mol [7].

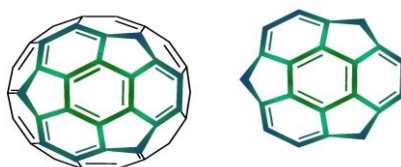


Figure 1. Fullerene and sumanene molecules.

2. COMPUTATIONAL METHODOLOGY

The GAUSSIAN 03 program was used for thoeretical calculations [8]. The geometry optimizations of all the structures were achieved at at B3LYP/6-31G(d), B3LYP/6-



31+G(d,p), X3LYP/6-31G(d), and X3LYP/6-31+G(d,p) level of theories.. Stationary points were characterized as minima or transition structures by way of an analytic evaluation of harmonic vibrational frequencies at the level of geometry optimization.

3. RESULTS AND DISCUSSION

In the first part of the study geometric parameters were calculated at the related levels. $\Delta 1$ and $\Delta 2$ are bond alternation of “hub” and “flank” benzene ring of halogenated sumanene, respectively.

$$\Delta 1 = \text{“rim”} - \text{“hub6”} \quad (1)$$

$$\Delta 2 = \text{“hub5”} - \text{“hub6”} \quad (2)$$

Bond alternations in the hub benzene ring ($\Delta 1$) and flank benzene ring of halogenated sumanene compounds obtained by replacing H atom with F, Cl and Br atoms were given in Table 1, Table 2 and Table 3, respectively.

Table 1. Bond alternations in the hub benzene ring ($\Delta 1$) and flank benzene ring ($\Delta 2$) of halogenated (F) sumanene at various level of theory (\AA)

Level	1Fa		1Fb1		1Fb2		2Fa		2Fb		12F	
	$\Delta 1$	$\Delta 2$	$\Delta 1$	$\Delta 2$	$\Delta 1$	$\Delta 2$	$\Delta 1$	$\Delta 2$	$\Delta 1$	$\Delta 2$	$\Delta 1$	$\Delta 2$
B3LYP 6-31G(d)	0.046	0.039	0.052	0.047	0.052	0.047	0.047	0.047	0.056	0.048	0.057	0.057
B3LYP 6-31+G(d,p)	0.046	0.037	0.051	0.047	0.053	0.048	0.047	0.045	0.055	0.048	0.056	0.059
X3LYP 6-31G(d)	0.047	0.039	0.052	0.047	0.053	0.047	0.048	0.047	0.056	0.048	0.057	0.057
X3LYP 6-31+G(d,p)	0.046	0.037	0.051	0.048	0.053	0.048	0.047	0.044	0.055	0.048	0.056	0.058

Table 2. Bond alternations in the hub benzene ring ($\Delta 1$) and flank benzene ring ($\Delta 2$) of halogenated (F) sumanene at various level of theory (\AA)

Level	1Cla		1Clb1		1Clb2		2Cla		2Clb		12Cl	
	$\Delta 1$	$\Delta 2$	$\Delta 1$	$\Delta 2$	$\Delta 1$	$\Delta 2$	$\Delta 1$	$\Delta 2$	$\Delta 1$	$\Delta 2$	$\Delta 1$	$\Delta 2$
B3LYP 6-31G(d)	0.047	0.045	0.048	0.046	0.050	0.047	0.048	0.057	0.050	0.047	0.048	0.071
B3LYP 6-31+G(d,p)	0.046	0.045	0.048	0.046	0.050	0.047	0.048	0.056	0.050	0.047	0.048	0.071
X3LYP 6-31G(d)	0.047	0.045	0.048	0.046	0.051	0.046	0.048	0.057	0.051	0.047	0.049	0.070
X3LYP 6-31+G(d,p)	0.047	0.045	0.048	0.046	0.050	0.047	0.048	0.056	0.050	0.047	0.049	0.070

Table 3. Bond alternations in the hub benzene ring ($\Delta 1$) and flank benzene ring ($\Delta 2$) of halogenated (F) sumanene at various level of theory (\AA)

Level	1Bra		1Brb1		1Brb2		2Bra		2Brb		12Br	
	$\Delta 1$	$\Delta 2$	$\Delta 1$	$\Delta 2$	$\Delta 1$	$\Delta 2$	$\Delta 1$	$\Delta 2$	$\Delta 1$	$\Delta 2$	$\Delta 1$	$\Delta 2$
B3LYP 6-31G(d)	0.046	0.044	0.048	0.046	0.049	0.046	0.048	0.053	0.050	0.046	0.047	0.060
B3LYP 6-31+G(d,p)	0.047	0.044	0.048	0.046	0.049	0.047	0.047	0.052	0.050	0.047	0.046	0.066
X3LYP 6-31G(d)	0.047	0.044	0.049	0.046	0.049	0.046	0.048	0.053	0.051	0.046	0.047	0.060
X3LYP 6-31+G(d,p)	0.047	0.044	0.048	0.046	0.050	0.048	0.048	0.052	0.050	0.047	0.047	0.065

In the next part of the study, bowl depth was estimated for each molecule at same level of theory. Bowl depth is the interplanar distance between the two planes formed by “hub” and the “rim” carbon atoms. Bowl depth exhibited fluctuations as a function of theory level. Close bowl depth values were obtained for 1Cla, 1Clb1, 1Clb2, 2Cla and 2Clb, while 12F compound showed significantly the lowest bowl depth values at all theory levels. For halogenated sumanene obtained by replacing H atoms with Br atoms, the bowl depth exhibited similar fluctuations as a function of theory level.



Table 4. Bowl Depth (BD) of halogenated (F) sumanene at various level of theory

Level	BD (Å)					
	1Fa	1Fb1	1Fb2	2Fa	2Fb	12F
B3LYP 6-31G(d)	1.106	1.144	1.154	1.117	1.155	1.152
B3LYP 6-31+G(d,p)	1.115	1.154	1.162	1.119	1.162	1.133
X3LYP 6-31G(d)	1.112	1.154	1.156	1.117	1.157	1.164
X3LYP 6-31+G(d,p)	1.116	1.155	1.179	1.121	1.168	1.140

Table 5. Bowl Depth (BD) of halogenated (Cl) sumanene at various level of theory

Level	BD (Å)					
	1Cla	1Clb1	1Clb2	2Cla	2Clb	12Cl
B3LYP 6-31G(d)	1.105	1.131	1.123	1.099	1.143	0.920
B3LYP 6-31+G(d,p)	1.118	1.140	1.126	1.101	1.147	0.922
X3LYP 6-31G(d)	1.107	1.133	1.124	1.100	1.147	0.925
X3LYP 6-31+G(d,p)	1.120	1.143	1.132	1.102	1.154	0.930

Table 6. Bowl Depth (BD) of halogenated (Cl) sumanene at various level of theory

Level	BD (Å)					
	1Bra	1Brb1	1Brb2	2Bra	2Brb	12Br
B3LYP 6-31G(d)	1.096	1.107	1.111	1.105	1.102	0.989
B3LYP 6-31+G(d,p)	1.103	1.113	1.128	1.110	1.118	0.896
X3LYP 6-31G(d)	1.100	1.109	1.115	1.107	1.107	0.992
X3LYP 6-31+G(d,p)	1.104	1.116	1.129	1.113	1.120	0.900

In conclusion, the obtained compounds by replacing the H atoms of sumanene with F have exhibited bowl-to-bowl inversion in a range from 16.5 kcal/mol to 20.7 kcal/mol. The bowl-to-bowl inversion values were calculated in a range from 13.4 kcal/mol to 20.1 kcal/mol for the halogenated sumanene compounds, obtained by replacing H atoms with Cl. For the halogenated compounds obtained by replacing H atoms with Br, bowl-to-bowl inversion values were calculated in a range from 12.7 kcal/mol, which is the lowest value, to 22.2 kcal/mol, which is the highest value.

ACKNOWLEDGMENT

This scientific work was supported by Balikesir University Scientific Research Projects Unit with the project number 2016-156.

REFERENCES

- [13]. D. Zhou, Gao, Y., Liu, B., Tan, Q., and Xu, B. *Organic Letters*, vol. 19, pp. 4628-4631, 2017.
- [14]. T. Amaya, H. Sakane, T. Nakata and T. Hirao, *Pure Appl. Chem.*, vol. 82 (4), pp. 969-978, 2010.
- [15]. N. Ngamsomprasert, G. Panda, S. Higashibayashi, and H. Sakurai, *J. Org. Chem.*, vol. 81, pp. 11978-11981, 2016.
- [16]. E. Tahmasebi, Biglari, Z., and Shakerzadeh, E. *Vacuum*, vol. 136, pp. 82-90, 2016.
- [17]. T. Amaya. And T. Hirao, *The Chemical Record*, vol. 15, pp. 310-321, 2015.
- [18]. U. D. Priyakumar, G. N. Sastry, *J. Phys. Chem*, vol. 105, pp. 4488-4494, 2001.
- [19]. S. Armaković, Armaković, S. J., Šetrajčić, J. P., and I. J. Šetrajčić, *Chemical Physics Letters*, vol. 578, pp. 156-161, 2013.
- [20]. M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A.



ICACChE

3rd International Conference on Applications
in Chemistry and Chemical Engineering

11 - 15 September 2019 **Skopje**

Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03. Revision C02, Gaussian, Inc., Pittsburgh, PA. 2003.



AMMONIA FOR THE HYDROLYSIS REACTION OF BORANE EFFECT OF YTTRIUM BASED RU-CO-Y ALLOY CATALYST ON HYDROGEN PRODUCTION

MEHMET SAIT IZGI^{a*}, ERHAN ONAT^b, ÖMER ŞAHİN^c

^aSIIRT UNIVERSITY

^bSIIRT UNIVERSITY

^cSIIRT UNIVERSITY

*saitizgi@gmail.com

Abstract:

Hydrogen is a clean energy source and a notable clean energy carrier, recently attracting great interest all over the world. Fossil fuels have a negative impact on the environment. In addition to influencing limited amounts that reserves are not sufficient for near future demands. Therefore; renewable, sustainable and clean energy resources need to be developed. Long Hydrogen close used in chemical industry for many years is the most promising alternative for the future.

In this study, a new ternary 85% Co, 10% Ru and 5% Yttrium ratio and 80% Co, 10% Ru and 10% Yttrium catalysts were synthesized by chemical reduction method, and their effects on ammonium boron hydride hydrolysis were investigated. At the same time, the effects of metal ratio, NaOH effect, different catalyst effect, different ammonia borane concentration effect and temperature were examined and their effects on ammonia borane were investigated separately.

Hydrogen is a clean energy source and a notable clean energy carrier, recently attracting great interest all over the world. Fossil fuels have a negative impact on the environment. In addition to influencing limited amounts that reserves are not sufficient for near future demands. Therefore; renewable, sustainable and clean energy resources need to be developed. Long Hydrogen close used in chemical industry for many years is the most promising alternative for the future.

In this study, a new ternary 85% Co, 10% Ru and 5% Yttrium ratio and 80% Co, 10% Ru and 10% Yttrium catalysts were synthesized by chemical reduction method, and their effects on ammonium boron hydride hydrolysis were investigated. At the same time, the effects of metal ratio, NaOH effect, different catalyst effect, different ammonia borane concentration effect and temperature were examined and their effects on ammonia borane were investigated separately.

Keywords: Yttrium, Nh_3bh_3 , Hydrolysis, Ru, Hydrogen



SYNTHESIS OF BENZO-AZA CROWN ETHERS BY MICROWAVE METHOD AND CHARACTERIZATIONS

BAKI ÇİÇEK^{a*}, ÜMİT ÇALIŞIR^b, AHMET SAPMAZ^c

^aBALIKESIR UNIVERSITY, FACULTY OF ARTS AND SCIENCES, CHEMISTRY
DEPARTMENT

^bBALIKESIR UNIVERSITY, INSTITUTE OF SCIENCE, CHEMISTRY DEPARTMENT

^cBALIKESIR UNIVERSITY, INSTITUTE OF SCIENCE, CHEMISTRY DEPARTMENT

*bcicek@balikesir.edu.tr

Abstract

Crown ethers are popular because of their interest in metal ions, cations and anions. However, obtaining crown ethers require the use of highly demanding methods with various disadvantages such as long reaction times, high dilution. Therefore, green chemistry have been used for many years in the synthesis of crown ethers. Crown ethers can be obtained more easily with the popularization of microwave assisted synthesis methods. Microwave synthesis has many advantages such as increased reaction rate, fast heating source, high efficiency, homogeneous heating, selective heating and being environmentally friendly. In this study, 2,2'-dithiodibenzo crown ether derivatives were synthesized by cyclisation reaction from 2,2'-dithiodidibenzo diamine and ethylene glycol dichloride compounds via S_N2 mechanism in nitrogen atmosphere by microwave synthesis method. The crown ether derivatives were purified by crystallization. Melting point, FT-IR, 1H -NMR, ^{13}C -NMR and LC-MS / MS techniques were used for structural characterization.

Keywords: Crown Ether, Aza-Crown ether, Microwave Synthesis

1. INTRODUCTION

The discovery of crown ethers date back to Pedersen's synthesis of benzo and oxo crown ethers. They are very popular because of their interest in metal ions, cations and anions. The crown ethers have an outer cavity of hydrocarbons and a hydrophilic inner cavity, in particular of elements such as nitrogen, sulfur and oxygen [1-8]. In the synthesis of crown ethers, methods that contradict green chemistry have been used for many years. Long reaction times, high dilution are some of these disadvantages. However, with the popularization of microwave assisted synthesis methods, crown ethers can be obtained more easily. Increased reaction rate, fast heating source, high efficiency, homogeneous heating, selective heating and being environmentally friendly are many advantages [9-17]. Green chemistry is the development of clean chemical products and methods by considering the environment. Green chemistry has a lot of chemical knowledge. Green chemistry is applied to the production of chemicals, use, destruction of chemicals, material consumption, effects on the health of living, to minimize damage to living organisms from toxic substances and chemicals. It makes this process economically feasible and cost effective. Green chemistry is



the most efficient chemistry application in the existing methods. While green chemistry is cost effective, it is a sustainable considering all the costs of chemical application, including hazards and possible environmental hazards [18-19]. Microwave synthesis has been an important advance in synthetic organic chemistry, because conventional heating is inefficient and time consuming. Microwave synthesis is the source of heating in organic synthesis chemistry. The development of microwave chemistry has been continuing for thirty years with the efforts of scientists and engineers. Using microwaves in synthesis; reaction rates are increased, higher yields are obtained and purer products are obtained. Today, microwave technology is used extensively in many laboratories for chemical reactions. In the future, microwave chemistry will be one of the most preferred synthesis methods in laboratories [20-21]. In this study, 2,2'-dithiodibenzo crown ether derivatives of 2,2'-dithiodidibenzo diamine and ethylene glycol dichloride compounds were synthesized by cyclisation reaction via S_N2 mechanism in nitrogen atmosphere by microwave synthesis method. The crown ether derivatives were purified by crystallization. Melting point, FT-IR, 1H -NMR, ^{13}C -NMR and MS / MS techniques were used for structural characterization.

2. MATERIAL AND METHOD

2.1. Material

Analytical purity chemicals are used in this study without purification. Synthesis has been conducted in a microwave digestion device (Milestone Startsynt).

2.2. Method

The synthesis of (1,8,14,21)-tetraaza-[2,3-6,7-15,16-19,20]-tetrabenzo-(4,5,17,18) tetrathio-(11,24)-dioxo-cyclohexacosane (A1) was carried out as illustrated in Figure 1.

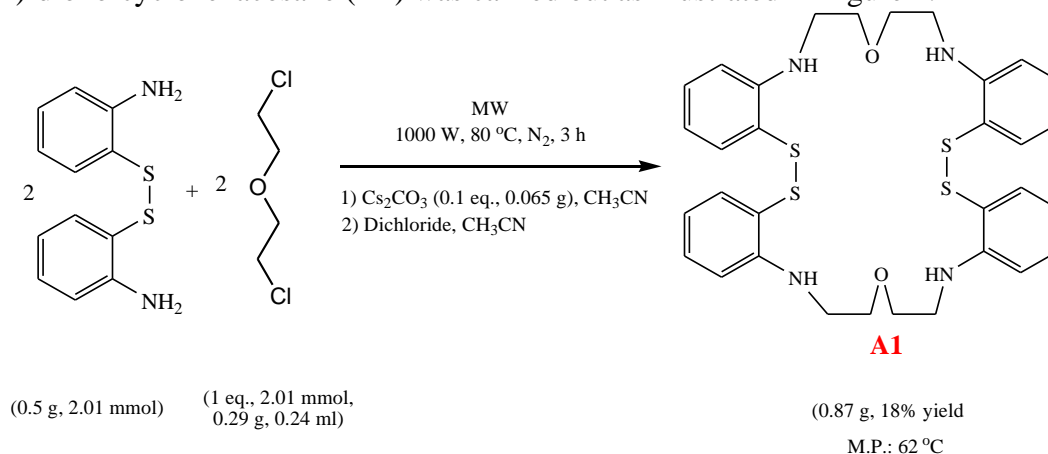


Figure 1: The microwave assisted synthesis procedure

3. RESULTS AND DISCUSSION

In this study, synthesis of 2,2'-dithio macrocyclic dibenzo crown ether were successfully synthesized by microwave method called **Green Chemistry**. The synthesis was carried out by using 2: 2 ring closure reaction in acetonitrile as a solvent with 2,2'-dithiodianiline and diethyleneglycol dichloride, Cs₂CO₃ catalyst using microwave synthesis device. The optimum conditions were determined using microwave method and 2,2'-dithio dibenzo crown ether was synthesized via S_N2 mechanism. Structural characterization of 2,2'-dithio dibenzo crown ether derivatives was determined using melting point, FT-IR, 1H -NMR, ^{13}C -



NMR and LC - MS / MS. The synthesized compound is (1,8,14,21) -tetraaza, [2,3-6,7-15,16-19,20] -tetrabenzo (4,5,17,18) tetrathio, (11,24) dioxo cyclohexacosane or Tetraaza tetrabenzo tetrathio dioxo -26-crown-8 (A1).

The structural characterization of A1, synthesized by nucleophilic cyclization reaction using microwave assisted synthesis method; The disappearance of the $-\text{CH}_2\text{-Cl}$ (Br) peak observed around 665 cm^{-1} , the loss of shear bending of the halide-bound CH_2 group observed around 1120 cm^{-1} , the loss of aromatic amine stress observed at 3375 and 3296 cm^{-1} , the formation of 3442 cm^{-1} NH stress, observed at the FT-IR spectrum. 3060 cm^{-1} aromatic CH stress and $2976\text{-}2857\text{ cm}^{-1}$ CH_2 asymmetric and symmetric stress observation, 1604 cm^{-1} aromatic benzene ring symmetric stress, 1445 cm^{-1} CH_2 group shear bending, $1184\text{-}1103\text{-}1016\text{ cm}^{-1}$ ether bends, 797 cm^{-1} NH bending (vag movement), 745 cm^{-1} NH ring off-plane bending indicates that the compound was synthesized. $^1\text{H-NMR}$ spectrum, 2.83 ppm (8H, t, $-\text{NH-CH}_2-$), 3.44 ppm (8H, t, $-\text{CH}_2-\text{O-}$), 4.56 ppm (4H, s, $-\text{NH-}$), 6.51 ppm (4H, t, C (sp^2)-H), 6.73 ppm (4H, t, C (sp^2)-H), 7.04 ppm (4H, dd, C (sp^2)-H), 7.24 ppm (4H, d, C (sp^2)-H) peaks were observed. $^{13}\text{C-NMR}$ spectrum, 33.21 ppm (NH- $\text{CH}_2\text{-CH}_2$), 68.64 ppm (NH- $\text{CH}_2\text{-CH}_2$), 114.30 ppm (C (sp^2)-), 116.39 ppm (C (sp^2)-), 131.10 ppm (C (sp^2)-), 135.10 ppm (C (sp^2)-), 135.37 ppm (C (sp^2)-) peaks were observed. The MS / MS (m / z) spectrum showed a molecular ion peak of 636.81 (Theoretical: 636.91).

4. CONCLUSION

The synthesis reaction of crown ethers are examined, that can be say, it is generally seen that the reaction time is long. But, in this study the original compounds were synthesized by nucleophilic ring closure reactions in the range of 3-7 hours using microwave synthesis method. FT-IR, $^1\text{H NMR}$, $^{13}\text{C-NMR}$ and LC - MS / MS analysis showed that the desired results were achieved. The synthesized compound, A1, contain different heteroatoms with multiple functional groups, shows the usability of the work such as biological activity, antimicrobial, antifungal, etc.

ACKNOWLEDGMENT

This study was supported by the Scientific Investigate Projects of Balıkesir University (BAP 2017/181).

REFERENCES

- [1] Parker, D., *Macrocyclic synthesis: a practical approach*, New York:Oxford University Press, (2002).
- [2] Ergün, A., "Makro halkalı tiyo-crown eterlerin sentezi ve karbonik anhidraz enzimi üzerinde inhibisyon etkilerinin araştırılması", Yüksek Lisans Tezi, Balıkesir Üniversitesi Fen Bilimleri Enstitüsü, Kimya Anabilim Dalı, Balıkesir, (2011).
- [3] Szczygelska, J.-Tao, J. Biernat, F., Kravtsov, V.C. ve Simonov, Y.A., "Crown ethers with an azo or azoxy unit and sulfur atom(s) in a 13-membered macrocycle" *Tetrahedron*, 55 (28), 8433-8442, (1999).
- [4] Çiçek, B., "Tetra-aza coronandların sentezleri ve kompleksleşme yeteneklerinin potansiyometrik, kondüktometrik ve sıvı-sıvı ekstraksiyon yöntemleri ile belirlenmesi" Doktora Tezi, Balıkesir Üniversitesi Fen Bilimleri Enstitüsü Kimya Anabilim Dalı, Balıkesir, (2002).
- [5] Dann, J.R., Chiesa, P. and Gates, J., "Sulfur-containing large-ring compounds The preparation of 4,7,13,16-tetraoxa-1,10- dithiacyclooctadecane and related compounds", 26



- (6), 1991-1995, (1961).
- [6] Yıldız, A., "Okso-tiyocrown eterlerin sentezi ve karakterizasyonları", Yüksek Lisans Tezi, Balıkesir Üniversitesi Fen Bilimleri Enstitüsü, Kimya Anabilim Dalı, Balıkesir, (2008).
- [7] Gregory, J., Shara, S.S., Clairalyn, L.B. and William, N.S., "Complexation and conformational analysis studies of 11-membered ring crown trithioethers", *Inorganica Chimica Acta*, 317 (1-2), 91-102, (2001).
- [8] John, M., Samuel, H., Robert, E. and Stephen, R., "Enhanced nickel (II) chelation by gem-dimethyl-substituted macrocyclic tetrathioethers", *Journal of the American Chemical Society*, 113 (23), 8663-8671, (1991).
- [9] Itoh, T., Takagi, Y., Murakami, T., Hiyama, Y. and Tsukube, H., "Crown ethers as regulators of enzymatic reactions: Enhanced reaction rate and enantioselectivity in lipase-catalyzed hydrolysis of 2-cyano-1-methylethyl acetate", *J.Org.Chem.*, 12 (43), 2456-2460, (1978).
- [10] Pedersen, C.J., "Macrocyclic polyethers: Dibenzo-18-crown-6 polyether and dicyclohexyl-18-crown-6 polyether", *Org.Synth.*, 66 (52), (1972).
- [11] Jing, Z., He-Le, L., De, C. and Xing-Hai, S., "Synthesis Of Anionic Sulphonate-Crown Ether Surfactants", *Chinese Chemical Letters*, 24 (12), 1137-1139, (2013).
- [12] Sergey, V., Vladimir, L., Artem, B., Evgeni, M., Valeri, V., Stephan, S., Konstantin, A., Stephanie, D. and Olga, A., "Synthesis, metal ion binding, and photochromic properties of benzo- and naphthopyrans annelated by crown ether moieties", *Tetrahedron*, 68 (38), 7873-7883, (2012).
- [13] Ryszard, O., "The synthesis of anthracene crown ethers derived from benzo- crown ethers", *Tetrahedron*, 54 (24), 6897-6902, (1998).
- [14] Pedersen, C.J., "Cyclic polyethers and their complexes with metal salts", *Journal of the American Chemical Society*, 89 (26), 7017-7036, (1967).
- [15] Corsaro, A. ve Pistar, V., "Conversion of the thiocarbonyl group into the carbonyl group", *Tetrahedron*, 54 (50), 15027-15062, (1998).
- [16] Zhao, Y., Hong, M., Liang, Y., Su, W., Cao, R. and Zhou, Z., "Syntheses and structural characterization of silver(I) complexes with versatile heterocyclic sulfur and nitrogen donor ligands", *Polyhedron*, 20 (20), 2619-2625, (2001).
- [17] Çalışır, Ü., and Çiçek, B. "Comparison of classic and microwave-assisted synthesis of benzo-thio crown ethers, and investigation of their ion pair extractions", *J.Of Molecular Structure*, 505-511, (2017).
- [18] Manahan, S.E., *Green Chemistry and the ten commandments and sustainability*, Columbia: ChemChar Research, (2006).
- [19] Hieresen, D., Boese, J. ve David, L., "Green Chemistry", *J.Chem.Educ.*, 12 (77), 1543-1547, (2000).
- [20] Başarır, M., "N-Süstitüe Pirel Türevlerinin Mikrodalga Etkisi Altında Sentezi.", Yüksek Lisans Tezi, Yıldız Teknik Üniversitesi Fen Bilimleri Enstitüsü, İstanbul, (2006).
- [21] Mukesh, D. ve Kruthiventi, A., "Green Chemistry & Engineering". Elsevier Science & Technology Books, 326, (2007).

Biography:

Prof. Dr. Baki ÇİÇEK is a teaching staff in Balıkesir University Chemistry Department. He works about physical organic chemistry, modification of nanotubes, conductometry, organic synthesis, crown ethers.



MINERAL ANALYSIS OF CANCEROUS AND NON-CANCEROUS PROSTATE TISSUE SAMPLES

BAKI ÇİÇEK^{a*}, ÜMİT ÇALIŞIR^b, EREN ALTUN^c

^aBALIKESIR UNIVERSITY, FACULTY OF ARTS AND SCIENCES, CHEMISTRY
DEPARTMENT

^bBALIKESIR UNIVERSITY, INSTITUTE OF SCIENCE, CHEMISTRY DEPARTMENT

^cBALIKESIR UNIVERSITY, FACULTY OF MEDICINE, MEDICAL PATHOLOGY

*bcicek@balikesir.edu.tr

Abstract

The prostate is a gland in male-only that surrounds the urethra, a channel that carries urine through the bladder. The prostate grows depending on age. Over time, symptoms of prostate cancer (PCa) and non-cancerous prostate enlargement (BPH) are due to pressure on the duct (urethra) that carries urine out of the body. This pressure blocks the flow of urine. The studies have observed differences in metal levels in patients with PCa and patients with BPH. In this study, prostate tissues from BPH patients and PCa patients were resolved by microwave digestion method. Macro, micro and heavy metals contents of solubilized tissue samples were analysed by inductively coupled plasma - mass spectroscopy (ICP-MS). Zinc, lithium, beryllium, boron, sodium, magnesium, phosphorus, calcium, titanium, vanadium, chromium, manganese, cobalt, nickel and arsenic levels were found to be low in malignant prostate tissues. In addition, beryllium, boron, titanium and vanadium concentrations were 4-5 times higher in BPH tissues.

Keywords: PCa, ICP-MS, Microwave Digestion, Heavy Metal

1. INTRODUCTION

Prostate is a gland found in every man and weighs 18-20 grams in young adult males. In an adult male, it reaches approximately the size of a walnut. It is located in the lower part of the abdominal organs after the bladder, just in front of the rectum. There are three common prostate-related conditions that begin at middle age; Prostate inflammation, Benign prostatic enlargement (Benign prostatic hyperplasia (BPH) and prostate cancer (PCa). Benign prostatic hyperplasia (BPH) is a very common condition in men over 40 years of age [1]. This tissue growth, thought to be due to BPH and androgen (secretory substance), increases with age and may cause urinary obstruction [2]. Prostate cancer (PCa) is the most common malignant tumour in men and has a lower mortality rate than other types of cancer [3]. Some studies have shown that the inherited cell mutations and environmental factors of androgens play a role in the pathogenesis of PCa. There are several epidemiological, clinical, and empirical studies linking PCa to heavy metal exposure [4-6]. It is believed that the accumulation of certain elements plays an important role in the development of cancers such as PCa. Some of them are given in Table 1. In this study, prostate tissues from BPH patients and PCa patients were resolved by microwave digestion method. 27 different metal/nonmetal element levels from solubilized tissue samples were analysed by ICP-MS. Meta- nonmetal levels in



cancerous and non-cancerous tissues were discussed.

Table 7: Some studies on the levels of minerals in PCa and BPH patients

Element	The Study and Results
Zinc (Zn)	1. Found a decrease in zinc levels in patients with prostate cancer [6-9,12-16]
Iron (Fe)	2. Low iron concentrations can transform benign tumours into more aggressive ones [6].
Cadmium (Cd)	3. High concentrations of cadmium can transform benign tumours into more aggressive ones [6].
Copper (Cu)	4. Increased copper concentrations may increase tumour grades [8].
Selenium (Se)	5. It has little importance in the prostate tissues that have started to grow [8]. However, in another study, it was observed that the amount of tissue cells is high [15].
Nickel (Ni) & Calcium (Ca)	BPH has been observed to be low in tissue cells [8].
Arsenic (As)	High intake of inorganic arsenic with drinking water and chronic exposure to this element is associated with prostate, skin, bladder and lung cancers [17] [18] [19].
Boron (B)	Dietary boron intake has shown that it affects steroid hormone levels and reduces PCa risk [20] [21].

2. MATERIAL AND METHOD

2.1. Material

Analytical purity chemicals are used in this study. The mixed calibration standards (Li, Be, Mg, P, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Sr, Mo, Cd, Sn, Sb, Tl, Pb, Pt, B, Na, and K) are prepared from single solutions of each element standard (Sigma Aldrich). Standards were prepared in 1% Suprapur nitric acid. In the microwave digestion process 65% nitric acid (Merck) and 30% hydrogen peroxide (Sigma Aldrich) are used directly. Microwave digestion device (Milestone Startsynt and SK-10) and ICP-MS device (Thermo Scientific iCAP Q) were used in analysis.

2.2. Method

All paraffinized samples were weighed directly in microwave teflon tubes and their amounts are recorded. 6 ml of concentrated HNO₃ and 2 ml of H₂O₂ were added to the tubes. It was kept half an hour in the fume hood in order to avoid any explosion. Then the samples were taken to the microwave digestion system.

Table 8: Microwave digestion procedure

Step	Time (minute)	Temperature (°C)	Power (W)
1.	5	100	1000
2.	15	100	1000
3.	5	150	1000
4.	15	150	1000

The optimum digestion procedure was given in Table 2. Teflon digestion tubes were cooled



to room temperature. All samples were transferred to the volumetric flasks and fulfilled to 25 ml. The total concentration of 27 elements in the samples was determined by ICP-MS.

3. RESULTS AND DISCUSSION

In this study, the data obtained for 27 elements were found to be similar to the literature data for benign and malignant prostate tissues. The investigated elements were arsenic, zinc, copper, nickel, cobalt, iron, manganese, chromium, vanadium, titanium, calcium, potassium, phosphorus, magnesium, sodium, boron, beryllium, lithium, lead, thallium, platinum, antimony, tin, cadmium, molybdenum, strontium, selenium. Zinc concentration in prostate tissue was low in PCa patients (adenocarcinoma) and high in BPH patients. This supports the relationship between PCa and zinc ($P = 0.001$). In addition, lithium, beryllium, boron, sodium, magnesium, phosphorus, calcium, titanium, vanadium, chromium, manganese and cobalt levels were found to be lower in malignant tissue (Figure 1).

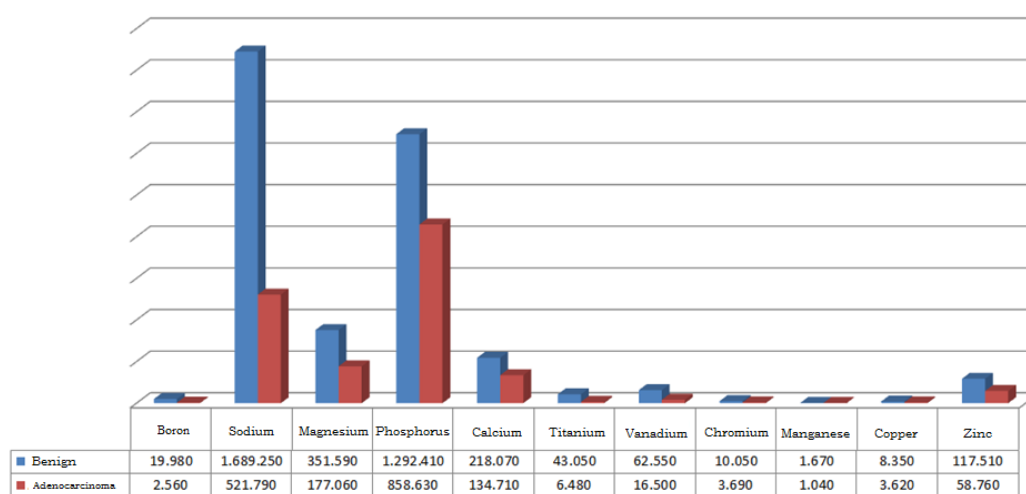


Figure 2: B, Na, Mg, P, Ca, Ti, V, Cr, Mn, Cu, Zn levels in Benign and Adenocarcinoma prostate tissue

Furthermore, beryllium, boron, titanium and vanadium concentrations were found to be five times or more in benign tissues (Figure 2).

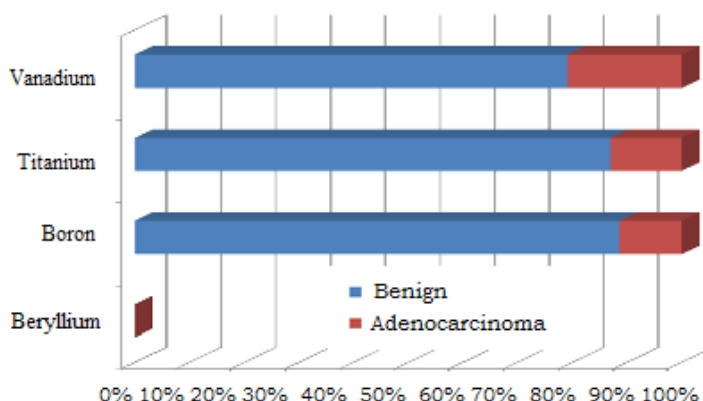


Figure 3: V, Ti, B, Be levels in PCa and BPH patients



4. CONCLUSION

In this study, 78 prostate patient tissue with cancerous and non-cancerous were analysed with ICP-MS to determine metal/non-metal deposition. There was a new microwave digestion method investigated given in Table 1. 27 element level were determined in Benign and adenocarcinoma patients. Some of element levels were different in Benign and adenocarcinoma patients. Zinc, lithium, beryllium, boron, sodium, magnesium, phosphorus, calcium, titanium, vanadium, chromium, manganese and cobalt levels were lower in Benign prostate tissue. When the obtained results were evaluated, it was found that there is a connection between metal non-metal levels and cancer types. This data can be supported by further studies.

ACKNOWLEDGMENT

This study was supported by the Scientific Investigate Projects of Balıkesir University (BAP 2017/205).

REFERENCES

- [1] E. D. CRAWFORD, "Epidemiology of prostate cancer chemoprevention," *Urology*, vol. 62, no. Suppl 6A, pp. 3–12, 2003.
- [2] T. R. Rebbeck, "Conquering cancer disparities: New opportunities for cancer epidemiology, biomarker, and prevention research," *Cancer Epidemiol. Biomarkers Prev.*, vol. 15, no. 9, pp. 1569–1571, 2006.
- [3] E. D. Crawford et al., "Early Stage Prostate Cancer An Approach Using PSA Levels of 1.5 ng/mL as the Cutoff for Prostate Cancer Screening in Primary Care," *Urology*, vol. 96, pp. 116–120, 2016.
- [4] A. K. Abbas and J. C. Aster, Vinay Kumar» MBBS» MD» FRCPath. .
- [5] M. R. Spitz et al., "Epidemiologic determinants of clinically relevant prostate cancer," *Int. J. Cancer*, vol. 89, no. 3, pp. 259–264, 2000.
- [6] A. G. Sarafanov et al., "Prostate cancer outcome and tissue levels of metal ions.," *Prostate*, vol. 71, no. 11, pp. 1231–8, 2011.
- [7] C. Neslund-dudas, "NIH Public Access," vol. 157, no. 2, pp. 107–112, 2015.
- [8] İ. Çelen et al., "Selenium, nickel, and calcium levels in cancerous and non-cancerous prostate tissue samples and their relation with some parameters," *Environ. Sci. Pollut. Res.*, vol. 22, no. 17, pp. 13070–13076, 2015.
- [9] J. Gumulec, M. Masarik, V. Adam, T. Eckschlager, I. Provaznik, and R. Kizek, "Serum and tissue zinc in epithelial malignancies: A meta-analysis," *PLoS One*, vol. 9, no. 6, 2014.
- [10] V. Zaichick, S. Nosenko, and I. Moskvina, "The effect of age on 12 chemical element contents in the intact prostate of adult men investigated by inductively coupled plasma atomic emission spectrometry," *Biol. Trace Elem. Res.*, vol. 147, no. 1–3, pp. 49–58, 2012.
- [11] V. Y. Zaichick, T. V. Sviridova, and S. V. Zaichick, "Zinc in human prostate gland: Normal, hyperplastic and cancerous," *J. Radioanal. Nucl. Chem.*, vol. 217, no. 2, pp. 157–161, 1997.



- [12] X. M. Li et al., "Measurement of serum zinc improves prostate cancer detection efficiency in patients with PSA levels between 4 ng/mL and 10 ng/mL," *Asian J. Androl.*, vol. 7, no. 3, pp. 323–328, 2005.
- [13] M. F. Leitzmann, M. J. Stampfer, K. Wu, G. A. Colditz, W. C. Willett, and E. L. Giovannucci, "Zinc supplement use and risk of prostate cancer," *J Natl Cancer Inst*, vol. 95, no. 13, pp. 1004–1007, 2003.
- [14] M. Yaman, D. Atici, S. Bakirdere, and I. Akdeniz, "Comparison of trace metal concentrations in malign and benign human prostate," *J. Med. Chem.*, vol. 48, no. 2, pp. 630–634, 2005.
- [15] B. P. Singh et al., "Status and Interrelationship of Zinc, Copper, Iron, Calcium and Selenium in Prostate Cancer," *Indian J. Clin. Biochem.*, vol. 31, no. 1, pp. 50–56, 2016.
- [16] F. Badalà, K. Nouri-mahdavi, and D. A. Raoof, "NIH Public Access," *Computer (Long Beach. Calif.)*, vol. 144, no. 5, pp. 724–732, 2008.
- [17] S. a Navarro Silvera and T. E. Rohan, "Trace elements and cancer risk: a review of the epidemiologic evidence," *Cancer Causes Control*, vol. 18, no. 1, pp. 7–27, 2007.
- [18] L. Benbrahim-Tallaa and M. P. Waalkes, "Inorganic arsenic and human prostate cancer," *Environ. Health Perspect.*, vol. 116, no. 2, pp. 158–164, 2008.
- [19] D. R. Intakes et al., *Dietary Reference Intakes*. 2000.
- [20] S. Orenay Boyacioglu, M. Korkmaz, E. Kahraman, H. Yildirim, S. Bora, and O. Y. Ataman, "Biological effects of tolerable level chronic boron intake on transcription factors," *J. Trace Elem. Med. Biol.*, vol. 39, pp. 30–35, 2017.
- [21] Y. Cui et al., "Dietary boron intake and prostate cancer risk," *Oncol. Rep.*, vol. 11, no. 4, pp. 887–892, 2004.

Biography:

Prof. Dr. Baki ÇİÇEK is a teaching staff in Balıkesir University Chemistry Department. He works about physical organic chemistry, modification of nanotubes, conductometry, organic synthesis, crown ethers.



SINGLE CELL PEM FUEL CELL DESIGN AND APPLICATION

SABIT HOROZ^{a*}, ARZU EKINCI^b

^aSIIRT UNIVERSITY

^bSIIRT UNIVERSITY

*sbt_fzk@hotmail.com

Abstract:

Due to increasing environmental pollution concerns and the possibility of fossil fuels being exhausted soon, the tendency towards alternative energy sources is increasing. Fuel cells are becoming more and more widespread with their efficiency up to 80%, quiet operation and modularity. The design and manufacture of single-cell or stacked components are the two most important processes in developing fuel cell technology. In general, the design and assembly of a fuel cell has a strong impact on its performance. In view of the materials and components used in the fuel cell, design and manufacturing should be optimized for the respective fuel cell power output to achieve the best performance. The main task of the fuel cell is to produce electricity of the desired power using an energy carrier such as hydrogen. The PEM electrolyser breaks down deionized water to produce hydrogen and oxygen at a given flow rate. The hydrogen and oxygen gases obtained are fed to the PEM fuel cell. Thanks to the load (resistors) connected to the PEM fuel cell, the performance curves (power and polarization) of the fuel cell are determined by means of voltmeter and amperemeter.

In this study, Pt / C catalyst supported single cell PEM fuel cell package was designed by using 117 nafion membranes. The production, modification and installation of fuel cells is also ensured. After completion of the test setup, fuel cell performance test studies were performed. The designed PEM fuel cell system was operated under constant pressure by giving H₂ gas for one hour and the current and voltage changes were examined against time. Then, voltage-current-power curves are drawn from the results of the data obtained under varying load. The open circuit voltage of the single-cell PEM fuel cell cell was measured as 1.1 V. The power of the fuel cell system was calculated as a maximum of 0.7 Watt. In PEM fuel cell application, average efficiency values according to power and ideal voltage were found to be 54% and 89%, respectively.

Keywords: Pem, Nafion Membrane, Voltage, Current, Power



INVESTIGATION OF PROPERTIES CDSE QUANTUM DOTS SYNTHESIZED BY LASER ABLATION

SABIT HOROZ^a

^aSIIRT UNIVERSITY

sbt_fzk@hotmail.com

Abstract:

Quantum dots (QDs) have great potential for applications in electronics and optoelectronics. They show special physical and chemical characteristics when their size is close to or smaller than the exciton Bohr radius, and this quantum confinement effect leads to tunable photoluminescence (PL) properties. In particular, their PL can be tuned by the size of the QDs, which gives them functionalities as sensitizers in photovoltaic solar cells. There are different ways to synthesize QDs, for example, solution-based methods for colloidal QDs and deposition-based methods such as successive ionic layer adsorption and reaction (SILAR), chemical bath deposition (CBD), and atomic layer deposition (ALD). It is desirable to develop QD-sensitized solar cells without ligands to achieve efficient electron transfer from the QDs to photoanode and improve the efficiency. Another attractive method to make QDs that retains the benefits of pulsed laser deposition (PLD) is laser ablation of solid targets in a liquid environment.

In this study, CdSe quantum dots (QDs) have been prepared by a facile and clean synthesis method—laser ablation in water. The structural and luminescent properties of the CdSe QDs have been investigated. The CdSe QDs of wurtzite crystal structure have an average particle size of about 5 nm. The QDs can be attached to ZnO nanowires making them ideal for applications in QD-sensitized nanowire solar cells. A uniqueness of the QDs attached to the ZnO nanowires by this laser ablation method is that they do not contain ligands, and the preparation avoids the complicated process of ligand exchange.

Keywords: Quantum Dots, Synthesis, Characterization, Cdse



EFFECT OF CO-CR-B CATALYST AMMONIA BORANE HYDROLYSIS

ERHAN ONAT^{a*}, MEHMET SAIT IZGI^b

^aBATMAN BILSEM

^bSIIRT ÜNİVERSİTESİ

*erhonat@gmail.com

Abstract:

Ammonia boron is one of the high energy density chemical compounds that eliminates the problem of storing hydrogen, which is a clean source of energy. Ammonia borane hydrolysis, hydrogen production efficiency and trial process. Clean energy sources are undoubtedly one of the biggest challenges humanity must face in one of the growing concerns about energy and environmental issues in the world. In the last city, hundreds of researchers in the nano-cities related to photovoltaic batteries and airlines have yielded significant improvements in environmental environmental research, energy conversion and storage. Your concerns about global, global warming and depletion of fossil fuels have become one of the promising and major sources of energy.

This study deals with the parameters of hydrogen production by hydrolysis in the presence of Co-Cr-B catalyst from ammonia boron. The synthesized catalyst was reacted with ammonia borane solution. Then, the amount of catalyst, different NaOH concentration and catalytic activity at different temperatures and optimum conditions for hydrolysis of ammonia borane were examined and the degree of reaction and activation energy determined.

Ammonia boron is one of the high energy density chemical compounds that eliminates the problem of storing hydrogen, which is a clean source of energy. Ammonia borane hydrolysis, hydrogen production efficiency and trial process. Clean energy sources are undoubtedly one of the biggest challenges humanity must face in one of the growing concerns about energy and environmental issues in the world. In the last city, hundreds of researchers in the nano-cities related to photovoltaic batteries and airlines have yielded significant improvements in environmental environmental research, energy conversion and storage. Your concerns about global, global warming and depletion of fossil fuels have become one of the promising and major sources of energy.

This study deals with the parameters of hydrogen production by hydrolysis in the presence of Co-Cr-B catalyst from ammonia boron. The synthesized catalyst was reacted with ammonia borane solution. Then, the amount of catalyst, different NaOH concentration and catalytic activity at different temperatures and optimum conditions for hydrolysis of ammonia borane were examined and the degree of reaction and activation energy determined.

Keywords: Ammonia Boron, Co-Cr-B, Catalyst, Hydrogen Energy



SYNTHESIS AND PROPERTIES OF LIQUID CRYSTALS COMPOUND

RAM ADEL PASHA^a

^aUMM ALQURA UNIVERSITY

ram.rom.nano@googlemail.com

Abstract:

The field of liquid crystals has become the focus of extensive research over the last century in terms of the design, synthesis and evaluation of novel materials, and the development of high technology applications, particularly displays. Virtually all current liquid crystal displays are based on the nematic phase, however, ferroelectric liquid crystal displays based on the chiral smectic C phase offers many advantages such as faster switching, higher resolution and contrast, bistability and wider angles of view. Although ferroelectric microdisplays are a commercial success, the technology is currently severely limited in their applicability because of problems in aligning the molecules in the ideal so-called bookshelf configuration. A wide range of novel materials has been designed, synthesized and evaluated. The main feature of the molecular design is the inclusion of a bulky group as part of a terminal chain, designed to cause a phase separation and preclude layer shrinkage on formation of the smectic C phase, and hence generate the desired bookshelf alignment. The synthesis was affected most efficiently using a range of synthetic methods, in particular low temperature lithiations and Suzuki coupling reactions. The materials were evaluated for structure and purity, and for mesomorphic and physical properties. The majority of the novel materials exhibit the smectic C phase over a wide temperature range, some compounds generate solely the smectic C phase whereas other additionally show the smectic A and nematic phases, and these results helps to establish patterns of how the mesomorphism relates to the structure of the bulky terminal group. Selected novel compounds were mixed with an established ferroelectric host mixture (KCHM211) to generate a range of novel ferroelectric host mixtures, which were doped with an established chiral dopant (BE8OF2N) to generate a range of novel ferroelectric mixtures, which were evaluated for their ferroelectric properties, namely tilt angle and spontaneous polarization. The results in terms of synthesis, mesomorphism and ferroelectric properties are discussed comparatively between novel compounds and known compounds.

Keywords: Chemistry, Organic Chemistry, Liquid Crystal



ELECTROCHEMICAL DETERMINATION OF DOPAMINE USING A GRAPHENE SCREEN-PRINTED CARBON ELECTRODE COUPLED WITH MAGNETIC SOLID-PHASE MICROEXTRACTION

HAYATI FILIK^{a*}, ASIYE ASLIHAN AVAN^b

^aISTANBUL UNIVERSITY-CERRAHPAŞA

^bISTANBUL UNIVERSITY-CERRAHPAŞA

*filik@istanbul.edu.tr

Abstract:

Dopamine is an important biogenic amine neurotransmitter in the human body. In biological fluids, the concentration of amine neurotransmitters is extremely low and their estimation has required that methods be used at the limit of their sensitivity. Sensitive and selective methods are required for the determination of dopamine due to its importance in brain chemistry. Thus, new preconcentration and/or separation method is usually necessary.

A magnetically separable Fe₃O₄@MWCNTs composite was prepared using the coprecipitation method and the magnetic Fe₃O₄@MWCNTs composites were used for separation and/or preconcentration of trace amounts of dopamine. For the detection stage, square wave voltammetry on disposable graphene screen-printed carbon electrode was successfully employed for the determination of dopamine. Graphene screen-printed carbon electrode exhibited excellent electroanalytical performance for dopamine and the linear concentration range was from 0.8 μM to 80 μM and the detection limit of 50 nM was obtained. In combination with the magnetic solid phase extraction method, the sensor response was linearly proportional to the concentration of dopamine in the range of 0.01–6.0 μM with a correlation coefficient of about 0.9992. The detection limit of the sensor was found to be 5.0 nM by square wave voltammetry method. At the end of the study, the combined methodology was successfully applied to detect dopamine in real urine samples with good recoveries ranging from 95–98%.

Keywords: Dopamine, Graphene, Magnetic Resin, Magnetic Microextraction, Combined Method, Voltammetry



FATTY ACID ETHYL ESTER SYNTHESIS FROM BEEF TALLOW USING SUPERCRITICAL ETHANOL

RICARDO GARCÍA MORALES^{a*}, OCTAVIO ELIZALDE SOLIS^b

^aINSTITUTO POLITÉCNICO NACIONAL

^bINSTITUTO POLITÉCNICO NACIONAL

*richo_garcia@hotmail.com

Abstract:

The use of renewable resources such as hydrogen, eolic and geothermal energy, as well as the development of biofuels are some examples of the substitution of fossil fuel resources(1). Due to the similarities of the properties of diesel and biodiesel (obtained from vegetable oils and animal fats) the latter is considered as a promising substitute(2). Biodiesel is produced with renewable raw materials, it is non-toxic and has low sulfur content. The main disadvantage is that the cost of biodiesel production is more expensive than the cost of diesel production. The cost of production is up to 70 % higher, depending on the raw material. Considering this, beef tallow (which is slaughterhouse waste) was suggested as raw material to minimize this disadvantage. In this work, transesterification reactions of beef tallow with supercritical ethanol were carried out at temperatures from 320 to 390 °C and pressures up to 450 bar.

A high pressure batch reactor made of Inconel 625 was used. Due to the operating conditions of this kind of reactors and that the molar ratio was fixed, the reactants were added to fully pack the reactor in order to reach supercritical conditions, obtained simply by raising the temperature. For covering the temperature range (320 - 390 °C), each reaction was set every 10 °C. The molar ratio for all the reactions was 45:1, ethanol:beef tallow. The reaction time was one hour with constant agitation. Once the reaction finished, the methanol excess was recovered by distillation; biodiesel and glycerol were separated by decantation..

The highest conversion was obtained at 370 °C and 450 bar, with no pretreatment needed for the raw material. The absence of catalyst led us not to wash the biodiesel. The cloud point results compared with those obtained with methanol are three Celsius below.

Keywords: Ethyl Esters, Supercritical Ethanol, Biodiesel, Transesterification

**This study is supported by Instituto Politécnico Nacional and COFAA*



AN EASY PROCEDURE FOR IDENTIFYING FAME, FAEE AND FABE OBTAINED WITH SUPERCRITICAL ALCOHOLS AND BEEF TALLOW

ABEL ZÚÑIGA MORENO^a

^aINSTITUTO POLITÉCNICO NACIONAL

abelzum@yahoo.com

Abstract:

Several reactions were performed to analyse the influence of temperature on supercritical transesterification with methanol, ethanol and isobutanol. From these reactions, a method was developed for the identification of the different products: fatty acid methyl esters FAME, fatty acid ethyl esters FAEE and fatty acid butyl esters FABE. Monitoring the reaction was performed by infrared spectroscopy (IR), which has immediate application in qualitative analysis (detection of the molecular structures present in the material).

FAME, FAEE and FABE were obtained with supercritical methanol, ethanol and isobutanol, respectively, and beef tallow. Reaction temperatures were from 320 to 400 °C. Molar ratio was 45:1 alcohol:beef tallow.

For the analysis, the spectra of the infrared zone for the samples were obtained with a Perkin Elmer Frontier FT-IR spectrophotometer, using a resolution of 2 cm⁻¹ and 20 scans per spectrum. Before analysis, the samples were filtered and centrifuged at 2000 rpm for 30 minutes. In the area of the IR electromagnetic spectrum with wavelengths between 400 and 1300 cm⁻¹, the assignment of the absorption bands to molecular vibrations is more difficult to perform, because each of them is generated by summed individual absorptions. It is the so-called fingerprint area.

In this area, small differences in the structure and constitution of the molecules give rise to important variations in absorption maxima, for the differentiation of the FAME, FAEE and FABE an easy-to-distinguish method of IR spectra in the region comprised from 1017 to 1035 cm⁻¹.

Keywords: Biodiesel, Transesterification, FTIR, Esters

**This study is supported by Instituto Politécnico Nacional and COFAA*



QUANTITATIVE DETERMINATION OF ACTIVE COMPONENTS IN A TABLET BY RATIO SPECTRA-DERIVATIVE METHOD

ÖZGÜR ÜSTÜNDAĞ^{a*}, ERDAL DİNÇ^b

^aANKARA UNIVERSITY FACULTY OF PHARMACY DEPT. OF ANALYTICAL
CHEMISTRY

^bANKARA UNIVERSITY FACULTY OF PHARMACY DEPT. OF ANALYTICAL
CHEMISTRY

*ustundag@pharmacy.ankara.edu.tr

Abstract:

New analytical methods or approaches play an increasingly important role in practical applications such as biomedical analysis, clinical analysis, pharmaceutical analysis, environmental monitoring, quality control of industrial manufacturing and forensic science. For these purposes, analytical chemists work to develop more powerful methods and to improve the reliability of existing analytical techniques to meet the demands for better chemical measurements or to get up desirable analysis results in many fields of science as well as the above mentioned areas this work, a ratio spectra-derivative spectrophotometric (RD) method has been developed for the simultaneous quantitative estimation of candesartan (CAN) and hydrochlorothiazide (HCT) in a tablet dosage form. The RD method was applied to the UV spectra of CAN and HCT. Calibration equations were obtained by measuring amplitudes at 243.1 nm for CAN and 262.7 nm for HCT. The validity and applicability of the proposed ratio spectra-derivative spectrophotometric method was carried out by analysing synthetic binary mixtures consisting of CAN and HCT by using an independent set consisting of CAN and HCT. In addition, standard addition technique and intra-day and inter-day tests were performed. The proposed method was successfully applied to the analysis of these active compounds in tablets.

Keywords: Quantitative, Determination, Ratio, Spectra, Derivative

References

1. I. Daubechies, Ten Lectures on Wavelets, Society for Industrial and Applied Mathematics, Philadelphia, 1992.
2. E. Dinç, D. Baleanu, Ö. Üstündağ, Spectr. Lett. 36 (2003) 341-355.



FUEL GAS PRODUCTION FROM GUAVA BY GASIFICATION WITH SUPERCRITICAL WATER

FRANCISCO JAVIER VERÓNICO SÁNC^{a*}, SANDRO GONZÁLEZ ARIAS^b, OCTAVIO
ELIZALDE SOLIS^c, ABEL ZÚÑIGA MORENO^d

^aINSTITUTO POLITÉCNICO NACIONAL

^bINSTITUTO POLITÉCNICO NACIONAL

^cINSTITUTO POLITÉCNICO NACIONAL

^dINSTITUTO POLITÉCNICO NACIONAL

*javi.ibq@hotmail.com

Abstract:

Gasification in Supercritical Water (GSCW) is an alternative technology for the gasification of biomass with a high moisture content. A large proportion of the residual biomass is wet biomass with a content greater than 70% water. In these cases, the GSCW process shows great expectations due to the supercritical water properties ($T_c > 374^\circ\text{C}$, $P_c > 22\text{ MPa}$) such as high diffusion rates, low viscosity and low dielectric constant, characteristics that not only make it an excellent solvent for organic materials but also weakens the hydrogen bond and contributes to the production of H₂ gas.

In 2015, Mexico presented an annual percent of food waste of 10,000,431 tons, that is, 37.26% of the national average. One of the most wasted foods present in this study is guava, since it is located in the first place, with a waste of 57.3% of its total production, which can be used as wet biomass for the generation of gaseous

A high pressure batch reactor made of Inconel 625 was used. Due to the operating conditions of this kind of reactors and that the molar ratio was fixed, the reactants were added to fully pack the reactor in order to reach supercritical conditions, obtained simply by raising the temperature. For covering the temperature range (320 - 390 °C), each reaction was set every 10 °C. The molar ratio for all the reactions was 45:1, ethanol:beef tallow. The reaction time was one hour with constant agitation. Once the reaction finished, the methanol excess was recovered by distillation; biodiesel and glycerol were separated by decantation.

This paper presents the results obtained from gasification in a batch reactor fed by a 1: 4 reaction (biomass / water) at 400 ° C and 35 MPa.

Keywords: Supercritical Gasification, Supercritical Water, Hydrogen Production

**This study is supported by Instituto Politécnico Nacional*



CERIUM OXIDE SUPPORTED NICKEL SCHIFF BASE COMPLEX AS A CATALYST FOR HYDROGEN PRODUCTION

DILEK KILINÇ^{a*}, ÖMER ŞAHİN^b

^aFACULTY OF SCIENCE AND LETTERS, DEPARTMENT OF CHEMISTRY, SIIRT UNIVERSITY, 56100 SIIRT

^bFACULTY OF ENGINEERING, DEPARTMENT OF CHEMICAL ENGINEERING, SIIRT UNIVERSITY, 56100 SIIRT

*dkilinc@siirt.edu.tr

Abstract:

NaBH₄ is a promising nominee, that has perfect hydrogen storage capability (10.8%), non-toxic water reaction. Because of entirely isolation with an external magnetic region, magnetic ground is take account as a promising material for a metal catalyst with a great efficiency and reusability [1].

In this presents we studied the cerium oxide supported of 5-Amino-2, 4-dichlorophenol-3, 5-ditertbutylsalisylaldimine-Ni complex [2] as a catalyst in NaBH₄ hydrolysis for H₂ production. Ni-Schiff Base complex catalyzed NaBH₄ hydrolysis was studied in different parameters as concentration of NaBH₄, concentration of NaOH, temperature effect, amount of catalyst and percentage of Ni complex. Also the catalyst was characterized with several analysis methods Finally the kinetic calculation of sodium borohydride hydrolysis reaction were studied at 30 °C-50 °C and it seen that Ni(II)-Schiff Base complex was an effective catalyst for NaBH₄ hydrolysis reaction.

Keywords: Complex, H₂ Production, NaBH₄

References

- [1] Chinnappan A, Puguan JMC, Chung W-J, Kim H. Hydrogen generation from the hydrolysis of sodium borohydride using chemically modified multiwalled carbon nanotubes with pyridinium based ionic liquid and decorated with highly dispersed Mn nanoparticles. *J Power Source*. 2015;293:429-36.
- [2] Kılınç D, Şahin Ö. Synthesis of polymer supported Ni (II)-Schiff Base complex and its usage as a catalyst in sodium borohydride hydrolysis. *International Journal of Hydrogen Energy*. 2018;43:10717-10727.