

## Progress Report (2023-24)

of

**Collaborative Research Project under  
Indo-Hungarian Strategic Research Fund (IHSRF) of Department of Science and  
Technology of India and National Research, Development and Innovation Office  
(NRDIO) of Hungary.**

**Title of the Project:** Applied Research and development for industrial realization of lignin recycling and conversion to value-added international market products.

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#### From Hungary Side:

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**PROJECT PROGRESS REPORT**  
(2023-2024)

<b>1. Project Title:</b> Applied research and development for industrial realization of lignin recycling and conversion to value-added international market products	<b>DST No:</b>  DST/INT/HUN/P-22/2020
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### 3. Broad area of Research

Green Chemistry

#### 3.1. Sub Area

Biotechnology and Renewable Energy

#### 4. Approved Objectives of the Proposal:

This project is a collaborative applied research and development between Department of Energy and Department of Chemical Sciences, University of Tezpur, Tezpur, India (TU) and Research Centre for Natural Sciences, Institute of Materials and Environmental Chemistry (RCNS) and its consortium partner 3R-BioPhosphate Ltd. company (3R) on the topic of "Biotechnology" and "Renewable Energy" of this call. The main purpose is to full utilization of lignin by-product. We develop innovative technologies for energy, chemical and agricultural applications. The basic objective is to acquire and apply new scientific knowledge to develop valuable market products from lignin. Instead of traditional burning, lignin is transformed into long-life, value-added products. The new products developed earlier are sold by the Hungarian consortium partner (3R) on the international market.

The benefit of the project is to establish circular economy at a number of sectoral levels, such as biotechnology aimed at re-use of by-products, renewable energy, environment and climate protection. Participants have the complementary knowledge, experience, research and development infrastructure necessary to achieve the objectives.

#### Date of Start:

01-04-2021 (Fund was received on 31-03-2020)

#### Total cost of Project:

**48,38,554**

#### Date of completion:

31-03-2024

#### Expenditure as on 31.03.2024:

2023-24: Rs 7,15,197/-

**Progress Reports for (2021-22) from Indian and Hungarian Sides are presented separately below:**

**Progress Report (INDIAN SIDE)**

**1. Objective:**

- To obtain lignin from samples and analyse the physiochemical properties of lignin
- Production of sulfonated activated carbon from Mimusops elengi seeds and Nahor seeds and compare its physiochemical properties.
- To depolymerise lignin using acid –based catalyst using hydrothermal autoclave
- Comparative analysis of depolymerised lignin obtained from reaction with sulfonated activated carbon catalyst.

**2. Methodology :**

Hungarian partners are working on upgrading depolymerised lignin. To obtain marketable products, phenolic compounds are required. Catalytic hydrodeoxygenation (HDO) is one of the depolymerisation upgrading routes, producing a large number of bulk aromatic compounds such as phenols, benzene, toluene, and xylene, as well as alkane fuels. Supported noble-metals and transition metals 24 are found to be active in HDO of Guaiacol (GUA) to cyclohexanone, but high amount of metal were applied. Oxide-supported transition and noble- metal catalysts have been prepared, characterized and tested in HDO reaction by Hungarian partner.

Indian partners are engaging on developing lignin depolymerisation method. Process on extracting Lignin from different biomass samples are going on. TU researchers are also involved in developing a solid acid catalyst to depolymerisation of lignin. Moreover, syntheses of bio-based renewable heterogeneous catalyst are undergoing to be used for lignin depolymerisation.

**3. Introduction:**

The global landscape of energy production and consumption is undergoing a dramatic change caused by various factors, including geopolitical uncertainty, environmental concerns, and technological advancements.<sup>1</sup> The dynamics of energy production and utilization are evolving very rapidly as the globe struggles with issues like pollution, climate change, and energy security. With the increase in population demands for increase in energy production and consumption. In year 2021, India was the third largest energy consumer in the world after China and the USA.<sup>2</sup> India's population is constantly expanding, thus, to fulfil the demands of both modernization and the country's growing population, the pace of energy production needs to keep advancing.

Coal, oil, and natural gas are examples of conventional energy sources that have long served as the foundation of the global energy infrastructure. These sources possess some serious disadvantages, too. Fossil fuel combustion contributes to climate change, air pollution, and negative health effects by releasing

greenhouse gases and other pollutants into the atmosphere. Furthermore, the exploitation and burning of fossil fuels puts the ecosystem at risk of issues like oil spills, water pollution, and habitat destruction. The limited quantity of fossil fuel reserves also adds to geopolitical tensions over resource ownership and accessibility, as well as worries about energy security and price volatility.<sup>3</sup>

In response to these challenges, there is a growing support for renewable energy sources which provide greener, more sustainable fuel substitutes than the traditional fuels. Renewable energy sources harnesses energy from natural processes such as wind, solar, water and biomass to generate heat and electricity. In contrast to fossil fuels, renewable energy technologies operate with little to no greenhouse gas emissions, which helps to reduce global warming and enhance air quality.<sup>4</sup> Moreover, renewable energy sources provide increased energy security and resilience because they are abundant widely distributed, and inexhaustible.<sup>5</sup> One of the most important source of renewable energy which is produced from organic resources such as crops, forestry residues, and organic waste is biomass. Biofuels, derived from biomass, offers liquid or gaseous substitutes for fossil fuels which are produced through a variety of conversion processes such as thermochemical, biochemical etc. Biomass and biofuels offer several advantages, including waste reduction, carbon neutrality and potential for rural development.<sup>6</sup>

Biomass can be categorized into different generations based on feedstock types and conversion technologies. First-generation biomass sources include food crops used to produce biofuel, while Second-generation biomass sources comprise of non-food crops, which offer high sustainability. Third-generation includes micro algae, which hold potential for producing bioethanol more effectively. Through advanced biochemical or thermochemical procedures, lignocellulosic biomass, such as woody plants and agricultural leftovers, can be transformed into bioethanol. Though its commercialization presents certain hurdles, microalgae—microscopic photosynthetic organisms—offer great biomass productivity and the possibility of producing bioethanol or biodiesel.<sup>7</sup>

The primary components of lignocellulosic biomass are composed of cellulose, hemicellulose, and lignin.<sup>8</sup> Lignocellulosic biomass is of particular interest because it is comprised of various plant residues such as wood chips, agriculture residues, and municipal waste.<sup>9</sup> The lignocellulosic biomass comprising plant residue can also be used as feedstock to produce biofuels, biochemical, and various bio-products through processes like physical, chemical, physio-chemical, and biological processes.<sup>10</sup>

Lignocellulosic biomass serves as an abundant and sustainable feedstock for a variety of applications, most notably to produce bioenergy. About 50% of the world biomass is considered as lignocellulosic biomass and its total annual production is estimated to be approximately 10–50 billion tons. Energy security and the reduction of greenhouse gas emissions are enhanced using lignocellulosic biomass for bioenergy, which also reduces reliance on finite fossil fuels.<sup>9</sup>

There are various benefits to using lignocellulosic biomass as a feedstock for ethanol production. Firstly, a steady and dependable supply is guaranteed by its broad availability from sources like forestry residues, energy crops, and agricultural residues. Additionally, lignocellulosic biomass is carbon-neutral or even carbon-negative, as the carbon dioxide emitted during ethanol combustion is offset by the carbon dioxide absorbed during biomass growth.<sup>11</sup>

As shown in the figure below, ethanol production from lignocellulosic biomass involves pre-treatment to

break down the biomass structure as it has a complex structure comprising cellulose, hemicellulose, and lignin. During pre-treatment, cellulose and hemicellulose complexes are hydrolysed with enzymes to release sugar. Yeast and bacteria ferment the sugar that is released during enzymatic hydrolysis. When enzymatic hydrolysis and fermentation take place in a single step, then the process is called simultaneous saccharification and fermentation (SSF). Finally, purification steps such as distillation and molecular sieve techniques are employed to obtain the final product, bioethanol. The remaining part of lignin, which is a natural polymer, can be purified, concentrated, and used to generate heat and electricity for the process.<sup>12</sup>

One of the products of valorization of lignocellulosic biomass produces lignin, which is a complex aromatic biopolymer responsible for providing structural support to plants.<sup>13</sup> Recently; lignin has gained a lot of interest in the field of research due to its unique property, its aromatic structure, and high carbon content. Depolymerisation of lignin is one of the most discussed topics as lignin can be transformed into various platform chemicals such as phenols, vanillin, and syringol which find applications in paint, adhesives, resins, etc.<sup>14</sup> For the depolymerisation of lignin, efficient catalysts are required for the efficient breakage of long molecular chains of lignin to low molecular weight platform molecules.<sup>13</sup>

Extensive study has been done over the use of second-generation biomass sources for energy production.<sup>15</sup> One of the most widely studied topics is the use of non-edible feedstock which does not compete with food and can be easily cultivated as a resource for renewable energy.<sup>16</sup> Nonedible seeds, as shown in the figure below, can be used to produce biodiesel as well as for producing catalysts.<sup>17</sup> Seeds like Nahor, Jatropha, Pongamia, etc., are used for biodiesel production because of their high oil content and suitability for cultivation on marginal lands unsuitable for food crops.<sup>18</sup> Oil is extracted from seeds using mechanical pressing, solvent extraction, or enzyme-assisted extraction and converted into biodiesel through a process called transesterification.<sup>19</sup> After the oil is extracted from the seeds, the leftover de-oiled cake can be utilized as a starting point for the synthesis of heterogeneous catalysts, which can be employed in a variety of chemical processes, including biodiesel production.<sup>20</sup> By repurposing the de-oiled cake for catalyst production, a valuable by-product of biodiesel production is utilized, contributing to resource efficiency and waste reduction.

#### **4. Materials and Methods:**

##### **4.1 Materials**

Wood chips and Coconut coir samples were collected from local market near Tezpur University. Both the samples were first dried in sunlight for two days and further oven—dried at 60°C for another day. It is further grounded and passed through Standard ASTM sieve (Mesh No. 70 and 0.21mm) and finally stored in an air-tight container. *Mimusops elengi* and *Mesua ferrea L.* seeds were collected from Tezpur University Campus, Tezpur (Assam), India. The seeds once collected were allowed to dry in an oven at 110°C to remove all moisture before removal of kernels and oil extraction. The process of oil extraction was done using Soxhlet extraction with the help of hexane as a solvent. Once oil is extracted from the seeds, remaining de-oiled waste cakes (DOWCs) was collected, dried, and grounded prior to carbonisation. Ortho-phosphoric acid and hexane were purchased from Rankem, Sulfanic acid, HCl (37%), H<sub>2</sub>SO<sub>4</sub> (98%) and Benzene were purchased from Merck Life Sciences Pvt. Ltd. The NaNO<sub>2</sub> were purchased from Emplura, Acetone from Fisher Scientific, Ethanol from Cofco Bio-Chemical Co. Ltd., Diethyl ether (98%) from Loba Chemie Pvt. Ltd. And Ethyl acetate from Sisco Research Laboratories Pvt. Ltd. India. All

chemicals were used as received.



(a)



(b)



(c)



(d)

**Fig 1** (a), (b) show raw biomass for catalyst and (c), (d) shows raw biomass for lignin

#### **4.2 Isolation of Lignin:**

It is evident from literature that linkages and functional groups present in the lignin varies from plant to plant and therefore, determination of the extract structure and bonding of lignin is a big challenge for researchers. There are various process such as Kraft lignin, Klason Lignin, organosolv, and soda process for the delignification of wood chips and coconut coir. In this work, Klason method is used for the isolation of lignin from the above-mentioned samples. The process of isolation of lignin from samples was done after the removal of extractives form wood. Extractives are the organic compounds such as resin, tannin, oils, and terpenes (aromatics & volatiles). Below is the description for obtaining extractives free samples.

Grounded Sawdust and Coconut coir each were extracted in a flask reactor and reflux condenser. Fresh sawdust 15 g was extracted with 200 ml ethanol-benzene solvent (1:2 v/v) for 6hrs keeping the liquid stably boiling. After boiling for 5 hrs. samples were transferred to Büchner Funnel to remove the excess solvent with suction. Samples were washed with ethanol to remove benzene and later was again returned to



extraction flask and extracted with 95% ethanol for another 4 hrs. Again, samples were transferred to Büchner Funnel to remove the excess solvent. Further washing was done by distilled water to remove ethanol. Finally, samples were transferred to 1000 ml Erlenmeyer flask and 500 ml of boiling distilled water was added. The flask was heated for an hour in the water bath at a boiling temperature. After the extraction, the sawdust samples and coconut coir were filtered in Büchner Funnel and washed with 500 ml of boiling distilled water. The samples were allowed to air dry thoroughly under room temperature. (TAPPIT264)

Two parallel samples were prepared from the extractive-free samples each 1g dry weight. Samples were placed in 100 ml beaker and 15ml of cold (10 to 15°C) 72% H<sub>2</sub>SO<sub>4</sub> was added. H<sub>2</sub>SO<sub>4</sub> was added gradually in small increments while the material was continuously stirred and macerated with the glass rod. Each beaker is kept at 20±1 °C bath during dispersion of the materials. After the samples were dispersed, each beaker was covered with a watch glass and was kept in a bath at 20±1 °C for 2 hrs. Samples were frequently stirred during the time to ensure complete dissolution. Solid solutions were transferred from beaker to flask separately. Add 300 ml of water in each flask. Further diluting the solution to a 3% conc. H<sub>2</sub>SO<sub>4</sub>. The solution was kept for boiling using flask reactor and reflux condenser for 4 hrs. Later, Lignin was transferred to the filter and hot water was used to wash lignin and further drying it to room temperature.

The acid-insoluble kason lignin contents were calculated in the samples by using the following equation (TAPPI T222 om-06).

$$\text{Lignin}\% = \frac{A \times 100}{W} \quad \dots\dots(1)$$

Where,

A= Weight of lignin (in grams),

W= Oven-dry weight of extractive free samples

Now, 1 gram of each sample of extractive- free sawdust and coconut coir were taken for estimation of % of lignin.

*Table 1: Acid- insoluble lignin contents in the samples*

Sample	No. of Trials	Weight of petri dish (grams)	Weight of petri dish + sample (grams)	Weight of lignin (grams)	% of lignin	Average lignin %
Wood Chips (Sawdust)	Trail 1	34.9603	35.3416	0.3813	38.13	37.7833
	Trail 2	34.6455	35.0121	0.3666	36.66	
	Trail 3	36.3802	36.7658	0.3856	38.56	
Coconut Coir	Trail 1	34.9603	35.3615	0.4012	40.12	41.4833
	Trail 2	34.6455	35.0655	0.4200	42.00	
	Trail 3	36.3802	36.8035	0.4233	42.33	

From the Klason method, 37.78% and 41.48% lignin yield were obtained in wood chips and coconut coir. To avoid any experimental error, all the isolation experiments were performed at least three times to check the reproducibility.



(a)



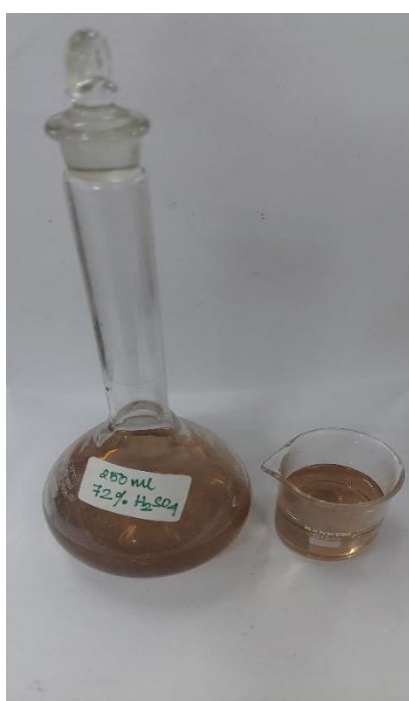
(b)



(c)



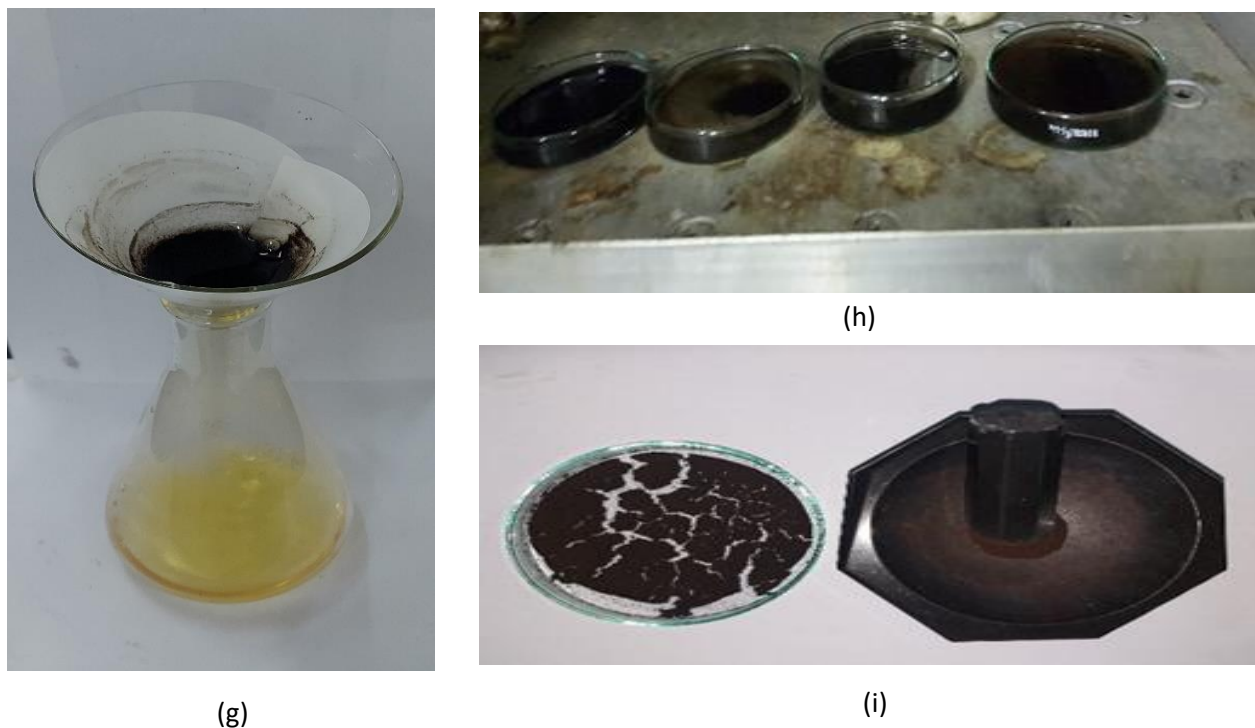
(d)



(e)



(f)



**Fig 2** (a), (b), (c), (d),(e), (f), (g), (h) & (i) show the steps for the isolation of lignin from the coconut coir

### 4.3 Catalyst Preparation:

In current study, chemical activation with phosphoric acid was used in catalyst preparation. In typical method, 20g of finely powdered DOCW of *Mimusops elengi* was soaked in 50% ortho-phosphoric acid at a 1:2 impregnation ratio for 24 hrs. The resulting material was calcined in a muffle furnace at 500 °C for 1 hr in a self-generated atmosphere. The black solid produced was consequently washed with 250 ml of double distilled water, HCl (0.01 mol l<sup>-1</sup>) and finally with 1000-1500 mL hot double distilled water until pH of 6-7 is obtained, followed by drying in oven overnight at 110 °C to obtain the *Mimusops Elengi*- derived activated carbon (MeAC). The carbonised materials were powered using a mortar and pestle and sieved through an ASTM no. 70 sieve to prepare particles with an average size of  $\leq 210\mu\text{m}$ .

Further, Sulfonation was achieved through the covalent attachment of 4-benzenediazoniumsulfonate radicals using two chemicals, i.e. Sulfanilic acid and NaNO<sub>2</sub>. Sufanilic acid is initially dispersed in 1 M HCl aqueous solution (300 mL) in a three-necked ground flask. The temperature is controlled to 3-5 °C with continuous stirring. Later, 10 % excess of NaNO<sub>2</sub> is added dropwise, a clear solution is obtained after addition of NaNO<sub>2</sub>. With continuous stirring of 1 hr at the same temperature, the white precipitate of 4- benzenediazoniumsulfonate is produced, which is filtered of, washed, and moved to a three-necked ground flask with double distilled water (200 mL) and ethanol (120 mL). Then, activated carbon (MeAC, 3g) was added maintaining the temperature at 3-5 °C. Subsequently, 30-32% H<sub>3</sub>PO<sub>2</sub> aqueous solution (100mL) was added. After stirring for 30 min, another 50 mL of H<sub>3</sub>PO<sub>2</sub> aqueous solution was added and allowed to stand for another 1 h with occasional stirring. The obtained



sulfonated AC (MeAC-SO<sub>3</sub>H) was intensively washed first with acetone and distilled water and then dried in the vacuum overnight.



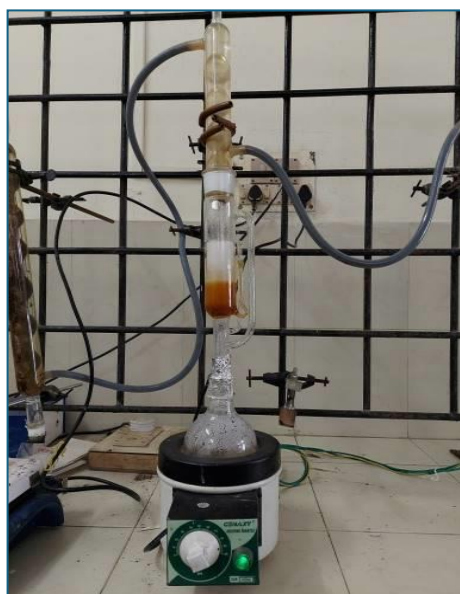
(a)



(b)



(c)



(d)

Fig 3 (a), (b), (c) & (d) show the steps for extraction of oil from *Mimosa elengi* seeds.

#### 4.4 Catalyst Run & Isolated Lignin:

The reaction was performed in a pressurised vessel using a Hydrothermal Autoclave purchased from Amar equipments pvt. Ltd. In a typical reaction, the mass ratio of Lignin/MAC is maintained at 1:1. Similarly, mass ratio of Lignin/solvent (EtOH/H<sub>2</sub>O 1:2v/v) is maintained at 1:60. Firstly, the reactor is

flushed with nitrogen, and the heating of the reactor was started under slow stirring (100 rpm). Once the reaction attains the desired temperature, the stirring rate was increased to 1000 rpm, which is considered to be the starting time of the reaction. Let the reaction cool at room temperature. The catalyst was separated from the reaction mixture by centrifugation and washed thoroughly with EtOH/H<sub>2</sub>O (1:2 v/v) in order to remove any adsorb lignin on the surface of catalyst. After the removal of catalyst from the reaction mixture, acidification of liquid layer was carried out with 2 N HCl solution until pH is 2. This process of acidification helps to separate out higher molecular weight products. Further, centrifugation and filtration process were carried out. The liquid and the solid fractions were subjected to the extraction process for the isolation of products. Organic solvents like DEE and EtOAc were used for lignin isolation. The soluble products were analysed using GC-MS



(a)



(b)



(c)

**Fig 4** (a), (b), (c)& (d) show reactor, resultant reaction mixture and hydrothermal autoclave setup.

## 5. Results and Discussions

With respect to above obtained lignin samples and catalysts are to be characterised using X-Ray diffraction, Energy dispersive X-Ray (EDX) analysis, Thermogravimetric Analysis, UV-Vis spectroscopy and Fourier Transform Infrared Spectroscopy. Similarly, the product obtained from the reaction mixture is to be characterized using GC, GC-MS, and HPLC to find the amount of aromatics compound in the

depolymerised lignin after the completion of the reaction.

### 5.1 FTIR Spectroscopy of Lignin:

The provided FTIR data reveals a complex mixture of compounds. Peaks at  $3444\text{ cm}^{-1}$  and  $1025\text{ cm}^{-1}$  indicate the presence of alcoholic and phenolic groups, as well as alcohols and ethers, respectively. The peak at  $2933\text{ cm}^{-1}$  suggests aliphatic hydrocarbons, while peaks at  $1508\text{ cm}^{-1}$  and  $1142\text{ cm}^{-1}$  confirm the presence of aromatic compounds. Carbonyl-containing compounds, such as ketones, aldehydes, esters, and carboxylic acids, are evident from peaks at  $1707\text{ cm}^{-1}$ ,  $1613\text{ cm}^{-1}$ ,  $1268\text{ cm}^{-1}$ , and  $1216\text{ cm}^{-1}$ , respectively. Additionally, the peak at  $863\text{ cm}^{-1}$  indicates substitutions in the aromatic ring or substituted phenolics. Overall, the sample appears to contain a diverse array of compounds, including alcohols, phenols, aliphatic and aromatic hydrocarbons, ethers, and various carbonyl-containing compounds, with potential substitutions on aromatic rings. The relative intensities and shapes of these peaks could provide further insights into the composition and structure of the sample.

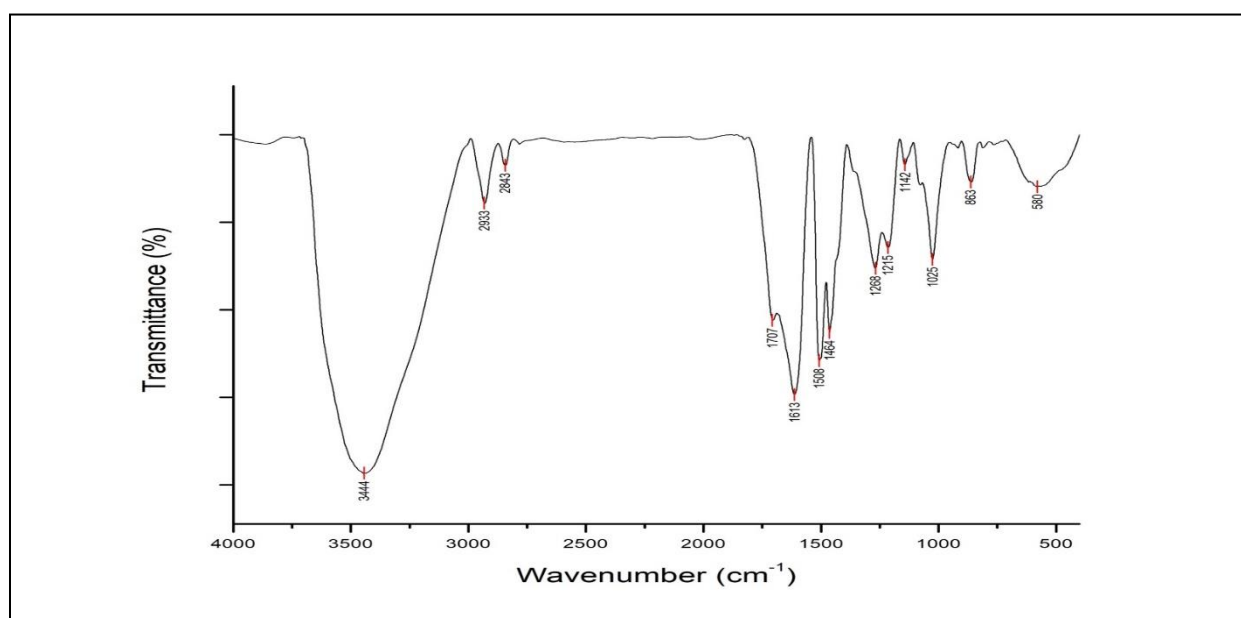


Fig 5: FTIR analysis of lignin

Table 2: Observed peak from FTIR Spectroscopy of lignin

Peaks	Inferences
3444	Alcoholic and phenolic -O-H stretching
2933	-C-H
1707	-C=O
1613	-C=O
1508	Aromatic skeleton vibrations
1464	-C-H bond vibration

1268, 1216	-C-C, -C-O, -C=O stretching
1142	-C-H bonds in aromatic ring
1025	-C-O Stretching in alcohol, ether
863	Substitutions in aromatic ring or substituted phenolics

## 5.2 FTIR Spectroscopy of Catalyst:

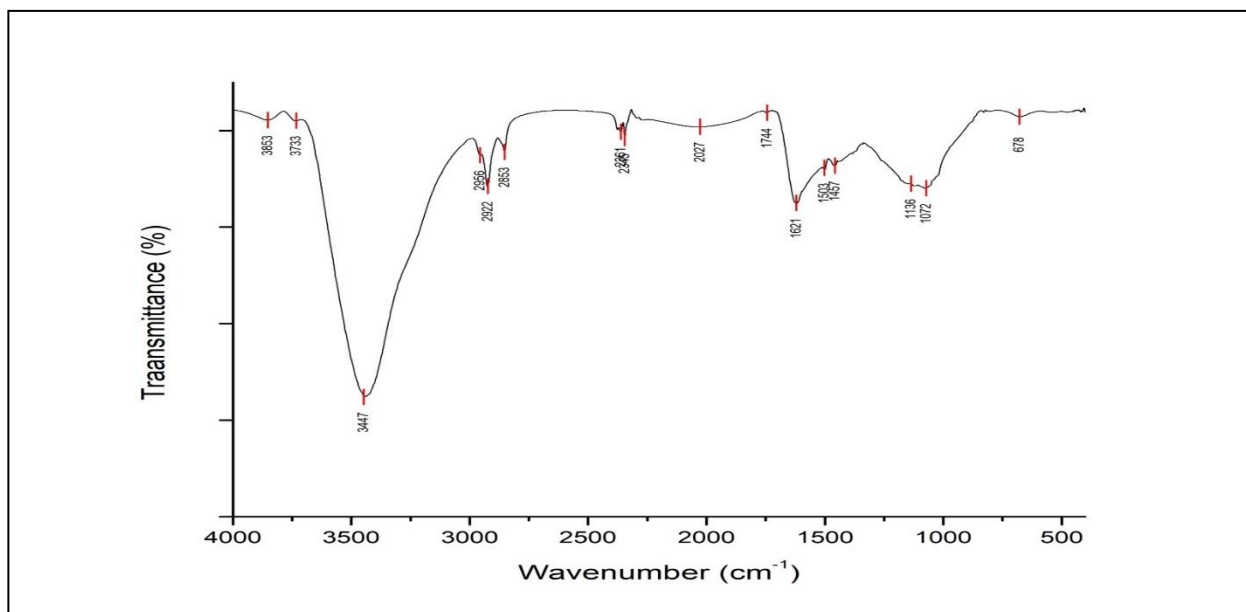


Fig 6: FTIR analysis of catalyst

Table 3: Observed peak from FTIR Spectroscopy of catalyst.

Peaks	Inferences
3447	-O-H
1744,1621	-C=O
1072	-S=O
1136	-SO <sub>3</sub> H

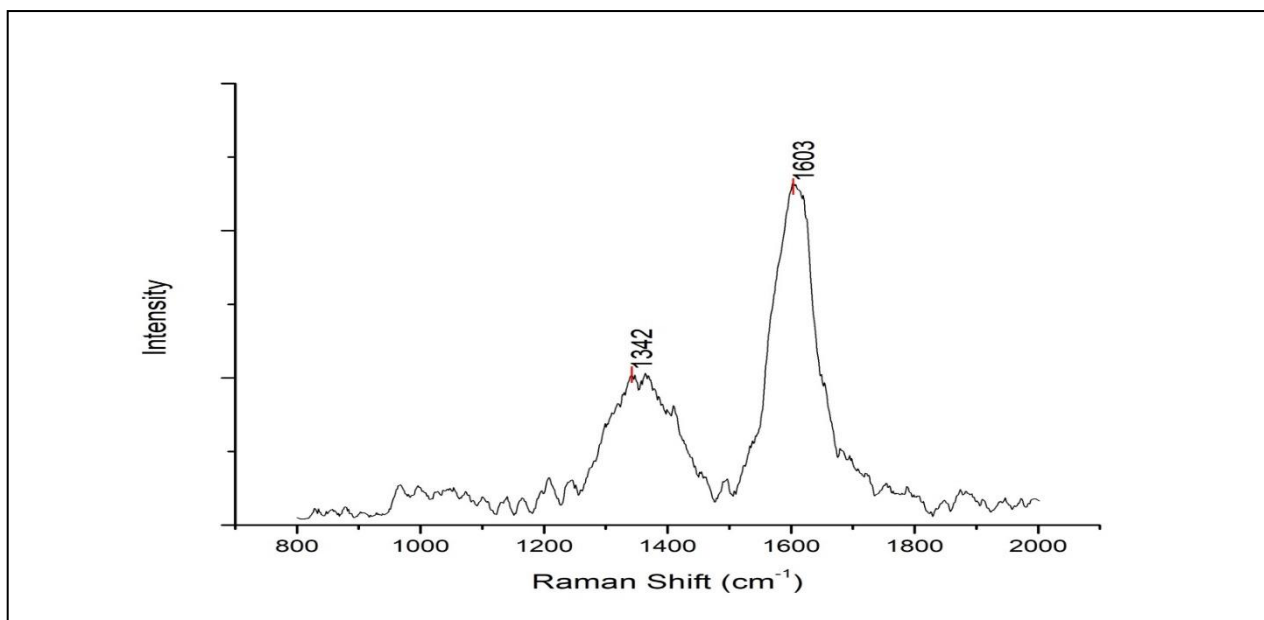
The provided FTIR data suggests the presence of specific functional groups within the sample. The peak at 3447 cm<sup>-1</sup> indicates the presence of hydroxyl groups (-OH), typically found in alcohols or phenols. Peaks at 1744 cm<sup>-1</sup> and 1621 cm<sup>-1</sup> indicate the presence of carbonyl groups (-C=O), which can be attributed to various compounds such as ketones, aldehydes, esters, or carboxylic acids. The peak at 1072 cm<sup>-1</sup> suggests the presence of sulfoxides (-S=O), indicating the presence of compounds containing sulphur. Additionally, the peak at 1136 cm<sup>-1</sup> indicates the presence of sulfonic acid groups (-SO<sub>3</sub>H). Overall, the data suggests the sample contains compounds with hydroxyl, carbonyl, sulfoxide, and sulfonic acid functional groups.

### 5.3 Raman Spectroscopy of catalyst:

The provided Raman spectroscopy data indicates the presence of characteristic peaks associated with graphene-like structures. The peak at  $1603\text{ cm}^{-1}$  corresponds to the G band peak, which represents the  $E_{2g}$  mode of vibration in graphitic carbon. This peak is associated with the planar configuration of  $sp^2$ -bonded carbon atoms in graphene sheets. It's a signature of the graphitic structure, indicating the presence of  $sp^2$  hybridized carbon atoms in a hexagonal lattice.

Additionally, the peak at  $1342\text{ cm}^{-1}$  corresponds to the D-band peak, which arises due to defects or disorder in the graphene structure. Specifically, it's associated with the breathing mode of  $sp^2$  carbon rings in disordered or defective regions. The D band is often used as an indicator of the degree of disorder or the presence of defects in carbon-based materials like graphene.

Therefore, based on this Raman spectroscopy data, it can be inferred that the sample contains graphene-like structures, with the G band peak confirming the presence of graphitic carbon and the D band peak indicating some level of disorder or defects within the graphene structure.



**Fig 7:** RAMAN analysis of catalyst

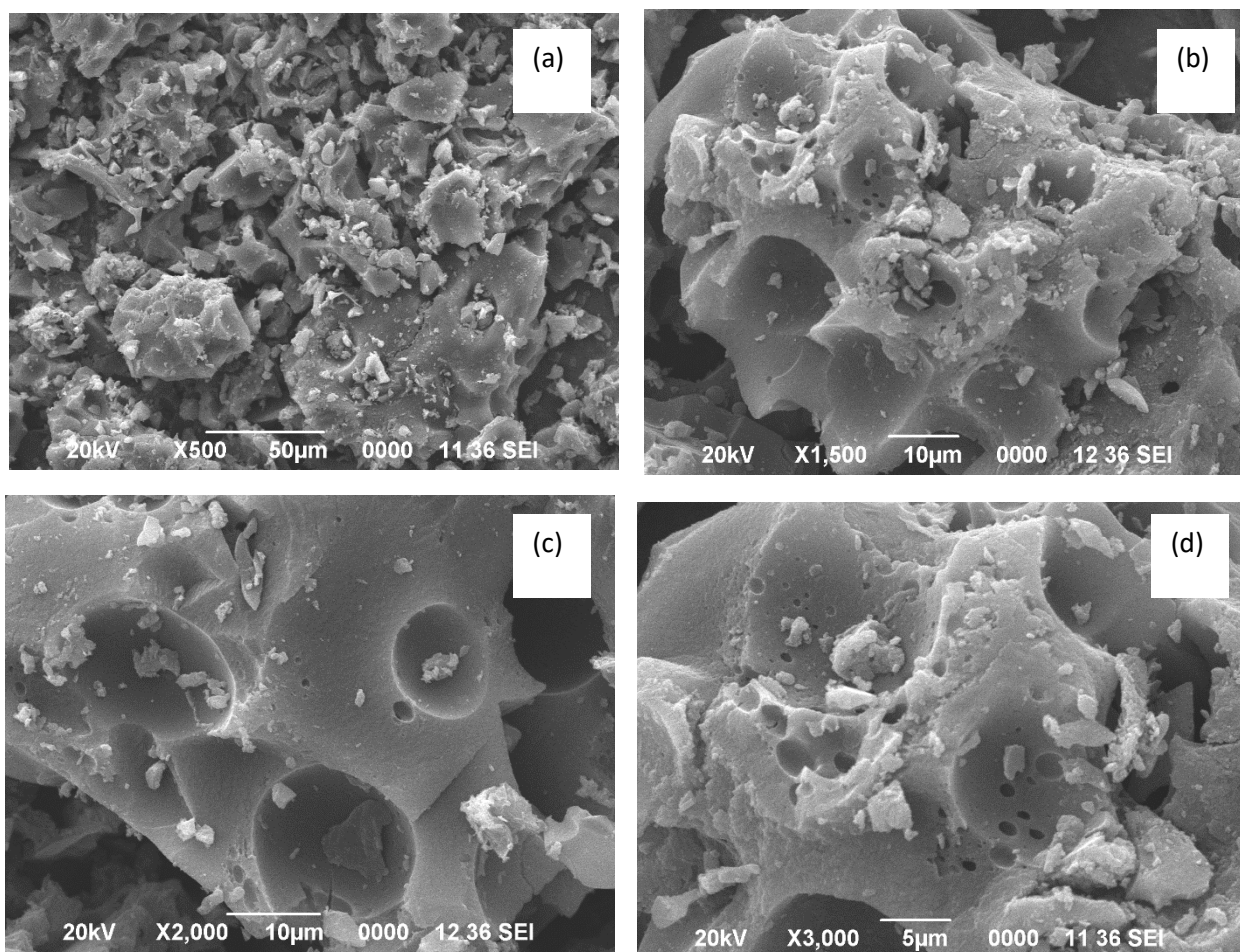
Table 4: Observed peak from RAMAN Spectroscopy of catalyst.

Peaks	Inferences
1603	G band peak (planar configuration $sp^2$ bonded carbon that constitutes graphene)
1342	D-band peak (ring breathing mode from $sp^2$ carbon rings)



#### 5.4 SEM images of catalyst:

Here are the SEM images of the MeAC catalyst at different magnification values. It can be observed from the above images that the catalyst shows the characteristics of high porosity and have irregular shapes. This non-uniformity in the pore size could affect catalytic activity in different regions of the catalyst. As shown in Fig a we can observe the large surface area, which is beneficial for catalytic reactions as it provides more active sites for molecules to interact.



**Fig 8:** SEM images of Catalyst

#### 6. New Observation:

- Klason method is considered as the superior option for the isolation of lignin as this provides accurate and precise measurements of lignin content. This process is much more specific as it targets the lignin fraction, thus reducing interference from other biomass components such as carbohydrates.
- The FTIR data for lignin indicates presence of various functional groups, such as alcohols, phenols, ethers, hydrocarbons, and carbonyl-containing compounds suggesting that the sample is originated from a naturally derived substance. This presence of diverse functional groups suggests that the depolymerised products could serve as versatile chemical feedstocks, which can be utilised in variety

of synthetic processes to create many different compounds and intermediates.

- The FTIR data of catalyst shows a prominent peak at  $3447\text{ cm}^{-1}$  indicating the presence of hydrogen bonding. The role of such bonding could enhance the catalytic activity by stabilizing transition states or intermediates in various chemical reactions. Also, peak  $1072$  and  $1136\text{ cm}^{-1}$  indicates the presence of sulfonic acids which are highly polar in nature and can significantly improve the catalyst's performance in acid-catalysed reactions.
- In Raman Spectroscopy, the presence of graphitic carbon (G band) is advantageous for catalytic applications as it can provide high electrical conductivity, stability, and a large surface area for catalytic reactions. The presence of defects (D band) within the graphene structure can play a significant role in catalysis. Defects can introduce active sites that enhance the reactivity of the catalyst. These sites can facilitate the adsorption and activation of reactants, thereby improving the overall catalytic efficiency.
- As the SEM image of catalyst indicates that the material is of high porosity and large surface area which will likely enhance the reactivity of the catalyst and lead to high conversion rates. But it also shows irregular pores which may cause mass transfer limitations, smaller pores might restrict the diffusion of larger reactant, while larger pores may not be as efficient in adsorbing smaller molecules.

**7. Innovations:** Production of renewable heterogeneous catalyst which is used for depolymerisation of lignin.

**8. Application Potential:**

**8.1 Long Term:** Following the global strategy for completely replacing carbon footprints, scientific advancement of its circle exploitation as a renewable energy source and carbon-reducing technologies, and creation of value-added biofuel and chemicals from lignocellulosic biomass.

**8.2 Immediate:** Chemical laboratory for replacing synthetically produced organic chemical by naturally synthesised chemicals in various chemical reactions.

**9 Any Other:** The incumbent JRF of the project was released from his assignment on 21-10-2019 as he joined in GATE Fellowship stream of Govt. of India and Mr Arun Kantholi was appointed as JRF in the project on 28-10-2021. In the year 2022, Mr. Arun Kantholi was released, and Ms. Aparna Rani Seal was appointed as Project Associate-I on 17<sup>th</sup> October 2022 till 31<sup>st</sup> March 2023. For the last financial year 2023-24, Ms. Aparna Rani Seal was appointed again as Project Associate-I for the tenure from 1<sup>st</sup> August 2023 to 31<sup>st</sup> March 2024.

**10 Research work which remains to be done under the project (for on-going projects)**

1. For clear understanding on the functional groups and bonding in the depolymerised lignin structure, FTIR and GC-MS is to be performed along with HPLC to confirm the formation of aromatics.
2. A comparative analysis of catalyst obtained from *Mimusops elengi* seeds and *Mesua Ferrea* L. on the depolymerisation of Klason lignin obtained from Coconut coir and Sawdusts.
3. Further characterisation of catalyst is to be performed.

**11 References:**

- [1] Sovacool, B. K. (2017). Reviewing, Reforming, and Rethinking Global Energy Subsidies: Towards a Political Economy Research Agenda. *Ecological Economics*, 135, 150–163.

<https://doi.org/10.1016/j.ecolecon.2016.12.009>

- [2] "BP Statistical Review of World Energy 2021," BP, June 2021. (<https://www.bp.com/en/global/corporate/energy-economics/statistical-review-of-world-energy.html>)
- [3] Davis, Steven J., et al. "Net-zero emissions energy systems." *Science* 360.6396 (2018): eaas9793.
- [4] Intergovernmental Panel on Climate Change (IPCC). (2018). Special report on global warming of 1.5°C. Retrieved from <https://www.ipcc.ch/sr15/>
- [5] REN21. (2020). Renewables 2020 Global Status Report. Retrieved from <https://www.ren21.net/reports/global-status-report/>
- [6] International Renewable Energy Agency (IRENA). (2019). Biofuels: a sustainable energy source. Retrieved from <https://www.irena.org/publications/2019/Jan/Biofuels-A-Sustainable-Energy-Source>
- [7] Kumar, A., Ergas, S., Yuan, X., Sahu, A., Zhang, Q., & Dewulf, J. (2019). A review on algae-based biofuel production and recent developments. *Sustainable Energy Reviews*, 107, 78-107.
- [8] Sun, S., Sun, S., Cao, X., & Sun, R. (2016). The role of pretreatment in improving the enzymatic hydrolysis of lignocellulosic materials. *Bioresource Technology*, 199, 49-58.
- [9] Cherubini, F. (2010). The biorefinery concept: using biomass instead of oil for producing energy and chemicals. *Energy Conversion and Management*, 51(7), 1412-1421.
- [10] Himmel, M. E., Ding, S. Y., Johnson, D. K., Adney, W. S., Nimlos, M. R., Brady, J. W., & Foust, T. D. (2007). Biomass recalcitrance: engineering plants and enzymes for biofuels production. *Science*, 315(5813), 804-807.
- [11] Sims, R. E., Mabee, W., Saddler, J. N., & Taylor, M. (2010). An overview of second-generation biofuel technologies. *Bioresource Technology*, 101(6), 1570-1580.
- [12] Hendriks, A. T., & Zeeman, G. (2009). Pretreatments to enhance the digestibility of lignocellulosic biomass. *Bioresource Technology*, 100(1), 10-18.
- [13] Ragauskas, A. J., Beckham, G. T., Biddy, M. J., Chandra, R., Chen, F., Davis, M. F., ... & Saddler, J. N. (2014). Lignin valorization: improving lignin processing in the biorefinery. *Science*, 344(6185), 1246843.
- [14] Zakzeski, J., Bruijninx, P. C., Jongerius, A. L., & Weckhuysen, B. M. (2010). The catalytic valorization of lignin for the production of renewable chemicals. *Chemical Reviews*, 110(6), 3552-3599.
- [15] Hosseini, S. E., Wahid, M. A., & Ganjloo, A. (2020). Biomass energy potential in South and Southeast Asia: Current status and future prospects. *Biomass Conversion and Biorefinery*, 10(2), 271-289.
- [16] Gnansounou, E., Dauriat, A., & Villegas, J. D. (2009). A comprehensive outlook of biofuels. *Bioresource Technology*, 100(17), 1649-1650.
- [17] Nasrin, R., Rahim, A., & Pang, S. F. (2016). A comprehensive review on biodiesel fuel production and recent technologies. *Renewable and Sustainable Energy Reviews*, 63, 160-173.
- [18] Kumar, A., Ergas, S., Yuan, X., Sahu, A., Zhang, Q., & Dewulf, J. (2019). A review on algae-based biofuel production and recent developments. *Sustainable Energy Reviews*, 107, 78-107.
- [19] Knothe, G. (2010). Biodiesel and renewable diesel: A comparison. *Progress in Energy and Combustion Science*, 36(3), 364-373.
- [20] Xu, Y., Su, B., Wu, X., & He, M. (2017). Acidic ionic liquid-functionalized rice husk ash as an efficient heterogeneous catalyst for biodiesel production. *Energy & Fuels*, 31(4), 3690-3698.

**12 Exchange Visits undertaken:** Yes, Principal Investigator, Dr. Dhanpati Deka and Project Associate- I, Ms. Aparna Rani Seal visited Institute of Materials and Environmental Chemistry, Research Centre for

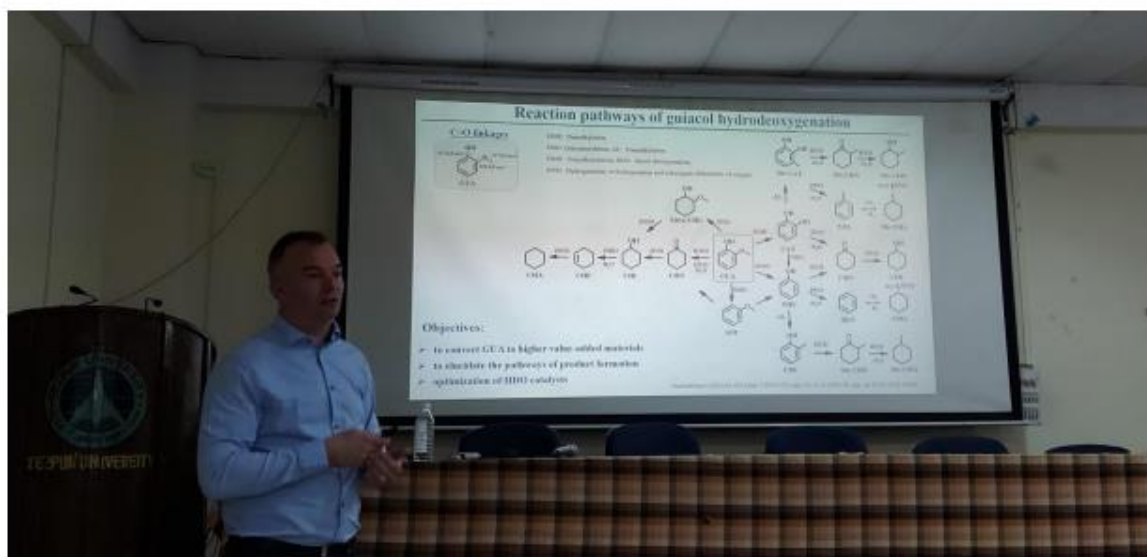
Natural sciences, Hungary on 28<sup>th</sup> January 2024 to 4<sup>th</sup> February 2024. During the visit, we have addressed the project's progress, highlighting key milestones achieved and challenges faced. We have also presented the detailed PowerPoint presentation, showcased findings and provided a comprehensive overview of the work completed. This was followed by an engaging discussion where both parties exchanged insights, identified potential solutions to overcome current limitations, and strategized on the next steps to ensure the project's successful continuation.

### **13 The Visit of Two Hungarian Scientist to the Department of Energy, Tezpur University**

Recently, our institute Tezpur University had the privilege of hosting two Scientist from Hungary, Dr. Gyula Novodárszki and Dr. Robert Barthos who are the researchers working on the project under the leader of Dr. Magdolna R. Mihályi. They have visited our Department of Energy on 23rd of November-30th November 2023.

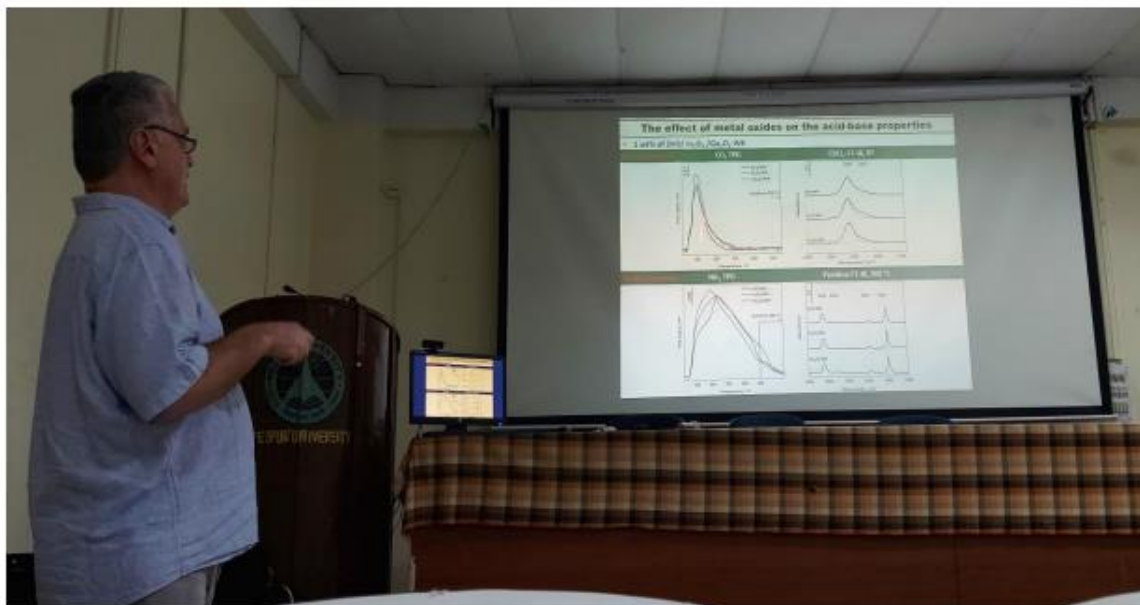
#### **Dr. Gyula Novodárszki**

During his visit to Tezpur University, he delivered a lecture on the topic 'Hydroconversion of lignocellulose-derived molecules over oxide-supported catalysts'. He discussed about the importance of lignocellulosic biomass conversion to different chemicals and fuels. He highlighted the need of quality improving treatment before utilization or storage of bio-oil obtained from lignin and how the catalytic hydrodeoxygenation of the bio-oils gives value-added products, such as fuel additives, industrial solvents, and precursors for the polymer and fine chemical industry.



Dr. Gyula also talked about his research work on hydroconversion of Guaiacol model feedstock over  $\gamma\text{-Al}_2\text{O}_3$  and phosphatized- $\gamma\text{-Al}_2\text{O}_3$  ( $\gamma\text{-Al}_2\text{O}_3(\text{P})$ ) supported Ni-based catalysts which resulted in products such as catechol methylcatechols and other partially and fully deoxygenated, saturated, and unsaturated products.

**Dr. Robert Barthos**



Dr. Robert Barthos presented a lecture on “Catalytic conversion of ethanol to butadiene over MgO-SiO<sub>2</sub> catalysts: effects of texture, structural heterogeneity and metal-oxide promoters on the catalytic activity’ during his visit. He shared insights in the production of butadiene from bioethanol. His research work where they have utilized MgO–SiO<sub>2</sub> samples, having the composition of natural talc (NT), as catalysts for the ethanol-to-1,3-butadiene reaction were discussed in detail during the presentation. He also talked about the role of promoters such as ZnO, Ga<sub>2</sub>O<sub>3</sub> and In<sub>2</sub>O<sub>3</sub> in increasing the surface concentration of the reactant and reaction intermediates, thereby increasing the rates of conversion and 1, 3-Butadiene (BD) yield.

During their visit, Dr. Gyula Novodárszki and Dr. Robert Barthos had the opportunity to tour our institute’s analytical centre, where they gained insight into the advanced technologies and resource available for scientific research. They went through all the working sophisticated machines required for clearer understanding over the characterization of samples crucial for synthesis of catalysis using biomass. They also visited different departments in the university and got opportunity to interact and discuss with other researchers and faculty members, fostering a broader exchange of ideas and expertise.

<b>PhDs produced no.: 1</b> (Ongoing)	<b>Technical Personnel trained: 2</b>	<b>Research Publications arising out of the present project: 2</b>
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**List of Publications from this Project (including title, author(s), journals, year(s) and Impact Factor****A. Papers published only in cited Journals (SCI)**

- [1] Hydroconversion of lignin-derived platform compound guaiacol to fuel additives and value-added chemicals over alumina-supported Ni catalysts. Gyula Novodárszki, Ferenc Lónyi, Balázs Csík, Magdolna R. Mihályi, Róbert Barthos, József Valyon, Anna Vikár, Dhanapati Deka, Zoltan Pászti, Yuting Shi and Hanna E. Solt. et. al. Applied Catalysis A, General, Elsevier (2024), Impact Factor: 4.7.
- [2] Ethanol Coupling Reactions over MgO–Al<sub>2</sub>O<sub>3</sub> Mixed Oxide-Based Catalysts for Producing Biofuel Additives. Vikár, A.; Lónyi, F.; Makoye, A.; Nagy, T.; Novodárszki, G.; Barthos, R.; Szabó, B.; Valyon, J.; Mihályi, M.R.; Deka, D.; et al. Molecules (2023), Impact Factor: 4.2

**B. Papers published in Conference Proceedings, Popular Journals etc.**

Nil

**Patents filed/ to be filed:** Nil

**Any Difficulty in carrying out the project (Bottlenecks):** Fund was not received timely & third instalment is not received till date.

**Major Equipment (Model and Make):** Nil

S.No.	Sanctioned List	Procured (Yes/ No) Model & make	Cost (Rs in lakhs)	Working (Yes/No)	Utilisation Rate (%)
	Nil				

**INDO-HUNGARIAN INTER-GOVERNMENTAL SCIENCE &  
TECHNOLOGY**

**COOPERATION PROGRAMME**

(HUNGARIAN SIDE)

**Title of the project:** *Applied research and development for industrial realization of lignin recycling and conversion to value-added international market products*

**Project Duration:** 3 years (1<sup>st</sup> February 2021- 31<sup>st</sup> January 2024)

**A. Research Centre for Natural Sciences and 3R- Bio phosphate Ltd. Signed a consortium cooperation agreement for the implementation of the project**

**1. Approved Objectives of the Proposal:**

**Research Centre for Natural Sciences (RCNS)**

- catalyst preparation and physio-chemical characterization by XRD, TEM, TPR, FT-IR spectroscopy
- determination of optimal catalytic HDO conditions
- development of lignin analysis for TU
- development of the analysis method for the fermentation products obtained from 3R

**3R-BioPhosphate Ltd.(3R)**

- selection of lignin decomposition fungi
- development of optimal conditions for the liquid and solid fermentation process
- development of analysis methods fermentation

**2. Description of the project including methodology**

**1. Research Centre for Natural Sciences (RCNS)**

Prepared 4 supported catalysts for the hydrodeoxygenation (HDO) of Guaiacol, a typical product of lignin depolymerization. They developed the exact recipe for preparing the catalyst. Noble metal (Pd) and transition metal (Ni) catalysts supported on phosphorus-modified and unmodified  $\gamma$ -alumina were prepared. The catalysts were characterized by physio-chemical and surface chemical methods. The optimal conditions for the catalytic HDO reaction were determined. An analytical system was developed to determine the qualitative and quantitative composition of liquid and gaseous reaction products.

With the cooperation of Tezpur University (TU) they applied and thoroughly investigated various lignin characterization procedures, such as CHNO elemental analysis, infrared spectroscopy, and size exclusion chromatography.

**2. 3R-BioPhosphate Ltd.(3R)**

Performed a qualitative laboratory study of the lignocellulosic activity to select the appropriate enzyme-producing saprophytic fungal strain. Based on the in-vitro enzyme activity test, 1 strain of lignin-degrading fungus - *Trichoderma reesei* ST4B strain - was successfully selected, which also successfully grew on wheat straw as a substrate containing lignocellulose. They determined the optimal conditions for the two-stage, liquid/solid phase fermentation process of the fungus strain in liquid fermenters with a capacity of 3x5 litres/batch and in a solid fermenter with a capacity of 10 kg/batch. They developed microscopic microbiological monitoring and cultivation on solid nutrients for liquid fermentation, while the progress of solid fermentation was followed by direct visual



detection, microscopic monitoring and CFU (colony forming unit) determination. They carried out material handling and technical tests in large laboratory conditions for the carbonization process of lignin-containing straw and horse manure to produce efficient biochar and bio-oil green power. They found that biochar production is technically and economically feasible. However, biochar can only be used as a small amount of biotechnological carrier material or as an additional material for compost. As of this July, due to a change in EU legislation, the agricultural utilization of biochar produced by pyrolysis from the lignin by-product of paper mills is not permitted, therefore 3R focused on the carbonization of lignocellulose.

### **3. Preparation and characterization of catalysts for the hydro conversion of lignin monomer**

Lignocellulose-based biomass is abundant on Earth, a carbon dioxide-neutral renewable raw material and energy source. Its processing is an alternative option to produce biofuels and chemicals. The economics of bio refineries can be significantly increased by catalytic value-added conversion of the lignin component of lignocellulose. Lignin is a biopolymer composed of substituted phenyl groups. Bio-oils obtained from the thermochemical/catalytic transformation, the so-called bio-oxygenates mainly contain oxygen-containing aromatic compounds. Their oxygen content can be significantly reduced by catalytic hydrogenation deoxygenation (HDO reaction). One of the constituent monomers of lignin is coniferyl alcohol. A similar phenol derivative is guaiacol (2-methoxyphenol, GUA). In catalytic hydrogenation, hydrogenolysis, dehydration and dehydroxylation reactions, demethylation, demethoxylation, alkylation/dealkylation/trans alkylation can be converted into chemical substances that can be, for example, chemical intermediates, polymer components, fuels, or solvents. It is a challenge to selectively transform them into aromatic and saturated compounds because they contain both C<sub>Ar</sub>-O, C<sub>Ar</sub>-O-C and aromatic unsaturated C=C bonds. The complex HDO reaction requires different catalytic functions; therefore, the presence of different catalytically active sites (metal, acid, base, or combinations thereof) is required in the catalyst.

In the first year of the project, our task was to produce oxide-supported heterogeneous catalysts suitable for the hydrogenation deoxygenation (HDO) of guaiacol/4-propyl-guaiacol, a typical product of lignin depolymerisation, and to determine their physicochemical characteristics. Furthermore, we aimed to optimize the guaiacol HDO reactions.

We prepared oxide supported noble metal and transition metal catalysts. The first step of the work process was the development of the catalyst preparation method. A commercial  $\gamma$ -alumina support was modified with phosphoric acid. The purpose of the surface modification was to reduce the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> Lewis acidity, the number of acid centres and the acid strength of the support. We chose a transition metal (Ni) and a noble metal (Pd) as components with hydrogenating activity. The modified and unmodified dehydrated, porous solid support was impregnated with an aqueous solution of metal precursors Pd(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> and Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O. We selected the optimal metal solution concentration, solution/solid support ratio, drying and thermal decomposition conditions. We determined the optimal metal content. The synthesized samples were characterized by

various physicochemical methods: specific surface area and porosity by N<sub>2</sub> isotherm method, morphology by transmission electron microscopy (TEM), phase composition by X-ray powder diffraction (XRD), acidity by pyridine adsorption infrared spectroscopy

(FT-IR), metal reducibility by hydrogen temperature- with programmed reduction (H<sub>2</sub>-TPR). Metal dispersion was determined by hydrogen chemisorption. In the case of Ni, we changed the reduction temperature for optimal metal dispersion. We determined the optimal conditions for the hydrogen conversion implemented in the GUA continuous-flow, fixed-bed micro reactor (reaction temperature, total pressure, catalyst mass, reactant feed (space time), hydrogen/reactant molar ratio).

The results of the preliminary experiments were presented as a lecture at the online International Conference on Reaction Kinetics, Mechanisms and Catalysis (RKMC21) May 20-22, 2021. ([RKMC website \(akcongress.com\)](http://akcongress.com))

We also dealt with the catalytic transformation of levulinic acid, which can be produced from the cellulose component of lignocellulose. The results of the joint work were presented as a poster at the 8th Conference of the Federation of European Zeolite Association (FEZA 2021) held virtually, on July 5-9, 2021. (8th Conference of the Federation of European Zeolite Associations (FEZA 2021) ([rsc.org](http://rsc.org)))

**In cooperation with the Indian partner (TU)**, we studied lignin characterization methods: size exclusion chromatography to determine molecular weight distribution, and Fourier transform infrared spectroscopy to examine the structure of lignin.

The planned exchange visits both the Indian and the Hungarian side was successfully performed in the month of January i.e. On 28<sup>th</sup> January 2024 to 6<sup>th</sup> Feb 2024.

#### **4. Microbiological preparation of lignin fermentation and biochar system design**

The task of the first year is the innovative biotechnological formulation of the microbial solid carrier of biochar or biophosphate from the carbonization process with integrated liquid and solid fermentation, as well as the selection of potential lignin-degrading fungal microorganisms from the *Trichoderma reesei* strain, which is well adapted to Central European and continental climatic conditions. During the selection of microorganisms, we considered the following aspects: isolation of natural soil microorganisms, which have favourable agronomic properties; they should be suitable for breaking down lignin and turning it into compounds that can be taken up by plants. The fungus is adapted to the surfaces of the microbial solid carrier, which is connected to the optimized integration of the existing biochar production system suitable for the carbonization of lignin. This project does not develop a biochar production pyrolysis thermal system, but rather optimizes and integrates the biochar system already successfully implemented by 3R to produce a product prototype for large-scale laboratory integrated liquid and solid fermentation. To produce biochar, which is also the microbial carrier during solid fermentation, we examined two main lignocellulose-containing raw materials: straw-containing horse stable manure and wheat straw, as well as paper sludge waste. In the process, it was established that in accordance with the EU 2019/1009 and EU 2021/2088

regulations, biochar (CMC14) produced from wheat straw as a plant/animal by-product and horse stable manure can be authorized as an EU crop-enhancing material and can then be marketed, but the biochar produced from industrial paper sludge pyrolysis material cannot be authorized or placed on the market for agricultural use after July 16, 2022. These clauses were adopted by the EU in 2021 during the detailed development of the main EU regulation 2019/1009. Therefore, in the future, our work aims at the production of an integrated liquid and solid fermentation product prototype of the biochar microbial carrier produced from plant/animal by-products, and we consider the paper sludge experiments to be closed. In general, *Trichodermas* are characterized by the production of extracellular enzymes (cellulases, chitinases, proteases) that break down biopolymers and substances with antibiotic effects, intense microparasitism and good saprobiont competition. The lignin-degrading fungus *Trichoderma reesei* ST4B occurs under natural conditions in soils, in decomposing organic matter, and has adapted to this environment during evolution. The task of the first year is to select economically available nutrients, to determine the optimal conditions for the liquid and solid fermentation process (time, selection of the fermentation method, pH, temperature, mixing, etc.), and to develop methods suitable for microbiological monitoring of the fermentation. Regarding the formulation of biological preparations, it was important to face one of the biggest challenges, to review and evaluate the fulfilment of the goal according to the challenge. The goal was to bridge the gap between the microbial cell mass produced in the laboratory on a special culture medium on a small scale, at high cost, and the formulated preparation suitable for commercial circulation. We carried out a qualitative study of the lignocellulose-decomposing activity to select the appropriate strain, as well as an examination of the cellulase enzyme activity and lignin-decomposing capacity of the *Trichoderma* strains. Based on this, we determined the optimal conditions for the liquid and solid fermentation process (time, choice of fermentation method, pH, temperature, mixing, etc.) and it was established that the application of the integrated two-stage, liquid-solid phase fermentation process provides an optimal opportunity and is suitable from an economic point of view to produce a preparation. We have also defined methods suitable for microbiological monitoring of fermentation.

## B. Hydrodeoxygenation of lignin-derived guaiacol on supported Pd and Ni catalysts using neat and phosphorous-modified $\gamma$ -alumina supports

### Gas-phase hydrodeoxygenation of lignin-derived guaiacol and phenol on Ni catalysts using neat and phosphorous-modified $\gamma$ -alumina supports

Gy. Novodárszki<sup>1\*</sup>, B. Szabó<sup>1</sup>, R. Barthos<sup>1</sup>, H. Solt<sup>1</sup>, J. Valyon<sup>1</sup>, E. Someus<sup>2</sup>, D. Deka<sup>3</sup>, F. Lónyi<sup>1</sup>, M.R. Mihályi<sup>1</sup>

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**Keywords:** guaiacol, phenol, hydrodeoxygenation, Ni/alumina

**Introduction.** Lignocellulosic biomass is a promising feedstock for the production of renewable chemicals and fuels. Lignin is polymeric component of lignocellulose, comprising of methoxylated phenylpropane monomers. In thermochemical and/or chemical processes, lignin can be converted into liquid products (bio-oils) with a high oxygen content, which mainly consist of aromatic compounds. The oxygen content of bio-oxygenates can be significantly reduced by catalytic hydrodeoxygenation (HDO) reaction [1]. Guaiacol (GUA), a representative component of bio-oil, is commonly used as a model compound in the HDO processes. Products obtained from GUA like cyclohexane (CHN), cyclohexanol (CHL), phenol (PHE), catechol (CAT), benzene (BEN), and toluene (TOL) can be used as fuel, solvent or precursors of nylons, chemicals, polymers, drugs, herbicides, cosmetics, and plastics [2]. The main objective of the present study is to understand the HDO reaction of GUA and PHE model compounds into value-added products. The effect of surface modification and the reaction conditions such as space time, temperature, and pressure as well as time-on-stream on the catalyst activity and selectivity was studied.

**Experimental/methodology.** Ni catalysts were prepared by wet impregnation using  $\gamma$ -alumina ( $\text{Al}_2\text{O}_3$ , Alfa Aesar) and phosphorous-modified  $\gamma$ -alumina ( $\text{Al}_2\text{O}_3(\text{P})$ ) supports. Modification was done with  $\text{H}_3\text{PO}_4$  solution. The Ni content was 5 and 20 wt%. The catalysts were characterized by XRD,  $\text{H}_2$ -TPR and FT-IR spectra of adsorbed pyridine and phenol. Catalytic experiments were carried out using a flow-through, tubular, fixed-bed microreactor at 10 bar total pressure in the 200–300 °C temperature range, whereas the space time was varied between 0.1 and 1.0  $\text{g}_{\text{cat}} \text{g}_{\text{GUA/PHE}}^{-1} \text{h}$ .

**Results and discussion.** Demethylation and transalkylation are the main reactions of GUA over Lewis acid  $\text{Al}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3(\text{P})$  supports giving CAT derivatives as main products. On 5Ni/ $\text{Al}_2\text{O}_3$  and 20Ni/ $\text{Al}_2\text{O}_3$  catalysts, O-free compounds like cycloalkanes and BEN derivatives were mainly formed at 300 °C and 10 bar. At higher temperatures, the thermodynamic equilibrium shifts toward dehydrogenation reaction resulting in mainly BEN derivatives. At lower temperature (225 °C) and/or space time CHL derivatives were also formed in larger quantities. However,  $\text{Al}_2\text{O}_3(\text{P})$  supported Ni catalysts were stable and selective in the formation of PHE derivatives. They catalyze demethylation and demethoxylation but do not initiate ring saturation. In order to clarify the different catalytic behavior, the adsorption complexes formed from PHE chemisorption was investigated by FT-IR spectroscopy. Results show that adsorbed phenolates species are formed on the neat  $\gamma$ - $\text{Al}_2\text{O}_3$  support, which is necessary for further deoxygenation. However, a weak interaction was observed on the  $\text{Al}_2\text{O}_3(\text{P})$  support. Phosphatization was shown to result in partial elimination of Lewis type acid-base pair sites and thereby lowering the surface concentration of phenol intermediates on these sites, which in turn hindered the hydrogenation of the aromatic ring. It was concluded that by using non-noble metal, supported on pure  $\gamma$ -alumina and phosphatized  $\gamma$ -alumina, and adjusting the reaction conditions, the GUA hydroconversion could be directed towards selective formation of required target compound.

#### Acknowledgments

The authors thank the Ministry of Innovation and Technology for its support from the National Research, Development and Innovation Fund within the framework of the 2019-2.1.13-TÉT\_IN program (Project No.: 2019-2.1.13-TÉT\_IN-2020-00043). The research was also supported by the ÚNKP-22-4 New National Excellence Program of the Ministry for Culture and Innovation from the source of the National Research, Development and Innovation Fund.

#### References

- [1] Kim, E. et al. *Green Chem.* **2019**, *21*, 3715–3743. [2] Li, X. et al. *Renew. Sustain. Energy Rev.*, **2017**, *71*, 296–308.



# Poster:



## Gas-phase hydrodeoxygenation of lignin-derived guaiacol and phenol on Ni catalysts using neat and phosphorous-modified $\gamma$ -alumina supports

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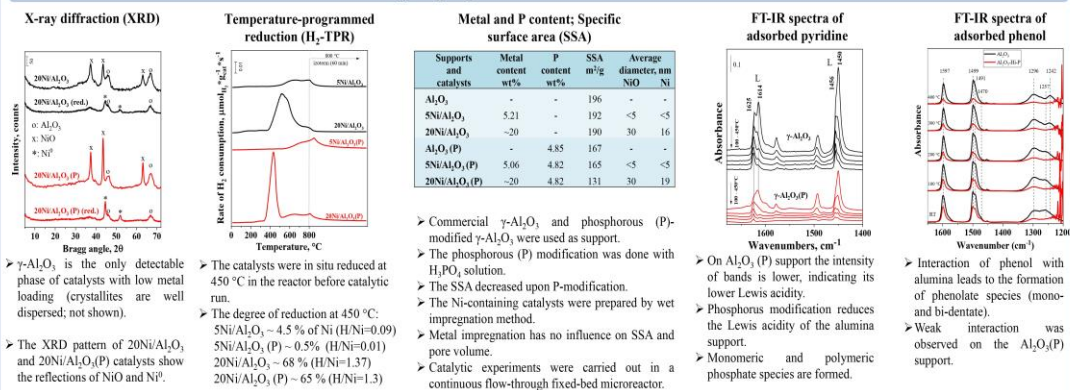


### Introduction

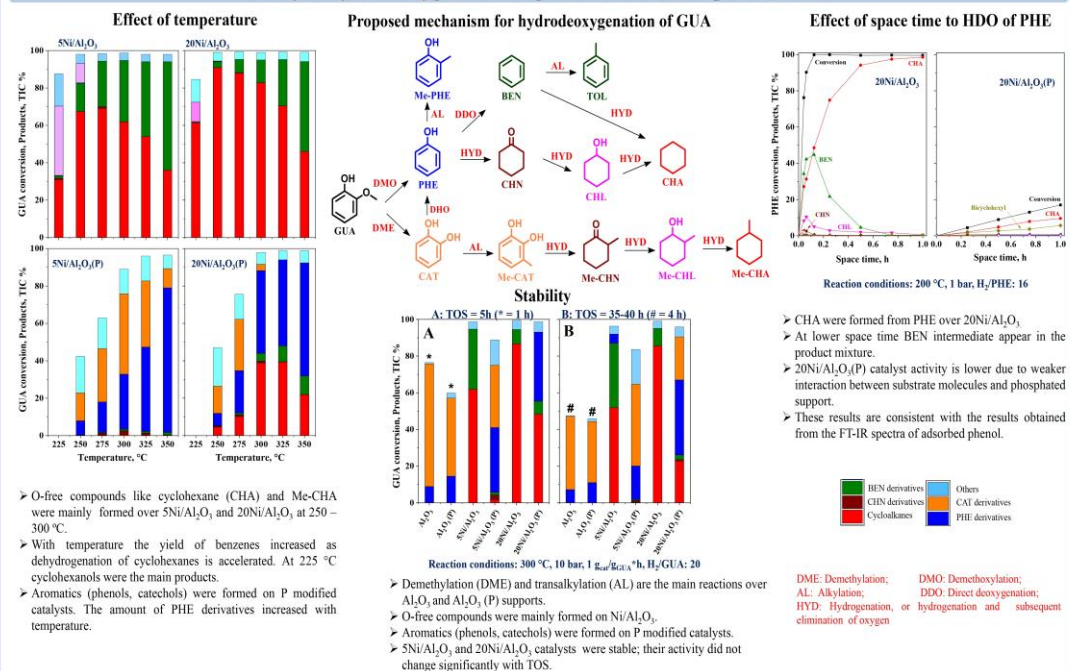
Lignocellulose is the major non-food component of biomass comprising three fractions such as cellulose, hemicellulose and lignin. Decomposition/depolymerizations of lignin results in lower molecular weight polymers and phenolic monomers. Guaiacol (GUA) is the most abundant product obtained from lignin, contains both major functional groups of lignin-derived phenolics, such as hydroxyl (-OH) and methoxy (-O-CH<sub>3</sub>). Catalytic hydrodeoxygenation (HDO) of GUA is a potential route to the value-added products [1]. Liquid hydrocarbons obtained by total HDO of GUA can be used as biofuel. The selective partial HDO of GUA results in the formation of oxygenated products like cyclohexanol (CHL). These oxygenates are industrial precursors of nylons. The demethylation and/or demethoxylation of GUA leads to the formation of aromatic products like benzene, toluene, xylenes (BTX), phenols and catechols, which are important precursors for many commercial chemicals and polymers [2,3]. In the present study  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and phosphorous-modified  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-supported Ni catalysts were investigated in HDO of GUA using a fixed-bed flow-through microreactor.

[1] Bioresource Technology 2015, 178, 108; [2] Fuel 2015, 150, 175; [3] Applied Catalysis B: Environmental 2021, 285, 119826

### Catalysts preparation and characterization



### Catalytic hydrodeoxygenation of guaiacol (GUA) and phenol (PHE)



### Conclusions

- The sequential steps of GUA hydroconversion can be controlled by modifying the alumina support.
- Demethylation of GUA on Al<sub>2</sub>O<sub>3</sub> and phosphorous modified Al<sub>2</sub>O<sub>3</sub>(P) supports leads to catechol formation.
- Ni/Al<sub>2</sub>O<sub>3</sub> catalyzed hydroconversion of GUA to O-free compounds like cyclohexane.
- At lower temperature and space time cyclohexanols were formed in large amounts.
- With temperature the yield of benzenes increased.
- Ni/Al<sub>2</sub>O<sub>3</sub>(P) catalysts are selective to aromatics. These catalysts remain active in demethylation and demethoxylation, but lose their ability to hydrogenate the aromatic ring. Weak interaction of phenol intermediate was observed on the Al<sub>2</sub>O<sub>3</sub>(P) support.

### Acknowledgment

The authors thank the Ministry of Innovation and Technology for its support from the National Research, Development and Innovation Fund within the framework of the 2019-2.1.13-TÉT-IN program (Project No.: 2019-2.1.13-TÉT-IN-2020-00043). The research was also supported by the UNKP-22-4 New National Excellence Program of the Ministry for Culture and Innovation from the source of the National Research, Development and Innovation Fund.



## C. Hydrodeoxygenation of levulinic acid over Pd/ZrO<sub>2</sub> catalyst

### 1. Introduction:

- Levulinic acid (LA) can be produced from sugar, which can be obtained for instance, from lignocellulosic waste and by-products, acid-catalysed process even at an industrial scale.[1]
- The most important product of LA hydrogenation (HDO) is  $\gamma$ -valerolactone (GVL) that can be blended with gasoline, and is intermediate to get liquid alkenes, polymers and fine chemicals.
- Both homogenous and heterogeneous Nobel metal (mainly Ru) and non-noble metal (Cu, Ni) catalysts are applied for the HDO of LA.[2]
- Pd, supported on carbon, silica or niobia were also investigated as catalysts. Only few papers have been published about utilizing Pd/ZrO<sub>2</sub> catalyst.
- Palladium chloride is a widely used precursor for the preparation of oxide-supported Pd catalysts. Thermal decomposition of the Pd precursor, impregnated on the support, results in a catalyst, retaining chloride that can either accelerates or suppress reactions.

#### Study of the chloride effect

- Development of novel preparation method to produce chloride-free zirconia-supported Pd catalyst (Pd/ZrO<sub>2</sub>(NH<sub>4</sub>)) for efficient HDO of LA to GVL.
- For comparison a catalyst was prepared by calcining H<sub>2</sub>PdCl<sub>4</sub>-impregnated zirconia (Pd/ZrO<sub>2</sub>(Cl)).

### 2. Catalyst preparation

#### Pd/ZrO<sub>2</sub>(NH<sub>4</sub>)

Physical mixture of commercial zirconia (MEI Inc.) and PdCl<sub>2</sub> was simply immersed and stirred in aqueous solution of ammonia. The thus formed Pd-tetraammine complex was reduced with hydrazine, depositing metallic Pd nanoparticles on the zirconia surface. By washing out the formed NH<sub>4</sub>Cl, the catalyst became totally chloride free.

#### Pd/ZrO<sub>2</sub>(Cl)

Wet impregnation with aqueous solution of the metallic precursor H<sub>2</sub>PdCl<sub>4</sub> (Vega and Camji 99.9%) on the ZrO<sub>2</sub> support.

Both catalysts were dried at 80°C for 24 h, calcined air flow at 400°C for 4 h. Before catalytic run the catalysts were in-situ reduced at 350°C for 1 h in H<sub>2</sub>.

### 3. Characterisation:

#### 3.1. Raman Spectroscopy

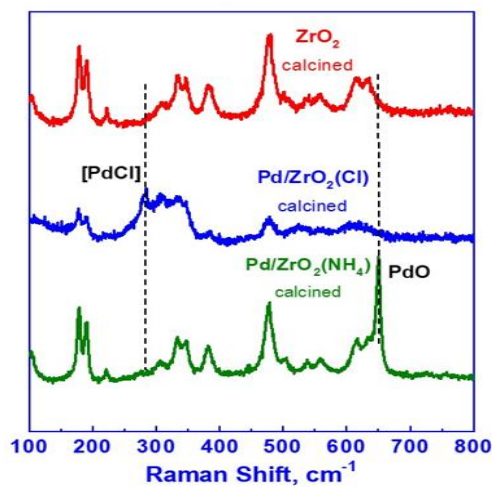


Figure 1: Comparison based on Raman Spectra

- Pd/ZrO<sub>2</sub> (Cl) contains chloride, bound to the zirconia support and/ or to the metal;
- Pd/ZrO<sub>2</sub>(NH<sub>4</sub>) has no chloride- containing species

#### 3.2. *In-situ* XRD in H<sub>2</sub> flow

- In H<sub>2</sub>- Pd-hydride (PdH) was formed in both catalysts at room temperature.
- At 350°C the PdH phase released hydrogen and metallic Pd is detected in Pd/ZrO<sub>2</sub>(NH<sub>4</sub>). Cooling the catalyst to room temperature the PdH phase reappeared.
- No metallic Pd was detected for the reduced Pd/ZrO<sub>2</sub>(Cl) catalyst, i.e., crystallite size was lower than 5nm. Pd is detectable in the presence of hydrogen only in PdH phase.

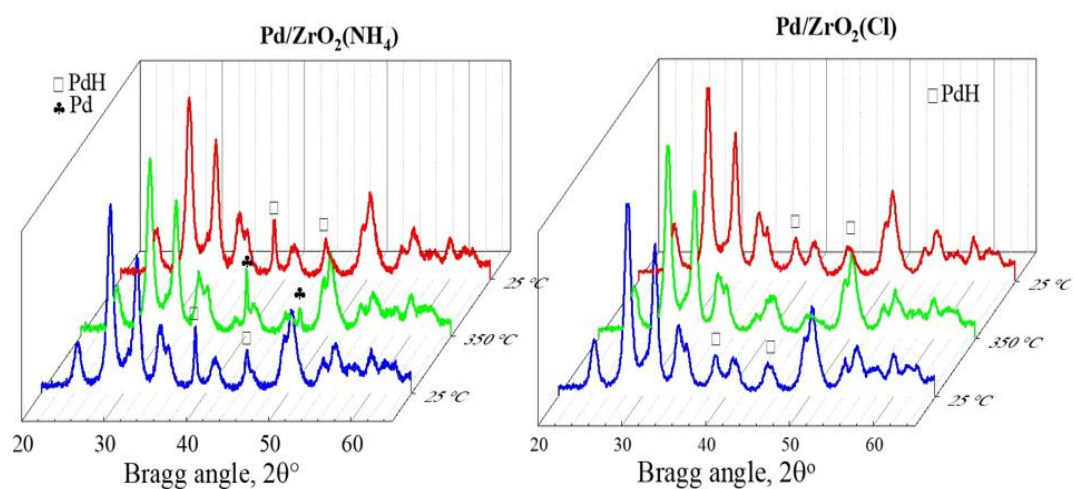
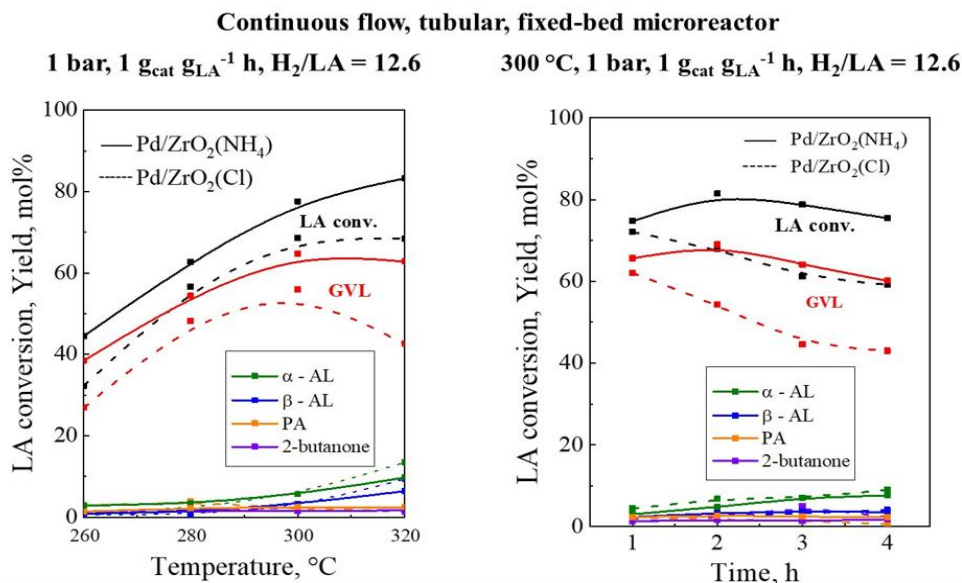


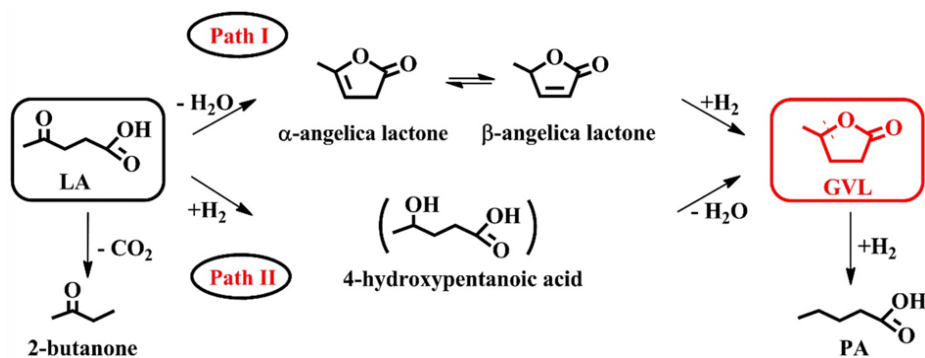
Figure 2- XRD analysis

#### 4. Catalytic activity and stability in the HDO OF LA



**Figure 3:** LA conversion yield vs Temperature(°C) and Time (h)

- The LA conversion and GVL yield are higher on the chloride-free catalyst (Pd/ZrO<sub>2</sub>(NH<sub>4</sub>)).
- The Pd/ZrO<sub>2</sub>(NH<sub>4</sub>) is more stable at 300°C.
- Angelica lactones intermediated ( $\alpha$ -AL,  $\beta$ -AL), pentanoic acid (PA) and 2-butanone by-products were also formed.



#### 5. Conclusion:

- Chloride-free zirconia-supported Pd catalyst was successfully prepared using Pd-chloride as Pd source.
- At atmospheric pressure, in presence of hydrogen, in the temperature range of 280-320°C, zirconia-supported Pd catalysts are active in LA hydrodeoxygenation to GVL through angelica lactone (AL) intermediate. LA is first dehydrated to unsaturated lactones and then hydrogenated to GVL.



- A fraction of  $\alpha$ - AL intermediate was isomerised to  $\beta$ - AL. Formation of a low amount of 2-butanone indicated that decarboxylation of levulinic acid also occurred. By-product pentatonic acid (PA) was formed in GVL hydrogenolysis.
- Although the Pd dispersion was higher in Pd/ZrO<sub>2</sub>(Cl) than in Pd/ZrO<sub>2</sub>(NH<sub>4</sub>), the latter catalyst showed better catalytic performance in LA hydrodeoxygenation. Higher LA conversion, higher selectivity to GVL and higher stability were achieved over the chloride- free catalyst than over the chloride- containing one.

## 6. References:

- [1] J.J. Bozell, L. Moens, D.C. Elliot, Y. Wang, G.G. Neuenschwander, S.W. Fitzpatrick, R.J. Bilski, J.L. Jarnefeld, *Resour. Conserv. Recyc.* **28**, 227 (2000)
- [2] S. Dutta, I.K.M. Yu, D.C.W. Tsang, Y.H. Ng, J.S. Ok, J. Cherwood, J.H. Clark, *Chem. Eng. J.*, **372**, 992 (2019). W.L.H. Wright, R. Palkovits, *Chem. Sus.Chem.* **5**, 1 (2012).

## D. Ethanol- Coupling reactions over MgO, MgO-SiO<sub>2</sub>, and MgO-Al<sub>2</sub>O<sub>3</sub> catalysts: The effect of promotion by transition metal oxide

### Ethanol-coupling reactions over MgO, MgO-SiO<sub>2</sub>, and MgO-Al<sub>2</sub>O<sub>3</sub> catalysts: The effect of promotion by transition metal oxide

B. Szabó<sup>1</sup>, Gy. Novodárszki<sup>1</sup>, B. Horváth<sup>2</sup>, E. Someus<sup>3</sup>, D. Deka<sup>4</sup>, J. Valyon<sup>1</sup>, R. Barthos<sup>4\*</sup>

<sup>1</sup>Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Magyar tudósok körútja 2, Budapest 1117, Hungary

<sup>2</sup>Slovak University of Technology in Bratislava, Faculty of Chemical and Food Technology, Ralinského 9, 81237 Bratislava, Slovakia

<sup>3</sup>3R-BioPhosphate Ltd., Kajászó, Hungary

<sup>4</sup>Biomass Conversion Laboratory, Department of Energy, Tezpur University, Tezpur, India

\*barthos.robert@ttk.hu

**Keywords:** ethanol, butanol, butadiene, MgO, MgO-SiO<sub>2</sub>, MgO-Al<sub>2</sub>O<sub>3</sub>,

**Introduction.** The formation of carbon-carbon bonds is of great importance in chemical technologies. Bioethanol, as a renewable source, can serve as raw material of important chemical products, such as, biofuels and biochemicals. Recently, the heterogeneous catalytic ethanol-coupling reactions, giving 1,3-butadiene (Lebedev reaction) or n-butanol (Guerbet reaction) were receiving special attention. It was proposed that the successive reactions of ethanol take place on a single multifunctional catalyst that either contains spatially separated active sites with hydrogenation/dehydrogenation, C-C coupling and optionally dehydrating activity, or on a catalyst in which ensembles of active sites are able to induce all the mentioned transformations of a 4-carbon activated surface complex.

A common intermediate of the Lebedev and Guerbet reactions is crotyl alcohol. The 1,3-butadiene is formed by dehydration, whereas butanol is obtained by hydrogenation of this intermediate. It is well known that over MgO-SiO<sub>2</sub> and MgO-Al<sub>2</sub>O<sub>3</sub> mixed oxide catalysts butadiene and butanol is formed, respectively, with high selectivity. Neat MgO is also known to have a high catalytic efficiency in ethanol coupling, mainly producing butanol and crotyl alcohol. Our present study concerns the role of transition metal oxide additives on the ethanol coupling reactions.

**Experimental/methodology.** Structure and properties of catalyst preparations was characterized by XRD, STEM, EDS, N<sub>2</sub> physisorption. The binding of acidic and basic adsorbates, such as CO<sub>2</sub>, CDCl<sub>3</sub>, and NH<sub>3</sub>, pyridine, respectively, to the catalyst surface was studied by TPD, and FT-IR measurements. Catalytic reactions were carried out using a fixed bed, continuous flow microreactor at atmospheric pressure. The adsorbed intermediate species formed in the reaction were identified by operando FT-IR measurements.

**Results and discussion.** Butadiene and butanol were the main ethanol conversion products formed over MgO-SiO<sub>2</sub> and MgO-Al<sub>2</sub>O<sub>3</sub> catalysts, respectively, whereas butanol and crotyl alcohol were obtained over pure MgO catalyst. The effect of transitional metal oxide promoters was investigated on the activity of pure MgO. Over Y<sub>2</sub>O<sub>3</sub>, Ga<sub>2</sub>O<sub>3</sub>, ZnO, and CuO promoted catalysts the product distribution was similar to that obtained by pure MgO catalyst under identical reaction conditions. However, the conversion was slightly higher due to the Lewis acidic character of the additives and butadiene also appeared among the products. Relative to above mentioned catalysts, promotion of MgO by Nb<sub>2</sub>O<sub>5</sub> or Ta<sub>2</sub>O<sub>5</sub> resulted in higher dehydrogenating activity, and high butadiene selectivity, while the formation of butanol and crotonaldehyde was suppressed. High acetaldehyde selectivity showed that In<sub>2</sub>O<sub>3</sub> promoter increased dehydrogenation activity. The modification ZrO<sub>2</sub> strongly enhanced dehydration, bringing about high butadiene and ethylene selectivities.

Catalytic test reactions using promoted mixed oxides are in progress, as well as, reactions of possible intermediates, and their mixtures.

#### Acknowledgments

The authors thank the Ministry of Innovation and Technology for its support from the National Research, Development and Innovation Fund within the framework of the 2019-2.1.13-TÉT\_IN program (Project No.: 2019-2.1.13-TÉT\_IN-2020-00043).

## Poster:

# Ethanol-coupling reactions over MgO, MgO-SiO<sub>2</sub>, and MgO-Al<sub>2</sub>O<sub>3</sub> catalysts: The effect of promotion by transition metal oxide

B. Szabó<sup>1</sup>, Gy. Novodárszki<sup>1</sup>, B. Horváth<sup>2</sup>, E. Someus<sup>3</sup>, D. Deka<sup>4</sup>, J. Valyon<sup>1</sup>, R. Barthos<sup>1\*</sup>

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<sup>2</sup>Slovak University of Technology in Bratislava, Faculty of Chemical and Food Technology, Ralinského 9, 81237 Bratislava, Slovakia

<sup>3</sup>3R-BioPhosphate Ltd., Kajászó, Hungary

<sup>4</sup>Biomass Conversion Laboratory, Department of Energy, Tezpur University, Tezpur, India

\*barthos.robert@ttk.hu

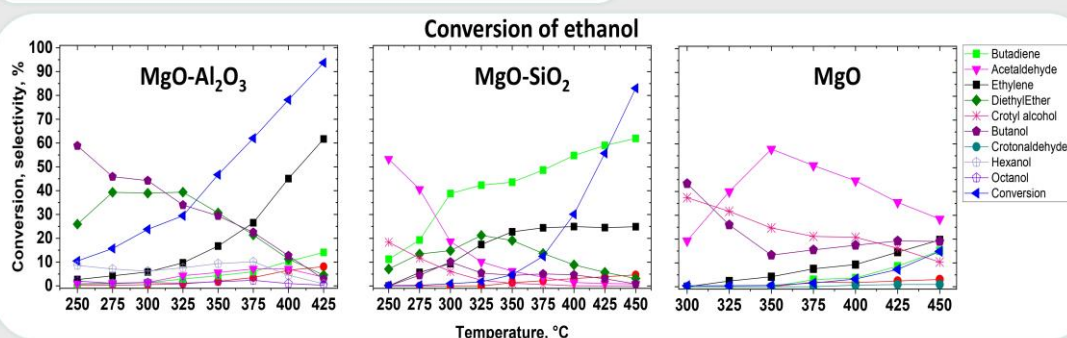


### Introduction

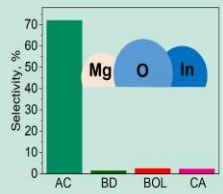
Bioethanol, as a renewable source, can serve as raw material of important chemical products. Recently, the heterogeneous catalytic ethanol-coupling reactions, giving 1,3-butadiene or n-butanol were receiving special attention. It was proposed that the successive reactions of ethanol take place on a single multifunctional catalyst that either contains spatially separated active sites with hydrogenation/dehydrogenation, C-C coupling and optionally dehydrating activity, or on a catalyst in which ensembles of active sites are able to induce all the mentioned transformations of a 4-carbon activated surface complex. The 1,3-butadiene is formed by dehydration, whereas butanol is obtained by hydrogenation of this intermediate. It is well known that over MgO-SiO<sub>2</sub> and MgO-Al<sub>2</sub>O<sub>3</sub> mixed oxide catalysts butadiene and butanol is formed, respectively, with high selectivity. Neat MgO is also known to have a high catalytic efficiency in ethanol coupling, mainly producing butanol and crotyl alcohol. Our present study concerns the role of transition metal oxide additives on the ethanol coupling reactions.

### Experimental/methodology

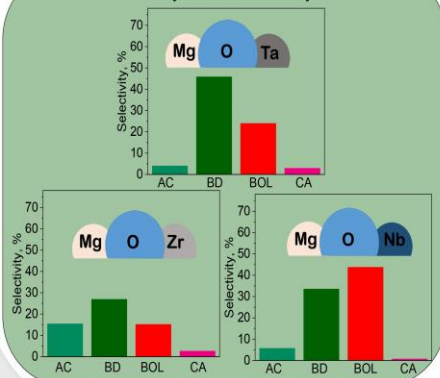
Catalytic reactions were carried out using a fixed bed, continuous flow microreactor at atmospheric pressure. The adsorbed intermediate species formed in the reaction were identified by operando FT-IR measurements. Structure and properties of catalyst preparations was characterized by XRD, STEM, EDS, N<sub>2</sub> physisorption. The binding of acidic and basic adsorbates, such as CO<sub>2</sub>, CDCl<sub>3</sub>, and NH<sub>3</sub>, pyridine, respectively, to the catalyst surface was studied by TPD, and FT-IR measurements



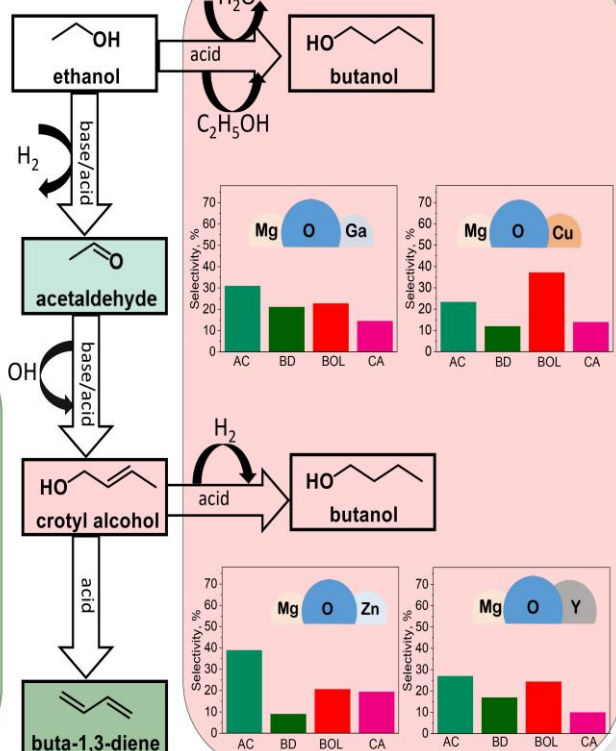
### Dehydrogenation activity



### Dehydration activity



### C-C coupling and dehydrogenation activity



### Results and discussion

Butadiene and butanol were the main ethanol conversion products formed over MgO-SiO<sub>2</sub> and MgO-Al<sub>2</sub>O<sub>3</sub> catalysts, respectively, whereas butanol and crotyl alcohol were obtained over pure MgO catalyst. The effect of transitional metal oxide promoters was investigated on the activity of pure MgO. Over Y<sub>2</sub>O<sub>3</sub>, Ga<sub>2</sub>O<sub>3</sub>, ZnO, and CuO promoted catalysts the product distribution was similar to that obtained by pure MgO catalyst under identical reaction conditions. However, the conversion was slightly higher due to the Lewis acidic character of the additives and butadiene also appeared among the products. Relative to above mentioned catalysts, promotion of MgO by Nb<sub>2</sub>O<sub>5</sub> or Ta<sub>2</sub>O<sub>5</sub> resulted in higher dehydrogenating activity, and high butadiene selectivity, while the formation of butanol and crotonaldehyde was suppressed. High acetaldehyde selectivity showed that In<sub>2</sub>O<sub>3</sub> promoter increased dehydrogenation activity, and high butadiene and ethylene selectivities. Catalytic test reactions using promoted mixed oxides are in progress, as well as, reactions of possible intermediates, and their mixtures.

## **E. Conference**

The three Hungarian researchers working on the project, participated in the "15th European Congress on Catalysis" international event organized in Prague between August 27 and September 1, 2023 (<https://www.europacat2023.cz>). The results of the project were presented in the form of a poster at a prestigious international conference closely related to the topic of the project. In the "Biomass to chemicals and fuels" section, "Gas-phase hydrodeoxygenation of lignin-derived guaiacol and phenol on Ni catalysts using neat and phosphorous-modified gamma-alumina supports" (BIO-P-105) and "Ethanol-coupling reactions over MgO, MgO-SiO<sub>2</sub>, and MgO-Al<sub>2</sub>O<sub>3</sub> catalysts: The effect of promotion by transition metal oxide" (BIO-P-143) was presented on August 29. (Posters-TUE-2.pdf (europacat2023.cz)). Researchers and industrial specialists from 53 countries, Europe and all over the world came to the conference.

## **F. Joint Paper**

A joint paper on the conversion of bioethanol produced from lignocellulose to 1-butanol using MgO-SiO<sub>2</sub> mixed oxide catalysts was published in the journal *Molecules* last year: Vikár, A.; Lónyi, F.; Makoye, A.; Nagy, T.; Novodárszki, G.; Barthos, R.; Szabó, B.; Valyon, J.; Mihályi, M.R.; Deka, D.; et al. Ethanol Coupling Reactions over MgO–Al<sub>2</sub>O<sub>3</sub> Mixed Oxide-Based Catalysts for Producing Biofuel Additives. *Molecules* 2023, 28, 3788. <https://doi.org/10.3390/molecules28093788>

Another paper on Hydroconversion of guaiacol (GUA) over  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and phosphatized- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>(P)) supported Ni catalysts was initiated by Lewis-sites and active Ni sites was published in the journal *Applied Catalysis A, General* in the year 2024. Gyula Novodárszki, Ferenc Lónyi, Balázs Csík, Magdolna R. Mihályi, Róbert Barthos, József Valyon, Anna Vikár, Dhanapati Deka, Zoltan Pászti, Yuting Shi and Hanna E. Solt, et.al. Hydroconversion of lignin-derived platform compound guaiacol to fuel additives and value-added chemicals over alumina-supported Ni catalysts. *Applied Catalysts A: General* 2024, 680, 119757. <https://doi.org/10.1016/j.apcata.2024.119757>.

## **G. The visit of the Indian project partner to RCNS**

In the framework of the Hungarian Indian TÉT cooperation, the head of the Department of Energy of Tezpur University, Professor Dhanapati Deka (PI) and his PhD student Ms. Aparna Rani Seal, who is working on the project, visited the Renewable Energy Research Group at the Institute of Materials and Environmental Chemistry of the Research Centre for Natural Sciences (IMEC RCNS), between January 28, 2024, and February 4. They met the projectleader Dr. Magdolna R. Mihályi, the other researchers working on the project, Prof. József Valyon, Prof. Ferenc Lónyi, Dr. Gyula Novodárszki, Dr. Róbert Barthos and Dr. Ágnes Szegedi, as well as the other members of the group. The Indian



researchers visited the institute's laboratory facilities.

The Hungarian and Indian partners reviewed the results achieved during the project year. They discussed the results of the physico-chemical characterization of the lignin depolymerization catalyst developed by the Indian partner from waste biomass, which was carried out at RCNS. The material of the joint manuscript submitted to the international journal on the catalytic conversion of lignin monomer was also discussed. It was established that the set goals were successfully achieved. They discussed possible forms of further cooperation.

On February 1, 2024, the Indian researchers presented their results to the researchers and PhD students at the Institute of Materials and Environmental Chemistry in a seminar on the following topics:

Professor Dhanapati Deka: Automated Modular Photobioreactor with Harvester (AMPH): Microalgae Cultivation System.

Ms. Aparna Rani Seal: Lignin Recycling for Value Added Global Products.

The Hungarian industrial partner of the project, the head of the 3R-BioPhosphate Ltd. (3R), Edward Someus, also participated in the institute seminar. After the seminar, the three project partners reviewed the results of the project and discussed the possibility of further cooperation in the future. The personal meeting further deepened the professional and human relationship between the partners.



Presentation by the Indian project leader Professor Dhanapati Deka at the IMEC RCNS seminar on February 1, 2024.



Presentation by the PhD student Ms. Aparna Rani Seal working on the project, at the IMEC RCNS seminar on February 1, 2024.



The three project partners and their colleagues in Budapest at the IMEC RCNS seminar on February 1, 2024. From left to right: Professor Emeritus Dr. Valyon József, the head of 3R Hungarian partner Edward Someus, the PI from India Prof. Dhanapati Deka, the PI from Hungary Dr. Magdolna R. Mihályi, PhD student Ms. Aparna Rani Seal and research associate Dr. Gyula Novodárszki.

## Annexure-II

**Statement of Expenditure**  
**Indo-Hungary project on "Applied Research and development for industrial realization of lignin recycling and conversion to value-added international market products"**  
**For the financial year 01.04.2023 till 31.03.2024.**

Sr No (I)	Sanctioned Heads (II)	Funds Allocated (indicate sanctioned) (III)	1 <sup>st</sup> year grant released	2 <sup>nd</sup> year grant released	3 <sup>rd</sup> year grant released	Expenditure Incurred			Total expenditure IV + V + VI (VII)	Balance as on 31-03-2024	Requirement of funds for 3 <sup>rd</sup> installment	Remarks (if any)
						1 <sup>st</sup> Year (1 <sup>st</sup> April, 2021 to 31 <sup>st</sup> March, 2022) (IV)	2 <sup>nd</sup> Year (1 <sup>st</sup> April 2022 to 31 <sup>st</sup> March, 2023) (V)	3 <sup>rd</sup> Year (1 <sup>st</sup> April, 2023 to 31 <sup>st</sup> March, 2024) (VI)				
1.	Equipment	8,00,000/-	8,00,000/-	-	-	7,87,326/-	-	-	7,87,326/-	-	Nil	-
2.	Manpower costs	26,17,920/-	8,55,360/-	2,70,000/-	-	1,53,864/-	3,20,613/-	2,49,161/-	7,23,638/-	20,830/-	4,79,520/-	@37,000/- pm+ 8% HRA for the proposed new fund.
3.	Consumables	3,00,000/-	1,00,000/-	92,782/-	-	93,363/-	-	55,750/-	1,49,113/-	37,032/-	1,00,000/-	-
4.	Contingencies	1,50,000/-	50,000/-	50,000/-	-	40,225/-	9,772/-	42,556/-	92,553/-	7,444/-	50,000/-	-
5.	Exchange visit (Indian Scientist to Hungary)	4,68,000/-	Nil	2,34,000/-	-	Nil	-	2,19,890/-	2,19,890/-	14,110/-	-	Visit was done in the 2 <sup>nd</sup> year during 28 <sup>th</sup> Jan 2024 to 04 <sup>th</sup> Feb 2024
6.	Exchange visit (Hungarian Scientist)	1,90,000/-	Nil	95,000/-	-	Nil	-	78,357/-	78,357/-	16,643/-	-	Visit was done in the 2 <sup>nd</sup> year during 22 <sup>nd</sup> Nov 2023 to 30 <sup>th</sup> Nov 2023
7.	Overhead expenses	3,12,634/-	1,48,029/-	69,483/-	-	1,45,127/-	2,901/-	69,483/-	2,17,511/-	0/-	50,362/-	-
	<b>Total</b>	<b>48,38,554/-</b>	<b>19,53,389/-</b>	<b>8,11,265/-</b>	<b>-</b>	<b>12,19,905/-</b>	<b>3,33,286/-</b>	<b>7,15,197/-</b>	<b>22,68,388/-</b>	<b>96,068/-</b>	<b>6,79,882/-</b>	<b>Rs. 4,00,198.00</b> as on 31- 12-2022 is returned to CNA (SERB) account name Research and Development SERB, Bank of Maharashtra, Press Enclave, Saket, New Delhi-110017, Account Number-60418655210, IFSC Code MAHB000593.

- Balance Rs. 96,068/- as on 31-03-2024 is returned as ZBS account.

(Dhanapati Deka) **Prof. Dhanapati Deka**  
 Name and Signature of Principal Investigator:  
 Date: 29/12/24  
 Department of Energy  
 Tezpur University  
 Tezpur, Assam, India

Signature of Competent financial authority: [Signature]  
 (With seal) Date: 29/12/24  
 Finance Officer  
 Tezpur University

- Note
1. Expenditure under the sanctioned heads, at any point of time, should not exceed funds allocated under that head, without prior approval of DST i.e. Figures in Column (VIII) should not exceed corresponding figures in Column (III)
  2. Utilization Certificate (Annexure III) for each financial year ending 31<sup>st</sup> March has to be enclosed along with request for carry-forward permission to the next financial year