# Záverečná karta projektu

Názov projektu **Katalytická depolymerizácia lignínu zo surovín na výrobu pokročilých biopalív**

Evidenčné číslo projektu **APVV-18-0255**

Zodpovedný riešiteľ **doc. Ing. Pavol Hudec, CSc.**

Príjemca **Slovenská technická univerzita v Bratislave - Fakulta chemickej a potravinárskej technológie**

**Názov pracoviska, na ktorom bol projekt riešený**

Fakulta chemickej a potravinárskej technológie STU v Bratislave
VURUP, a.s., Bratislava
Prirodovedecká fakulta UK Bratislava
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**Názov a štát zahraničného pracoviska, ktoré spolupracovalo pri riešení**

žiadne

**Udelené patenty/podané patentové prihlášky, vynálezy alebo úžitkové vzory, ktoré sú výsledkami projektu**

žiadne

**Najvýznamnejšie publikácie (knihy, články, prednášky, správy a pod.) zhrňujúce výsledky projektu – uveďte aj publikácie prijaté do tlače**

Indexované v databáze Scopus a WOS:

1. Horňáčková M., Plavčan J., Horňáček M., Hudec P., Veis P.: Heavy Metals Detection in Zeolites Using the LIBS Method (2019) Atoms, 7(4), art. no. 98.
2. Horňáček M., Hudec P., Jorík V., Čaplovičova M., Čaplovič L., Kaliňak M., Smieškova A.: Dehydroaromatization of methane over Mo/ZSM-5 zeolites: influence of aluminum distribution in the crystals (2020) Reaction Kinetics, Mechanisms and Catalysis, 131 (2) , pp. 889-904.
3. Mališová M., Horňáček M., Mikulec J., Hudec P., Hájek M., Peller A., Jorík V., Frolich K., Hadvinová M., Hájeková E.: Transesterification of Camelina sativa Oil Catalyzed by Mg/Al Mixed Oxides with Added Divalent Metals (2020) ACS Omega, 5 (49) , pp. 32040-32050.
4. Mališová M., Hájek M., Kocián D., Malina J., Peller A., Horňáček M.: The influence of various anions in Mg-Al mixed oxides on presence of sodium ions in transesterification of oil (2022) Fuel, 319, art. no. 123781
5. M. Slezáčková, A. Peller, J. Mikulec, M. Banič, J. Blaško, E. Hájeková: Catalytic hydroprocessing of camelina oil/AGO mixtures over NiMoP/ γ-Al2O3 catalysts, Catalysis Today 2022, v tlači

Príspevky z konferencií v zahraničí:

1. HORŇÁČEK, Michal - MALIŠOVÁ, Miroslava - JORÍK, Vladimír - HUDEC, Pavol. Hierarchical ZSM-5 – Preparation and Characterization. In 51. Symposium on Catalysis:

Program, Book of abstracts. 1. vyd. Praha: Ústav fyzikální chemie J. Heyrovského AV ČR, 2019, S. Po12. ISBN 978-80-87351-55-0.
2. HUDEC, Pavol - HORŇÁČEK, Michal - JORÍK, Vladimír - OLLÉOVÁ, Marta. Preparation and characterization of Ni-USY/gama-alumina extrudate catalysts for catalytic decomposition of lignin. In 51. Symposium on Catalysis: Program, Book of abstracts. 1. vyd. Praha: Ústav fyzikální chemie J. Heyrovského AV ČR, 2019, S. Po19. ISBN 978-80-87351-55-0.
3. MALIŠOVÁ, Miroslava - HORŇÁČEK, Michal - HUDEC, Pavol - MIKULEC, Jozef - JORÍK, Vladimír - HÁJEKOVÁ, Elena - SLEZÁČKOVÁ, Martina. Transesterification of Camelina sativa oil on heterogeneous catalyst hydrotalcite to prepare biodiesel. In 51. Symposium on Catalysis: Program, Book of abstracts. 1. vyd. Praha: Ústav fyzikální chemie J. Heyrovského AV ČR, 2019, S. Op03. ISBN 978-80-87351-55-0.
4. HORŇÁČEK, Michal - MALIŠOVÁ, Miroslava - HUDEC, Pavol. The utilization of hierarchical structured ZSM-5 zeolite in chemical processes. In 15th Pannonian International Symposium on Catalysis: Program and Abstracts. 1. vyd. Lublin, Poľsko: New Chemical Syntheses Institute, 2022, S. 115-115. ISBN 978-83-965789-0-7.
5. HUDEC, Pavol. Studies of different zeolite catalysts in petrochemical and refinery conversions of hydrocarbons in Slovakia. In 15th Pannonian International Symposium on Catalysis: Program and Abstracts. 1. vyd. Lublin, Poľsko: New Chemical Syntheses Institute, 2022, S. 40-40. ISBN 978-83-965789-0-7.
6. HUDEC, Pavol - MIKULEC, Jozef - HORŇÁČEK, Michal - PELLER, András - BLAŠKO, Jaroslav. Catalytic transformation of Lignin into valuable fractions and individual hydrocarbons. In 15th Pannonian International Symposium on Catalysis: Program and Abstracts. 1. vyd. Lublin, Poľsko: New Chemical Syntheses Institute, 2022, S. 147-147. ISBN 978-83-965789-0-7.
7. MALIŠOVÁ, Miroslava - FÖTTINGER, Karin - PACHOLIK, Gernot - ALVES, Gustavo Andrade Silva - HORŇÁČEK, Michal. Impact of different synthesis methods of Ni-Mg/Al hydrotalcite on properties and catalytic activity in CO2 hydrogenation. In 20th International Zeolite Conference: Book of Abstracts. 1. vyd. Valencia, Španielsko: GEZ, 2022, S. 1083-1086. ISBN 978-84-09-42100-8.
8. HORŇÁČEK, Michal - OLLÉOVÁ, Marta - HUDEC, Pavol. Hierarchical structured zeolite ZSM-5: application and characterization. In 52nd Symposium on Catalysis: Book of abstracts. 1. vyd. Praha, Česko: J. Heyrovsky Institute of Physical Chemistry of Czech Academy of Sciences, 2021, S. 31-31. ISBN 978-80-87351-58-1.
9. HORŇÁČEK, Michal - KUPCOVÁ, Kristína - JORÍK, Vladimír - HUDEC, Pavol. Hierarchical structured materials: characterization and application. In 8th FEZA Virtual Conference. 1. vyd. Brighton, UK: Federation of European Zeolite Associations, 2021, S. 124-124.
10. HORŇÁČEK, Michal - HUDEC, Pavol. Preparation, characterization and application of hierarchical structured materials. In CHISA 2021, 1. vyd. Praha: Publisher Czech Society of Chemical Engineering, 2021, S. [1-2].
11. HORŇÁČEK, Michal - MIKULEC, Jozef - BLAŠKO, Jaroslav - HUDEC, Pavol. Catalytic hydrotreatment of wheat straw lignin residue to cycloalkanes and aromatics. In CHISA 2021, 1. vyd. Praha: Publisher Czech Society of Chemical Engineering, 2021, S. [1-2].
12. HUDEC, Pavol - HORŇÁČEK, Michal - OLLÉOVÁ, Marta - MIKULEC, Jozef - BLAŠKO, Jaroslav - KUBINEC, Róbert. Two-steps catalytic decomposition and deoxygenation of lignin over acid and difunctional catalysts. In 52nd Symposium on Catalysis: Book of abstracts. 1. vyd. Praha, Česko: J. Heyrovsky Institute of Physical Chemistry of Czech Academy of Sciences, 2021, S. 13-13. ISBN 978-80-87351-58-1.
13. HUDEC, Pavol - HORŇÁČEK, Michal - MIKULEC, Jozef - JORÍK, Vladimír. Catalytic decomposition of lignin over zeolite catalyst. In 8th FEZA Virtual Conference. 1. vyd. Brighton, UK: Federation of European Zeolite Associations, 2021, S. 129-129.
14. MALIŠOVÁ, Miroslava - HORŇÁČEK, Michal - HÁJEK, Martin - HUDEC, Pavol. Preparation of hydrotalcite catalyst for lignin decomposition. In 52nd Symposium on Catalysis: Book of abstracts. 1. vyd. Praha, Česko: J. Heyrovsky Institute of Physical Chemistry of Czech Academy of Sciences, 2021, S. 22-22. ISBN 978-80-87351-58-1.
15. MALIŠOVÁ, Miroslava - HORŇÁČEK, Michal - HUDEC, Pavol - PELLER, Andras - HÁJEKOVÁ, Elena. Impact of different nickel incorporation methods into hydrotalcite to heterogeneous transesterification of Camelina Sativa oil. In 53rd Symposium on Catalysis:

Book of abstracts. 1. vyd. Praha, Česko: J. Heyrovsky Institute of Physical Chemistry of Czech Academy of Sciences, 2022, OP-7. ISBN 978- 80- 87351- 63- 5.
16. HORŇÁČEK, Michal - MALIŠOVÁ, Miroslava - HUDEC, Pavol. The chemical and thermal dealuminated zeolite Y as a catalyst for alkylation of benzene with 1-tetradecene. In 53rd Symposium on Catalysis: Book of abstracts. 1. vyd. Praha, Česko: J. Heyrovsky Institute of Physical Chemistry of Czech Academy of Sciences, 2022, Po-09. ISBN 978-80- 87351- 63- 5.
17. HORŇÁČEK, Michal - HUDEC, Pavol - MALIŠOVÁ, Miroslava- VRETENÁR, Viliam. Characterization of hierarchically structured materials prepared by recrystallization of ZSM-5 zeolites. In 53rd Symposium on Catalysis, Book of abstracts. 1. vyd. Praha, Česko: J. Heyrovsky Institute of Physical Chemistry of Czech Academy of Sciences, 2022, Po-10. ISBN 978- 80- 87351- 63- 5.
18. Kafková V., Ondrejíčková P., Hruška M.: CHEMICAL PRETREATMENT OF INDUSTRIAL LIGNIN BY DISSOLVING IN ORGANIC SOLVE, Proceedings of the 9th International Conference on Chemical Technology, 9th ICCT Mikulov, ČR, 25.-27.4.2022, full text, p. 345-350, ISBN 978-80-88307-11-2,
Citácie:
Horňáčková M., Plavčan J., Horňáček M., Hudec P., Veis P.
Heavy Metals Detection in Zeolites Using the LIBS Method
(2019) Atoms, 7(4), art. no. 98
1) Nisah, K., Rahmi, Ramli, M., Iqhrammullah, M., Mitaphonna, R., Hartadi, B.S., Abdulmadjid, S.N., Md Sani, N.D., Idroes, R., Safitri, E.
Controlling the diffusion of micro-volume Pb solution on hydrophobic polyurethane membrane for quantitative analysis using laser-induced breakdown spectroscopy (LIBS)
(2022) Arabian Journal of Chemistry, 15 (6), art. no. 103812.
2) Iqhrammullah, M., Suyanto, H., Rahmi, Pardede, M., Karnadi, I., Kurniawan, K.H., Chiari, W., Abdulmadjid, S.N.
Cellulose acetate-polyurethane film adsorbent with analyte enrichment for in-situ detection and analysis of aqueous Pb using Laser-Induced Breakdown Spectroscopy (LIBS)
(2021) Environmental Nanotechnology, Monitoring and Management, 16, art. no. 100516.
3) Iqhrammullah, M., Abdulmadjid, S.N., Suyanto, H., Rahmi, Marlina, Kemala, P.
A Review of Membrane-Facilitated Liquid-Solid Conversion: Adding Laser-Induced Breakdown Spectroscopy (LIBS) Multi-Applicability for Metal Analysis
(2021) Journal of Physics: Conference Series, 1951 (1), art. no. 012044.
4) Harmon, R.S., Senesi, G.S.
Laser-Induced Breakdown Spectroscopy – A geochemical tool for the 21st century
(2021) Applied Geochemistry, 128, art. no. 104929.
5) Senila, M., Cadar, O., Miu, I.
Development and validation of a spectrometric method for Cd and Pb determination in zeolites and safety evaluation
(2020) Molecules, 25 (11), art. no. 2591.
6) Iqhrammullah, M., Marlina, Hedwig, R., Karnadi, I., Kurniawan, K.H., Olaiya, N.G., Mohamad Haafiz, M.K., Abdul Khalil, H.P.S., Abdulmadjid, S.N.
Filler-modified castor oil-based polyurethane foam for the removal of aqueous heavy metals detected using laser-induced breakdown spectroscopy (LIBS) technique
(2020) Polymers, 12 (4), art. no. 903.
Horňáček M., Hudec P., Jorík V., Čaplovičova M., Čaplovič L., Kaliňak M., Smieškova A.
Dehydroaromatization of methane over Mo/ZSM-5 zeolites: influence of aluminum distribution in the crystals
(2020) Reaction Kinetics, Mechanisms and Catalysis, 131 (2) , pp. 889-904.
1) Nazari, M., Yaripour, F., Shifteh, S.
Systematic evaluation and optimization of crystallization conditions for an ethanol-templated ZSM-5 zeolite using response surface methodology
(2021) Advanced Powder Technology, 32 (12), pp. 4621-4634.
2) Wang, Z., Ma, A., Yu, Z., Qu, Y., Wang, J.
Mechanism of propane formation during n-butane aromatization over ZSM-5 zeolite
(2021) Reaction Kinetics, Mechanisms and Catalysis, 134 (1), pp. 419-440.
Mališová M., Horňáček M., Mikulec J., Hudec P., Hájek M., Peller A., Jorík V., Frolich K., Hadvinová M., Hájeková E.

Transesterification of Camelina sativa Oil Catalyzed by Mg/Al Mixed Oxides with Added Divalent Metals
(2020) ACS Omega, 5 (49) , pp. 32040-32050.
1) Arshad, M., Mohanty, A.K., Van Acker, R., Riddle, R., Todd, J., Khalil, H., Misra, M.
Valorization of camelina oil to biobased materials and biofuels for new industrial uses: a review
(2022) RSC Advances, 12 (42), pp. 27230-27245.
2) Bitire, S.O., Jen, T.-C., Belaid, M.
Synthesis of beta-tricalcium phosphate catalyst from Herring fishbone for the transesterification of parsley seed oil
(2022) Environmental Technology (United Kingdom), 43 (20), pp. 3175-3187.
Mališová M., Hájek M., Kocián D., Malina J., Peller A., Horňáček M.
The influence of various anions in Mg-Al mixed oxides on presence of sodium ions in transesterification of oil
(2022) Fuel, 319, art. no. 123781
1) Karcz, R., Napruszewska, B.D., Walczyk, A., Kryściak-Czerwenka, J., Duraczyńska, D., Płaziński, W., Serwicka, E.M.
Comparative Physicochemical and Catalytic Study of Nanocrystalline Mg-Al Hydrotalcites Precipitated with Inorganic and Organic Bases
(2022) Nanomaterials, 12 (16), art. no. 2775

**Uplatnenie výsledkov projektu**

Výsledky výskumu sú využiteľné pri vývoji pilotnej jednotky na spracovanie odpadného lignínu z bylinnej biomasy (pšeničná slama, kôrovie z kukurice) ako zdroj frakcie cyklánov a aromátov pre budúce udržateľné letecké palivá. V roku 2025 by mali výrobcovia leteckých palív v EÚ pridávať minimálne 2% takých zložiek do leteckých palív.

**Súhrn výsledkov riešenia projektu a naplnenia cieľov projektu v slovenskom jazyku (max. 20 riadkov)**

Výskumom bolo podrobne analyzované zloženie surového lignínu, ktorý vzniká pri pilotnom projekte rozkladu pšeničnej slamy technológiou parnej explózie pri výrobe bioetanolu. Surový lignín obsahoval zvyšku cukrov, popol a nezanedbateľný podiel nepremennej celulózy, hemicelulózy a časti proteínov. Tieto látky významným spôsobom ovplyvňujú zloženie produktov depolymerizácie a následného upgradingu produktov depolymerizácie. Pre výrobu palív je vhodnejšie surový lignín vyčistiť, ale to zvyšuje náklady na jeho spracovanie. Z testovaných katalyzátorov sú na depolymerizáciu klasické sulfidovaný NiMoP/Al2O3 katalyzátor, ktoré nie je citlivý na prítomnosť zlúčenín síry a dusíka. Vhodné sú aj kyslé katalyzátory na báze Sapo11 a klinoptilolit. Na upgrading produktov depolymerizácie mali najvyššiu aktivitu sulfidovany NiMoP/Al2O3 a Ni-Cu/ zmesný oxid. Vzhľadom k rýchlej deaktivácii katalyzátora je potrebná trojstupňová technológia: prvý a druhý stupeň musí byť realizovaný slurry proces s možnosťou pridávania aktívneho katalyzátora a odoberania deaktivovaného. V treťom stupni je potrebné dohydogenácia prítomných olefínov a oxygenátov.
Proces predstavuje nádejnú technológiu výroby cyklanickej zložky bio-benzínov a najmä cyklanickej a aromatickej časti udržateľných leteckých palív z lignínu, ktorý využíva najmä na výrobu energie. Ciele projektu boli v plnom rozsahu splnené.

**Súhrn výsledkov riešenia projektu a naplnenia cieľov projektu v anglickom jazyku (max. 20 riadkov)**

The composition of the crude lignin produced in a pilot project for the decomposition of wheat straw by steam explosion technology for the production of bioethanol was analysed in detail. The crude lignin contained residual sugars, ash and a non-negligible proportion of non-variable cellulose, hemicellulose and some protein. These substances significantly influence the composition of the depolymerization products and the subsequent upgrading of the depolymerization products. For the production of fuels, it is preferable to refine the crude lignin, but this will increase the cost of processing. From the tested catalysts, the classical sulphidated NiMoP/Al2O3 catalysts for depolymerization are not sensitive to the presence of sulphur and nitrogen compounds. Acid catalysts based on Sapo11 and clinoptilolite are also appropriate. For upgrading the depolymerization products,

NiMoP/Al2O3 sulfided and Ni-Cu/mixed oxide had the highest activity. Due to the rapid deactivation of the catalyst, a three-stage technology is required: the first and second stage must be realized by a slurry process with the possibility of adding active catalyst and removing the deactivated one. In the third stage, dohydrogenation of the olefins and oxygenates present is necessary.
The process represents a promising technology for the production of the cyclanic component of bio-gasoline and in particular the cyclanic and aromatic part of sustainable aviation fuels from lignin, which it uses mainly for energy production. The objectives of the project have been fully met.