



Science, Technology and Innovation Platform

**Annual Activity Report** 

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# Photocatalytic reactions for conversion of lignocellulosic materials to value-added fuels and chemicals

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### Abstract

Application of photocatalytic processes for conversion of sugars which can be derived from lignocelluloses to energy and chemicals is considered a new promising environmentally friendly alternative which will play an important role in biorefinery and bioindustry related to the valorization of sugars and agricultural wastes. This project aims to advance our technology on photocatalyst design based on the close collaboration with Prof. Dr. Takashi Sagawa, Kyoto University, under the JASTIP Renewable Energy program between NSTDA and Kyoto University (2015-2019). The project themes cover (1) continual research on fabrication and modification of photocatalysts for conversion of sugars to high-value chemicals (e.g. functional sugar derivatives) by improving the catalyst's specificity by fabrication techniques or surface modification, and (2) design and assembly of a prototype photocatalytic reactor. The concept of "photo-conversion on renewable biomaterials" will lead to the development of a "photo-bio flow reactor" and will provide a strong platform for the conversion of sugars to value-added chemicals in integrative biorefinery.

**Keyword:** Biorefinery; Lignocellulosic biomass; Photocatalysis; Sugar conversion to derivatives

### **Research Summary**

(1) Improvement of the catalyst's specificity by fabrication techniques or surface modification:

One of the challenges for the photocatalytic reaction is to develop up-scalable processes. Continuous flow has attracted considerable attention due to possible scale-



up and low energy input. To solve the problem of catalyst separation and recovery, TiO<sub>2</sub> catalyst is coated on several supports (ceramic balls, glass beads, and alumina balls). The surface morphology of three different supporting materials (*i.e.* ceramic ball, alumina ball, and glass bead) and Ag-N/TiO2 coated on these supports are shown in Figure 1. After coating with Ag-N/TiO2, the surface morphology of ceramic balls and glass beads were covered with Ag-N/TiO2 in the form of nanoparticles, and agglomeration of nanoparticles can be also observed. This result indicated that the catalyst-coated ceramic balls achieved particles with very fine size and well dispersion compared to glass beads and alumina balls. Ag-N/TiO<sub>2</sub> coated on ceramic balls showed the highest photocatalytic performance for degradation of organic dye (methylene blue; MB), which had entirely been converted (*viz.* almost 100% degradated) after UV irradiation for 2 h as indicated in Figure 1D.



**Figure 1.** Photo- and SEM-images of three different supporting materials (A1) ceramic ball, (B1) alumina ball, and (C1) glass bead. Numbers 2 refer to Ag-N/TiO<sub>2</sub> coated on supporting material at image magnifications of 30k (scale bar = 1 mm) and (D) Photocatalytic degradation of MB (5 ppm) by Ag-N/TiO<sub>2</sub> on the three different supporting materials under the UV irradiation.

Coating of Ag-N/TiO<sub>2</sub> on the ceramic balls were performed by dip coating, dip coating with the binder (polyvinylalchohol; PVA), impregnation, aging, and evaporation



method and compared their photocatalytic activities. Impregnation process obtained Ag-N/TiO<sub>2</sub> nanoparticles in small particles size and the particles were well packed on the surface of ceramic balls. Among the several coating techniques tested, the impregnation process resulted in the highest efficiency for photocatalytic degradation of MB as shown in Figure 2A. The stability of catalysts under operational conditions is important for their reusability as indicated in Figure 2B. In this experiment, the remained photocatalytic activity of the used catalysts was determined after three reaction cycles performed under the optimized conditions. The decrease in degradation efficiency was not significant (12%) for Ag-N/TiO<sub>2</sub> prepared by impregnation technique, whereas the catalyst prepared by dip-coating showed a slight decrease in photocatalytic activity from 98% to 83% after three reaction cycles.



**Figure 2.** (A) Photocatalytic degradation of MB (5 ppm) by Ag-N/TiO<sub>2</sub> on the ceramic ball coated through five different coating techniques under the UV irradiation and (B) three repeated photocatalytic degradations of MB by recycled Ag/N-TiO<sub>2</sub> on the ceramic ball.

Effective and selective photodegradation of environmental pollutant (methyl red; MR) was investigated by using morecular imprinted TiO<sub>2</sub> hollow nanofibers (MIHNF-TiO<sub>2</sub>). MIHNF-TiO<sub>2</sub> was prepared from the mixture of methyl red, Ti(OiPr)<sub>3</sub>Cl, acetyl acetone, polyvinylpyrrolidone (PVP), and Ti(OBu)<sub>4</sub> in EtOH through electrospinning biased under 15 kV with 15 cm of distance at 3.0 mL h<sup>-1</sup> of feeding rate. After the dryness under the atmospheric conditions followed by dipping into 1% NH<sub>3</sub> aq, the obtained fibers were calcined at 600 °C for 3 h. SEM images of the obtained MIHNF-TiO<sub>2</sub> were indicated in Figure 3.





**Figure 3.** SEM images of the obtained MIHNF-TiO<sub>2</sub> (imprinting ratio of MR/Ti = 2%). Relatively fragmental short fibers were observed with their slightly rough surface.

Photodegradation of MR (6.25, 12.5, 25, and 50 ppm) by MIHNF-TiO<sub>2</sub> in water (pH 7.0) under the irradiation of 500 W Xe lamp at RT was performed and monitored the decrease of the absorbance of MR. The time-course changes of the concentration of MR obeyed the pseudo-first order kinetics with good linearity and the estimated rate constants were replotted as Lineweaver Bulk plot. Michaelis constant ( $K_m$ ) and apparent maximal rate constant ( $V_{max}/K_m$ ) after formation of MR-TiO<sub>2</sub> complex were summarized in Table 1. As the reference,  $K_m$  and  $V_{max}/K_m$  values of non-imprinted TiO<sub>2</sub> hollow nanofibers (HNF-TiO<sub>2</sub>) were also indicated.

	• •	0	5
	<i>K</i> m <i>[</i> M]	V <sub>max</sub> [M min <sup>-1</sup> ]	V <sub>max</sub> /K <sub>m</sub> [min <sup>-1</sup> ]
MIHNF-TiO <sub>2</sub>	6.81 x 10 <sup>-5</sup>	1.57 x 10 <sup>-5</sup>	0.231
HNF-TiO <sub>2</sub>	3.64 x 10 <sup>-4</sup>	3.48 x 10 <sup>-5</sup>	0.0956

Table 1. Kinetic parameters for photodegradation of MR by MIHNF-TiO<sub>2</sub> and HNF-TiO<sub>2</sub>

It was found that the affinity (*viz.* comparison of  $1/K_m$  value) of the molecular imprinted TiO<sub>2</sub> for MR is 4 times higher than that of the non-imprinted one. Larger  $V_{max}/K_m$  of molecular imprinted TiO<sub>2</sub> than that of non-imprinted one was reflected by the predominant formation of MR-TiO<sub>2</sub> complex through molecular imprinting, which might be able to create the specific binding cavity for MR on the surface of TiO<sub>2</sub>. Further optimization in terms of the enhancement of the selectivity of the catalysts and the extension of the materials design of the target molecule as the template for imprinting are under progress.

(2) Design and assembly of a prototype photocatalytic reactor:

Photocatalytic degradation of MB in a photo-bio flow reactor using Ag-N/TiO<sub>2</sub> immobilized on ceramic balls was studied. The different flow rates from 20-150 ml min<sup>-1</sup> were investigated in a flow-through reactor in order to determine the optimal flow rate for



degradation of MB using the optimal catalyst design. The optimized flow-through process using the optimal catalyst design showed that the flow rate at 100 ml min<sup>-1</sup> exhibited the highest MB degradation efficiency of 100% for 5 h with the volume of solution equal to the volume of the reactor are shown in Figure 4A. The degradation of dye wastewater from the textile industry was studied in the flow-through reactor using immobilized Ag-N/TiO<sub>2</sub> on ceramic balls. The flow-through system was in equilibrium as controlled by the solution flow rate at 100 ml min<sup>-1</sup> with the photocatalyst loading of 3 kg. The color of the wastewater was analyzed by the ADMI method. The highest industrial dye wastewater degradation of 91.89% was achieved with an average degradation of 91.57% after. The ADMI value was decreased from 2800  $\pm$  43 to 236  $\pm$  14 which meeted the standard to be released into the environment according to Industrial Effluent Control Standard B.E. 2559 (2016) from the ministry of natural resource and environment of Thailand as shown in Figure 4B. The use of immobilized photocatalysts in the flow-through processes allowed no cost in the catalyst recovery step and reusability of the catalyst.



**Figure 4.** (A) Degradation of MB (5 mg L<sup>-1</sup> methylene blue solution, 2000 ml) under UVC irradiation on Ag-N/TiO<sub>2</sub> coated on the ceramic ball with different solution flow rates of 20, 50, 100, and 150 mL min<sup>-1</sup> and (B) degradation of wastewater from textile industry) under UVC irradiation using Ag-N/TiO<sub>2</sub> coated on the ceramic ball.

Photocatalytic performance of Ag-N/TiO<sub>2</sub> immobilized on ceramic balls was applied for photocatalytic glucose conversion in the flow-through reactor. The results show that 10% H<sub>2</sub>O/90% ACN showed the high performance of photocatalytic glucose conversion of 14% is shown in Figure 5A. For product distribution, it was found that the solvent ratio of 10% H<sub>2</sub>O/90% ACN showed the yield of gluconic acid, arabinose, xylitol, and formic of 2.7%, 6.9%, 0.6%, and 3.6%, respectively after UV irradiation for 6 h (Figure 5B). In addition, the rate of glucose conversion was increased with an increase in the flow rate because more glucose molecules can contact catalyst surfaces per unit of time. The flow rate of 100 mL min<sup>-1</sup> showed the highest glucose conversion of 50% for 6 h with high selectivity of arabinose, xylitol, and formic acid. The process and



system developed in this study provide a platform for further process optimization for glucose conversion and also for dye-containing wastewater treatment in the next step.



**Figure 5.** (A) Photocatalytic conversion of glucose over Ag/N-TiO<sub>2</sub> nanoparticles with different solvent ratios and (B) product yields of photocatalytic glucose conversion over Ag/N-TiO<sub>2</sub> nanoparticles after UV irradiation for 6h.

In terms of economic evaluation of photo-bioreactor, the overall results were evaluated to study economic optimization including mass balance, operating condition, and all individual responses. The process diagram is illustrated in Figure 6. This study was assumed the chemical recovery with 99% related to the chemical make-up with 1%. The photocatalyst was assumed to be recovered and regenerated during the process. It was found that the main operating cost was solvent use resulting in 89% of overall. In addition, the profit was 0.57 baht/batch. In order to calculate the profit per annum, the uptime was assumed at 350 days/year. This resulted in 1,400 of operation time. Thus, the total profit per annum was 798 baht/annum. Since the fixed cost (equipment utility) of this study was approximately 120,000 baht. It was observed that the overall result in a photo bio-flow reactor seems not to be feasible in the economy. In order to improve the economic feasibility, further optimization on glucose concentration from 1 g L<sup>-1</sup> to 20 g L<sup>-</sup> <sup>1</sup> was also conducted to optimize the profit. It was found that the basis of glucose concentration at 20 g L<sup>-1</sup> achieved a profit up to 11.46 baht/batch resulting in 20-fold of starting substrate. This indicated that the starting concentration is the main criteria to improve the economic feasibility. The solvent used is also one of the affected parameters to reduce the operating cost when the modified photocatalyst is applicable in pure water. Moreover, improving the performance in terms of yield and selectivity is also purposed in the photocatalytic process which is related to the properties of the modified photocatalyst.



#### Condition



**Figure 6.** Overall mass balance of glucose conversion in photo bio-flow reactor under optimal condition.

### Publications and Presentations

- Roongraung K, Chuangchote S, Laosiripojana N (2020) Enhancement of Photocatalytic Oxidation of Glucose to Value-Added Chemicals on TiO<sub>2</sub> Photocatalysts by A Zeolite (Type Y) Support and Metal Loading. Catalysts. 10, 423 (JIF = 3.520)
- Suriyachai N, Chuangchote S, Laosiripojana N, Champreda V, Sagawa T (2020) Synergistic Effects of Co-Doping on Photocatalytic Activity of Titanium Dioxide on Glucose Conversion to Value-Added Chemicals. ACS Omega 5, 20373–20381 (JIF = 2.870)

### Group Workshops, meetings, and researcher exchange

- 1. Annual Group Workshops (Online), March 19, 2021 Other outcomes
  - N.A



### **Development of Bio-based Carbon Materials for Energy Storage Applications**

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### Abstract

Development of viable technologies in converting abundant biomass feedstocks to higher value products is part of a Bio Circular Green Economy (BCG) model in which Thai government has energetically been promoting. This BCG model promoted the use of under-utilized biomass resources, for example, palm empty fruit bunch (PEFB). Most of it remain unused. They could be utilized as a feedstock for high value-added materials such as electrode materials, compounds, and nanomaterials for energy, environment and other applications.

This study aims to synthesize activated carbon from oil palm biomass for highperformance supercapacitors, and improve the supercapacitor performance made of biobased activated carbon. A unique combination between chemical and surface modification processes have been carried out using hydrothermal and hetero-elemental doping techniques to achieve high surface area activated carbon with designed pore and surface properties. This research is an extension of the previous success work in producing activated carbon from palm empty fruit bunch (PEFB) and palm shell (PS) which exhibit a capacitance higher than that of commercially available activated carbon in an aqueous electrolyte. (JASTIP, phase I)

Hydrothermal carbonization followed by post-treatment process, i.e., chemical activation and surface modification, would provide activated carbons with high porosity which are generally suitable for energy storage applications. The chemical activation is, in general, conducted with the presence of porogen such as phosphoric acid, potassium hydroxide, sodium hydroxide or zinc chloride. The different porogens are expected to enhance pore generation both micropore and mesopore which will be investigated on biobased activated carbon from oil palm biomass i.e., palm empty fruit bunch (PEFB). In addition, the effect of elemental nitrogen doping will be preliminary studied for the surface modification of activated carbon. It was reported from previous research that nitrogen functional groups formed on the surface of activated carbon could promote the surface ion transportation in supercapacitors. Thus, nitrogen doping when combined with chemical activation process could enhance the electrochemical properties of activated carbon when used as an electrode in either aqueous or organic electrolyte supercapacitors.



#### **Research Summary**

# 1.Study of chemical activation using different porogens in enhancing the porosity within activated carbon from oil palm biomass

High surface area activated carbon (AC) has been produced from oil palm biomass i.e., palm empty fruit bunch (PEFB) by using hydrothermal carbonization and chemical activation processes. Hydrothermal carbonization (HTC) was used to convert biomass to biochar, and the effect of activating agent (porogens) and amount of activating agent on biochar was studied. The activating agent:char ratio, weight ratio, could affect the surface and pore properties of activated carbon. The research methodology and results are reported.

### 1.1 Production of oil palm bio-based activated carbon using potassium hydroxide (KOH) as an activating agent

Biochar from hydrothermal carbonization (HTC) of palm empty fruit bunches (PEFB) is mixed with potassium hydroxide (KOH) with KOH:char weight ratios of 0.5:1, 1:1 and 1:2. Then the char mixture was activated in a furnace at 700-900°C under CO<sub>2</sub> atmosphere at a flow rate of 60 ml/min for 2 h. The activated carbon was washed to remove any residue impurities. The final PEFB activated carbon samples were characterized for specific surface area (BET) and porosity of activated carbon by adsorption of nitrogen gas at -196°C using a surface analyzer Micromeritics ASAP 2460.

Bio-based activated carbon samples from hydrothermal carbonization were made into an electrode with 11 mm diameter. A Swagelok cell with 1 M H<sub>2</sub>SO<sub>4</sub> electrolyte was assembled and employed on the electrochemical test, galvanostatic charge-discharge (GCD), to evaluate the supercapacitor performance. The galvanostatic charge-discharge test was performed by charging and discharging between 0 - 0.6 V using constant current levels of 0.1, 0.2, 0.5, 1 and 2 A g<sup>-1</sup> of activated carbon. The overall hydrothermal process and electrochemical test schematic is shown in Figure 1.



Grind 0.5:1, 1:1, 2:1 700-900°C KOH : Char Under N Mix Activate **Biomass** Hydrothermal Carbonization Powder Wash (HTC) Current Collecto Carbon Electrode Separator Electrochemical test Activated Swagelok Cell (1M H<sub>2</sub>SO<sub>4</sub>) Carbon Galvanostatic Charge-Discharge (GCD) measurement

Activated carbon from hydrothermal carbonization (HTC)

Figure 1 The overall schematic of hydrothermal process and electrochemical test of oil palm biomass activated carbon

#### Experimental results

The specific surface area and pore properties of PEFB Activated Carbon (KOH-activation) The specific surface area (BET) and pore distribution plot of KOH-activated PEFB activated carbon are shown in Figure 2. All activated carbons have high surface area which contained mostly micropore (<2 nm). It was found that when the KOH:char ratio was increased, the specific surface area of activated carbon was also increased. From Figure 2, the activated carbon produced using a KOH:char ratio of 2, has the largest amount of pore volume. The majority of pore size is ~ 0.6-0.7 nm which is able to accommodate the ion in aqueous electrolyte systems. This results in the bio-based PEFB activated carbon with improved properties and enhances the electrical capacitance when used as an electrode in supercapacitors.

#### Electrochemical test, GCD result of PEFB Activated Carbon (KOH-activated)

The capacitance (specific gravimetric capacitance) results of the activated carbon produced from PEFB and activated by KOH in ratios of 1:1 and 2:1 at 700°C were calculated from GCD test. PEFB-KOH2 activated carbon exhibits a peak capacitance of 175 F g<sup>-1</sup> when discharged at a current density of 0.1 A g<sup>-1</sup> which is higher than YP50F, a commercial activated carbon as shown in Figure 3.





Figure 2 Adsorption-desorption isotherm and pore size distribution plot of PEFB activated carbon produced with KOH and YP50F commercial activated carbon as a benchmark



Figure 3 Capacitance results from GCD test of PEFB activated carbon produced with KOH and YP50F commercial activated carbon as benchmark



# 1.2 Production of oil palm bio-based activated carbon using zinc chloride (ZnCl<sub>2</sub>) as an activating agent

PEFB biochar from HTC process was mixed with zinc chloride at ZnCl<sub>2</sub>:char weight ratios of 1:1 and 2:1. It was then activated in a furnace at 700°C under CO<sub>2</sub> atmosphere. The overall process was similar to the aforementioned section 1.1 except a different activating agent was used. Another PEFB activated carbon samples using ZnCl<sub>2</sub>:char ratio of 2:1 activated at 800°C also produced and designated as HWZ-EFB-21-800. All ZnCl<sub>2</sub>-activated carbon were made into electrode and the capacitance values were calculated from GCD tests. The results of supercapacitor performance (specific gravimetric capacitance) are reported below.



Figure 4 Capacitance results from GCD test of PEFB activated carbon produced with  $\mbox{ZnCl}_2$ 

As shown in Figure 4, zinc chloride activation at ratios 1:1 and 2:1 activated at 700°C showed no significant difference in electrical specific capacitance at 76 and 80 Fg<sup>-1</sup>, respectively. When PEFB activated carbon was produced with  $ZnCl_2$ :char ratio of 2:1 and activated at 800°C, the capacitance reported is as high as 102 F g<sup>-1</sup>. Thus, for  $ZnCl_2$ -activation, the optimum activating temperature for bio-based activated carbon is at 800°C.

# 1.3 Production of oil palm bio-based activated carbon using sodium hydroxide (NaOH) as an activating agent

NaOH-activated carbon was made from PEFB biochar from HTC process with NaOH:char ratios of 1:1, 2:1 and 3:1. It was then activated in a furnace at 700°C under CO<sub>2</sub> atmosphere. The overall process was similar to the aforementioned section 1.1 The NaOH-PEFB activated carbon samples were made into electrode and the capacitance values were calculated from GCD tests. The results of capacitance from GCD tests are shown in Figure 5. NaOH-activated carbon samples have low tapped density, which cause the electrode fabrication more difficult. However, at NaOH:char ratio of 3:1, the activated carbon provides the highest capacity value of 106 F g<sup>-1</sup>, which is higher than a commercial activated carbon (YP50F) tested under the same condition.







#### Conclusions

Bio-based activated carbon produced from oil palm empty fruit bunches (PEFB) using KOH, ZnCl<sub>2</sub> and NaOH as activating agents were successfully produced. It was found that the activated carbon from ZnCl<sub>2</sub>:char ratio at 2:1 activated at 800°C gave the highest tapped density and good capacitance value of 102 F g<sup>-1</sup>. The KOH-activated carbon has a high surface area and contained mainly micropore. The KOH-activated activated carbon also exhibits the highest capacitance. This is expected to be the results of the high amount of pore volume of the KOH-activated carbon. For the NaOH-activated carbon, the 3:1 ratio shows the best capacitance value of 106 F g<sup>-1</sup>.

The ZnCl<sub>2</sub>-activated carbon contained more mesopore than KOH- or NaOHactivated carbons which could be suitable to be utilized in an organic solvent electrolyte supercapacitor since organic electrolyte has a larger ion size than aqueous electrolyte. However, choosing the right activated carbon production process for different electrolytes may be complicated since many process parameters must be considered. In summary, we had achieved three selected processes to produce PEFB activated carbons with high supercapacitor performance which are, 1) via KOH activation using 2:1 KOH:char ratio, 2) via ZnCl<sub>2</sub> activation using 2:1 ZnCl<sub>2</sub>:char ratio, and 3) via NaOH activation using 3:1 NaOH:char ratio. All three PEFB activated carbons show higher capacitance than the benchmark commercial activated carbon (YP50F) in the aqueous electrolyte supercapacitor.



# 2.Study the influence of nitrogen doping on PEFB bio-based activated carbon for supercapacitor applications

PEFB hydrochar from hydrothermal carbonization (HTC) of palm empty fruit bunches was mixed with  $ZnCl_2$  and N-source (NH<sub>4</sub>Cl) and activated at 700°C under CO<sub>2</sub> atmosphere. The activated carbon was used as electrode materials in a swagelok cell for GCD test. Figure 6 shows a schematic of the overall process.



Biobased activated carbon from hydrothermal carbonization with nitrogen addition

Figure 6 The schematic of a production process of N-doped PEFB activated carbon

The preliminary capacitance value of nitrogen doped PEFB activated carbon is shown in Figure 7. The specific capacitance value from GCD test of the N-doped activated carbons is higher than the undoped activated carbon. This promising preliminary result of the N-doped PEFB activated carbon shows that it has high opportunity to improve the biobased PEFB activated carbon supercapacitor performance.





Figure 7 Capacitance from GCD test of N-doped PEFB activated carbon, undoped PEFB activated carbon and YP50F commercial activated carbon as a benchmark

### **Publications and Presentations**

- Vituruch Goodwin, Thanathon Sesuk, Parinya Jitreewas, Pimpa Limthongkul and Sumittra Charojrochkul, "Activated Carbon from Palm oil Biomass via Hydrothermal Carbonization as Electrodes for Supercapacitors", the Materials Thailand 2021 conference (AMF-AMEC-2021), 7<sup>th</sup> – 9<sup>th</sup>, 2021, Bangkok, Thailand.
- Parinya Jitreewas, Thanathon Sesuk, Vituruch Goodwin, Pimpa Limthongkul and Sumittra Charojrochkul, "Nitrogen-doped of Hydrothermal Palm Shell Activated Carbon for Supercapacitor Electrode", the Materials Thailand 2021 conference (AMF-AMEC-2021), 7<sup>th</sup> – 9<sup>th</sup>, 2021, Bangkok, Thailand.
- Thanathon Sesuk, Vituruch Goodwin, Pimpa Limthongkul and Sumittra Charojrochkul, "Microporous Activated Carbon from Wood Chip and Durian Peel for Application in Supercapacitor", the Materials Thailand 2021 conference (AMF-AMEC-2021), 7<sup>th</sup> – 9<sup>th</sup>, 2021, Bangkok, Thailand.

#### Group Workshops, meetings, and researcher exchange

#### Other outcomes

Thailand petty patent title "Method of producing activated carbon from oil palm biomass for supercapacitor applications" filed on 17 June 2021.



# Nanocarbon Materials for Sustainable Production and Storage of Green Fuels and Platform Chemicals

#### 1. Research team

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### 2. Purpose of Collaborative Research

The effects of climate change caused by the anthropogenic CO<sub>2</sub> emission has increased the average global temperature by 1 °C above the pre-industrial level. If this current trend is continued, the average global temperature is expected to inevitably elevate by 4-5 °C by 2100. To slow down this global crisis, the greenhouse gas emission must be drastically reduced towards zero emission within this century. These need has led to the blossom of green technological concepts including biorefinery and bio-energy devices where renewable resources replace the need for fossil fuel in the future. The catalytic productions of carbon-based materials, biofuels, and biochemicals are at the heart of biorefinery industry. The collaborative researches carried out by the groups in NANOTEC/NSTDA (Faungnawakij's team) and Kyoto University (Sano's team) aim to develop new and innovative knowledge on biomass conversion to useful materials and development of bio-energy devices.

In this year, 3 major research activities have been done as follows.

- Development of fast and low-energy method to synthesize activated carbon using microwave plasma
- Rational Design of Metal-free Doped Carbon Nanohorns Catalysts for Efficient Electrosynthesis of H<sub>2</sub>O<sub>2</sub> from O<sub>2</sub> Reduction
- The Efficient Conversion of D-Fructose to 5-Hydroxymethylfurfural using Organic Acids as Catalytic Promoters



### 3. Research Outcome

3.1 Development of fast and low-energy method to synthesize activated carbon using microwave plasma: Controllability of pore structures by KOH-to-carbon ratio in feed and activating time

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**ABSTRACT**: Recently, it was found that the activation by microwave-induced plasma (MiWP-KOH) can be used to prepare high-surface-area activated carbon (AC) within a few minutes. In the present study, microwave-activation time and KOH concentration in the feed mixture are focused as key factors governing the pore formation. The volumes of micorpores and mesopores in addition to BET surface area were measured to evaluate the structures of resulted AC prepared by MiWP-KOH activation. The experimental results show that activated carbon with specific surface area of 1251 and 2718 m<sup>2</sup>g<sup>-1</sup> can be obtained within 80 and 270 s. It was suggested that the increases of the activation time and KOH concentration resulted in the increase of micro and mesopore volumes, but excessively long activation time was not useful to increase these volumes. It was observed that the concentration of KOH should be high enough to stabilize the pore structures. It was suggested that the hierarchical pore structure can be controlled as function of the KOH concentration, so that the microporosity can be increased by increasing KOH concentration. Besides, the AC prepared by MiWP-KOH activation shows a mass yield percentage of 12.3 wt-% in the conditions to achieve the stabilized values of micropore volume and specific surface area, which seems higher than the mass yield percentage of the AC prepared by a conventional activation using electric furnace.

### INTRODUCTION

A high surface activated carbon (AC) is a porous carbon material, which has specific surface area of 1000-3000 m<sup>2</sup> g<sup>-1</sup>. It has been used widely owing to its high surface reactivity, hierarchical pore structure, and high surface area provided more adsorption-site (Sayğılı et al., 2015). It can be used in purification and separation processes. For example, H<sub>2</sub> purification ( He et al., 2020), glycerol purification (Habaki et al., 2019), and syngas purification (Pena et al., 2020). Moreover, it was used as a catalysts or catalyst supports for syngas production (Su et al., 2020), phosgene formation (Rossi et al., 2020), and phenols production (Huo et al., 2020). AC can be used as electrode materials for supercapacitors (Inal et al., 2020, Jiang et al., 2020, Cossutta et al., 2020). Owing to those varieties of application, the demand for AC has been increasing worldwide.

AC has a hierarchical pore structure consisting of micropores (pore diameter is smaller than 2 nm), mesopores (pore diameter is between 2-50 nm), and macropores (pore diameter is larger than 50 nm) (Lozano-Castello et al., 2002, Aroua et al., 2008, Ahmed et al., 2016a, Ahmed et al., 2016b, Rashidi et al., 2017). Although AC with microporous structure has high adsorption efficiency for small molecules (acetone,



dichloromethane, ethyl formate), it is not so effective for large molecules or ions. On the contrary, AC with mesoporous structure are suitable to adsorb macromolecules such as dyes, proteins, antibiotics, and polycyclic aromatic compounds (Benhouria et al., 2015). The large molecule can diffuse into mesopores and be adsorbed onto the surface of the pores.

Various activating agents can be used to produce the AC with mesoporous structure. For example, steam (Lam et al., 2019, Yek et al., 2019), CO<sub>2</sub> (Xin-hui et al., 2011), ZnCl<sub>2</sub> (Nasrullah et al., 2019), H<sub>3</sub>PO<sub>4</sub> (Liu et al., 2010, Koyuncu et al., 2018), NaOH (Zhang et al., 2019, Boujibar et al., 2019, Yu et al., 2019), K<sub>2</sub>CO<sub>3</sub> (Deng et al., 2010, Foo and Hameed, 2012) and KOH (Li et al., 2019, Erdoğan et al., 2017). To prepare the AC with high surface area and mesoporous structure, carbon precursors (feed materials) must be mixed with the activating agents and heated at high temperature for several hours (Selvaraju and Bakar, 2018, Loya-González et al., 2019, Zabaniotou et al., 2004, Zhang et al., 2019). Among activation methods mentioned above, KOH activation is a well-established method that can be used to prepare high-surface-area AC in industrial scale (Liang et al., 2018). Previous study reported that the high-surface-area AC with micro and mesoporous structures can be prepared by mixing KOH with the carbon precursor using KOH/carbon mass ratio of 6 (Njoku et al., 2014).

In a conventional process, the mixture of the carbon precursors and the activating agents was heated at 700-850 °C for 0.5-2.5 h to get the AC with specific surface area in the range of 647-2413 m<sup>2</sup> g<sup>-1</sup> (Li et al., 2019, Nasrullah et al., 2019, and Sulaiman et al., 2018). The long activation time limits the AC preparation process to be operated in batch systems, which cannot efficiently produce AC in large scale. If the activation time becomes shorter (several minutes), the AC preparation process can be operated in continuous system.

Many researchers have been seeking for a new method to reduce activation time by applying microwave irradiation to the KOH activation. For example, previous study (Deng et al., 2010) reported that AC can be synthesized using KOH activation with microwave irradiation, suggesting that AC with specific surface area of 729 m<sup>2</sup> g<sup>-1</sup> can be prepared within 10 min. In another study, AC was prepared by microwave-KOH activation (Foo and Hameed, 2011), suggesting that the mixture of carbon precursors and KOH was heated by microwave irradiation for 7 min to obtain AC with specific surface area of 752 m<sup>2</sup> g<sup>-1</sup>. Furthermore, AC with specific surface areas of 972 m<sup>2</sup> g<sup>-1</sup> and 1229 m<sup>2</sup> g<sup>-1</sup> can be prepared within 12 min (Njoku et al., 2014) and within 3 min (Liang et al., 2018), respectively, using microwave-KOH activation. In these studies, the preparation methods required at least 3 min to get high-surface-area AC, and none of them report the synthesis of AC of which specific surface area is above 2000 m<sup>2</sup> g<sup>-1</sup>. And, none of them report the generation of the plasma in the reaction zone, but only electromagnetic heating of the feed.

Recently, we found that the activation by microwave-induced plasma with KOH (MiWP-KOH activation) can prepare AC with high specific surface area of 1007 and 2084  $m^2 g^{-1}$  using microwave-activation time of 80 and 330 s (Kuptajit and Sano, 2019). Economically, the consumed energy and the cost for the preparation of AC should depend on the activation time. The preparation of high-surface-area AC with micro and



mesoporous structures in a short-time is considered to be very important from an energy point of view.

Previous studies suggested that activation time and concentration of the activating agents in the feed mixture play an important role in pore formation of AC prepared by a conventional method (Zhu et al., 2017, Üner and Bayrak, 2018, Huber and Hauser, 2019). Therefore, this work aims to investigate the influence of the concentration of the activating agents, KOH, to use MiWP-KOH activation for the preparation of AC with high specific surface area (higher than 2000 m<sup>2</sup> g<sup>-1</sup>) and its hierarchical pore structures with micropores and mesopores. Also the effect of the microwave-activation time was investigated on the pore structures, with relating the effect of the KOH concentration.

### MATERIAL AND METHODS

**Preparation of AC.** A synthetic carbon gel has been used as a carbon precursor in this study. According to Mukai et al. (2005), the carbon gel can be prepared by mixing phenol and formaldehyde in the presence of sodium carbonate, which served as catalyst. Here, phenol and formaldehyde concentration were fixed at 0.5 and 1.0 mol L<sup>-1</sup>. The ratio of phenol to sodium carbonate was set at 1.5. The solution was heated at 95 °C for 72 h before being left at room temperature for 72 h to terminate the reaction. Then, a purple gel, so called synthetic carbon gel, was obtained. This synthetic carbon gel was dried at 110 °C for 1 h. Then, it was carbonized at 700 °C for 1 h under N<sub>2</sub> atmosphere to get carbonized carbon gel (CCG).

CCG was activated by MiWP-KOH activation (Kuptajit and Sano, 2019) under various conditions by adjusting the microwave-activation time (80, 180, and 270 s) as well as KOH concentration (9-91 wt-%) in the feed mixture, which is CCG-KOH mixture. The MiWP-KOH activation was carried out in a modified household microwave oven (Sanyo Electric EM-LA1(HL)) in nitrogen flow with a flowrate of 300 cm<sup>3</sup> min<sup>-1</sup> in a quartz tube. The microwave oven was operated at 500 W and 2.45 GHz. The resulting mixture was washed with distilled water after being cooled in nitrogen flow at room temperature until the filtrate became neutral. The AC was dried at 50 °C for 12 h before being collected and measured its weight to evaluate mass yield percentage using eq. (1).

Mass yield percentage =  $\frac{\text{Mass of AC}}{\text{Mass of CCG}}$  x 100% (1)

**Investigation of activation temperature.** Microwave-induced plasma can be clearly observed as a uniquely bright plasma above the CCG-KON mixture bed. The previous report indicated that the temperature of this plasma was estimated to be above 5000 K from the analysis of the emission spectra (Kuptajit and Sano, 2019). The contact of this hot plasma with the CCG-KOH mixture bed should enhance the fast increase of its temperature.

It was observed that thermocouples were corroded heavily by KOH at high temperature, suggesting that commonly-used thermocouples protected by metallic sheath cannot be used to measure the temperature of the CCG-KOH mixture in the MiWP-KOH



activation. Therefore, the temperature-change of the CCG-KOH mixture was observed using a radiation thermometer (Japan Sensor, FTHX-0200S V-1563).

**Characterization of AC via N**<sub>2</sub> **sorption isotherms.** Pore structures of the AC was studied by obtaining N<sub>2</sub> adsorption-desorption isotherms using an automated physisorption surface area analyzer (MicrotracBEL, BELSORP-miniII-S). The samples were outgassed at 200 °C in vacuum for 4 h before the measurements. The isotherms was used to evaluate pore properties of the AC.

The total pore volume was assessed, corresponding to volume of N<sub>2</sub> adsorbed at relative pressure ( $P/P_0$ ) of 0.90. Micropore volume was calculated by applying *V*-*t* plot method (Lippens et al., 1965) to N<sub>2</sub> adsorption data. Mesopore volume was calculated from the difference between total pore volume and micropore volume.

Specific surface area was calculated by Brunauer–Emmett–Teller (BET) equation using N<sub>2</sub> adsorption isotherms of  $0.01-0.03P/P_0$  (Brunauer et al., 1938). The calculation considered the molecular cross-sectional area of N<sub>2</sub> at 77 K to be  $0.162 \text{ nm}^2$ .

Microporosity was calculated by eq. (2) to indicate the degree of microporedomination in AC structure.

$$Microporosity = \frac{\text{micropore volume}}{\text{total pore volume}} \times 100$$
(2)

### **RESULTS AND DISCUSSION**

Activating temperature. The temperature-change of CCG-KOH mixture was recorded as illustrated in Fig. 1. It is shown that the temperature rises along with microwave irradiation time to about 450 °C by 80-90 s with almost same temperature-elevating rate in all KOH-concentration cases, and the difference can be seen in the temperature elevation rate after this time range. The result shows that the maximum activation-temperature was 505, 787, and 860 °C when KOH to CCG ratio is 4:1, 6:1, and 10:1, respectively. It indicates that the activation-temperature increases along with the increasing of KOH concentration in feed material.

**Pore formation of AC.** Fig.2 presents N<sub>2</sub> adsorption-desorption isotherms of the AC prepared using various KOH concentration in the feed mixture. Figs.2 (a), (b), and (c) show sorption isotherms of the AC prepared using microwave-activation time of 80, 180, and 270 s, respectively. The sorption isotherms show adsorption of N<sub>2</sub> at low relative pressure ( $P/P_0 < 0.01$ ), indicating microporous structure in AC (Schneider, 1995, Sing, 1982). The results suggested that the adsorbed volume of N<sub>2</sub> at low  $P/P_0$  tends to increase with an increase of the KOH concentration, leading to an increase of micropore volume. In addition, each isotherm shows a hysteresis loop, indicating mesoporous structure (Sing, 1982, Schneider, 1995, Thommes, 2010, Cychosz and Thommes, 2018). The size of the hysteresis loops seem to be wider as the KOH concentration increase of the KOH concentration.





Fig. 1 Temperature-change of CCG-KOH mixture in the MiWP-KOH activation with varied KOH:Carbon ratio.



Fig. 2  $N_2$  adsorption-desorption isotherms of AC prepared by MiWP-KOH activation with microwave-activation time of (a) 80, (b) 180, (c) 270 s.



Fig.3 presents the specific surface area of AC prepared using different KOH concentration in the feed mixture and the activation time. Figs.3 (a), (b), and (c) show specific surface area of the AC prepared using microwave-activation time of 80, 180, and 270 s, respectively. It can be shown that the maximum specific surface area are 1266, 2189, and 2332 m<sup>2</sup> g<sup>-1</sup> in AC obtained by microwave-activation time of 80, 180, and 270 s, respectively. The results illustrate that specific surface area tends to increase as the KOH concentration increases.



Fig. 3 Effect of KOH concentration on specific surface area of AC prepared by MiWP-KOH activation using different KOH concentration and microwave-activation time of (a) 80, (b) 180, (c) 270 s.



Here, "stable zone" is defined as the operating conditions used to produce AC with pore properties that have narrow fluctuation-range. The stable zone can be observed in the results of AC prepared by microwave-activation time of 180 and 270 s. However, no stable zone can be seen in the results of AC prepared by microwave-activation time of 80 s. This tendency suggests that it takes time more than 80 s to realize uniformity of heating. It should be noted that the electrical conductivity of carbon increases with temperature (Morgan, 1971), and the electrical conductivity of CCG may become high enough to cause the uniform plasma at higher than 450 °C of CCG temperature, when the microwave irradiation time exceed 80 s. It seemed in the experiments that when the average CCG temperature is not high enough, the plasma above the GGC-KOH mixture becomes narrowly localized, so that the CCG can be activated just in non-uniform manner.

One should be reminded that, unless the KOH concentration is substantially high, the stable zone can not be seen even if the average temperature of CCG-KOH is high enough. It seems that KOH is vaporized during the microwave-activation process. Thus, if the amount of KOH in GGC-KOH mixture is not large enough, the uniformly-occurred reaction between carbon and KOH can not be preserved during the microwave-activation process.

Similarly to a previous study (Kuptajit and Sano, 2019), it can be shown here that the specific surface area of AC significantly increases as microwave-activation time increases until microwave-activation time becomes 120 s. When microwave-activation time is longer than 120 s, the specific surface area of the AC seem to increase very slowly with an increase of microwave-activation time. This tendency might be due to the loss of KOH from CCG-KOH mixture by the vaporization of KOH.

The analytical results of micropore volume show the similar tendency with those of the specific surface area. Fig.4 shows the micropore volume of AC prepared using different KOH concentration and the microwave activation time. Figs.4 (a), (b), and (c) show the micropore volume of the AC prepared using microwave-activation time of 80, 180, and 270 s, respectively. The results show that micropore volume tends to increase as the KOH concentration increases. Moreover, the stable zone can be observed in the results of the AC prepared by microwave-activation time of 180 and 270 s at the high KOH concentration range. However, no stable zone is shown in the results of AC prepared by microwave-activation time of 80 s. The results indicate that in the suitably high ranges of KOH concentration and microwave-activation time, the stable zone can be secured for specific surface area and micropore volume.

Fig.5 presents mesopore volume of the AC prepared using different concentration of KOH and microwave activation time. Figs.5 (a), (b), and (c) show mesopore volume of the AC prepared using microwave-activation time of 80, 180, and 270 s, respectively. The results show that mesopore volume increases with an increase of the KOH concentration. Also, the mesopore volume increases with the time of the microwave activation time. The influence of the time of the microwave activation time seems similar to the cases of the specific surface area and the micropore volume. However, differently from the cases of the specific surface area and the micropore volume, the mesopore volume does not exhibit the stable values in the high KOH concentration range, which corresponds to the stable zone to the specific surface area and the micropore volume.





Fig. 4 Effect of KOH concentration in feed mixture on micropore volume AC prepared by MiWP-KOH activation using different KOH concentration and microwave-activation time of (a) 80, (b) 180, (c) 270 s.





Fig. 5 Effect of KOH concentration in the feed mixture on mesopore volume of AC prepared by MiWP-KOH activation using different KOH concentration and microwave-activation time of (a) 80, (b) 180, (c) 270 s.

Fig. 6 shows the N<sub>2</sub> sorption isotherms of AC synthesized at 82 and 86 wt-% of KOH concentration with 270 s of the microwave activation time. These conditions are categorized into the stable zone to obtain the stable values of high specific surface area and the micropore volume. One can notice that the shapes of in these isotherms are



different in the relatively high pressure range, where the one synthesized at 82 wt-% of KOH concentration is expected to contain well-grown mesopres and the other should not contain significant volume of the mesopores. The reason why mesopore volume is difficult to control can be explained as follows.







Fig. 7 Effect of KOH concentration on mass yield percentage of AC prepared by MiWP-KOH activation using microwave-activation time of 180 and 270 s. The plots marked by square are the one obtained when high-surface-area AC with surface area larger than 1500 m<sup>2</sup> g<sup>-1</sup> was synthesized in the stabilized zone.

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In the MiWP-KOH activation, the growth of micropores can be proceeded since activation time is short, but mesopores grow much slower at the high temperature while the CCG-KOH is heated by the plasma (Kuptajit et al., 2021). In fact, the timing to start stable plasma that can heat CCG-KOH mixture uniformly is not well repeatable. Therefore, if the timing to obtain such stable plasma is late, the duration of such plasma until the activation is terminated is not long enough to obtain well-grown mesopores, but this duration can be long enough to form well-grown micorpores. If the timing to start such stable plasma is early, the both of micro and mesopores can be grown well. To improve the stability of mesopore volume, further study to investigate the reaction conditions to stabilize the timing to obtain such stable plasma will be necessary.

**Mass yield percentage in MiWP-KOH activation.** Fig.7 illustrates the mass yield percentage of AC prepared using microwave-activation time of 180 and 270 s. The mass yield percentage was calculated using eq. (1). The average value of the mass yield percentage for the condition when high-surface-area AC with surface area larger than 1500 m<sup>2</sup> g<sup>-1</sup> was synthesized in the stabilized zone is 12.3 %. It is higher than the mass yield percentage of the AC prepared by conventional activation method, which is normally in the range of 4.5-5.1 (Sulaiman et al., 2018).

**Comparison with past studies.** A comparison of the present study with past studies about the use of microwave to produce AC is summarized in Table 1. Here, the values of the maximum specific surface area of AC obtained by each of the past studies are shown. This table also shows the information of some reports of the conventional activation. By looking the comparison in this table, it could be said that the present study exhibits the best microwave performance. Koyuncu et al. (2018) reported that AC with specific surface area of 1021 m<sup>2</sup> g<sup>-1</sup> was obtained within 40 s, but the power to generate microwave used by them was 900 W. On the other hand, the power used by the present MiWP-KOH activation to produce the AC with similar surface area was only 500 W. Liu et al., (2010) used the even lower power, 350 W, to obtain AC with specific surface area of 1410 m<sup>2</sup> g<sup>-1</sup>, but a long microwave-activation time such as 20 min was required there. Other works used longer time and higher power to make the microwave activation. And importantly, none of the microwave activation methods except MiWP-KOH activation realized the synthesis of AC of which specific surface area was above 2000 m<sup>2</sup> g<sup>-1</sup>.

Table 1 Comparison of pore properties of various AC prepare from microwave and conventional activation.

Carbon precursor	Activatio n method	Activati ng Agent	Activati on time / min	Activati on temper ature / °C	Microwav e power / W	Surface Area / m² g⁻¹	Microp orosity / percent	Refere nce
CCG	Microwa ve	КОН	1:20		500	1266	90.76	

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	(Present study)							
	,		3:00		500	2189	80.58	
			4:30		500	2238	74.89	
Mandarin shells	Microwa ve	H <sub>3</sub> PO <sub>4</sub>	0:40		900	1021	3.12	Koyunc u et al., 2018
Orange peel	Microwa ve	K <sub>2</sub> CO <sub>3</sub>	6:00		600	1104	40.16	Foo et al., 2012
Rice husks	Microwa ve	K <sub>2</sub> CO <sub>3</sub>	7:00		600	1165	42.31	Foo et al., 2011
Rice husks	Microwa ve	КОН	7:00		600	752	40.63	Foo et al., 2011
Cotton stalk	Microwa ve	K <sub>2</sub> CO <sub>3</sub>	8:00		660	621	28.95	Deng et al., 2010
Banana peel	Microwa ve	KOH + NaOH	10:00		700	1038	38.36	Liew et al., 2018
Cotton stalk	Microwa ve	КОН	10:00		680	729	68.42	Deng et al., 2010
Rambutan	Microwa ve	КОН	12:00		600	972	25.23	Njoku et al., 2014
Bamboo	Microwa ve	H <sub>3</sub> PO <sub>4</sub>	20:00		350	1432	72.27	Liu et al., 2010
Palm kernel shells	Microwa ve	Steam	30:00		700	419	76.06	Lam et al., 2019
Coal	Conventi onal	КОН	60:00	800		1001	74.58	Erdoğa n et al., 2017
Anthracite	Conventi onal	NaOH	60:00	850		1200	94.00	Boujiba r et al., 2019
Phenol/for maldehyd e resol	Conventi onal	КОН	90:00	700		1410	52.05	Lv et al., 2012



One can see in this table that the conventional methods can be used to prepare AC with high specific surface area, but they need 60-90 min to finish the activation (Lv et al., 2012, Erdoğan et al., 2017, Boujibar et al., 2019). One may imagine that such time-consuming activation of MiWP-KOH may result in high energy consumption. As a feature of the pore structure of AC prepared by MiWP-KOH activation, the microporosity seems to be relatively high. The characteristics of the MiWP-KOH activation which need relatively short activation time and less power to generate microwave may indicate the potential to realize the energy saving process to produce high-surface-area AC.

**Controllability of microporosity. Fig. 8** shows the microporosity calculated by eq. 2 for the results obtained with all of the KOH concentration and microwave activation time adopted in this study. The results suggest that the microporosity trends to increase as KOH concentration increases. On the other hand, the influence of the microwave-activation time is not clearly seen.

The relation between the microporosity and KOH concentration within the observed KOH concentration range seem to be described by a linear equation, although relatively large variations from this correlation line can be seen. This correlation line can be written as (Microporosity) = (0.529)(KOH concentration [wt-%]) + 22.65, where coefficient of determination R<sup>2</sup> is 0.414.

The mesoporosity defined here is considered to be a kind of criteria to know how much the micropores dominate the porous structures. When one needs to use AC to adsorb relatively large molecules, or wants quick adsorption with high diffusivity of adsorbate molecules in AC, the activation condition with high KOH concentration can be recommended. The result here can be used to synthesize AC by MiWP-KOH activation to answer such demands for the pore structures of AC.



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Fig. 8 Microporosity of AC prepared by MiWP-KOH activation defined by eq. 2 related with microwave-activation time and KOH concentration in feed-material.

### CONCLUSIONS

MiWP-KOH activation can be used to prepare a high surface area AC with specific surface area of 1251, 2250, and 2718 m<sup>2</sup> g<sup>-1</sup> within 80, 180, and 270 s. The MiWP-KOH activation can be done rapidly because the high-temperature plasma may support the quick heating of the feed material. It was suggested that the increases of the activation time and KOH concentration resulted in the increase of micro and mesopore volumes, but excessively long activation time was not useful to increase these volumes. It was observed that the concentration of KOH should be high enough to stabilize the high values of the micropore volume and the specific surface area of resulted AC. This condition is referred to as "stable zone" in this study. The stable zone can not be observed for mesopore volume at this stage. The mass yield percentage of the AC prepared by MiWP-KOH activation was 12.3 wt-% in average in the stable condition. This mass yield percentage is higher than the mass yield percentage of the AC prepared by the conventional activation. The result about microporosity indicates that the microporous structure become more dominant when KOH concentration become higher. The results obtained here may be useful to control the pore structures of AC with high specific surface area for various demands for adsorption applications.

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### REFERENCES

- Ahmed, M. B., Zhou, J. L., Ngo, H. H., Guo, W., 2016a. Insight into biochar properties and its cost analysis. Biomass Bioenergy. 84, 76-86.
- Ahmed, M. B., Zhou, J. L., Ngo, H. H., Guo, W., Chen, M., 2016b. Progress in the preparation and application of modified biochar for improved contaminant removal from water and wastewater. Bioresour. Technol. 214, 836-851.
- Aroua, M. K., Daud, W. M. A. W., Yin, C. Y., Adinata, D., 2008. Adsorption capacities of carbon dioxide, oxygen, nitrogen and methane on carbon molecular basket derived from
- polyethyleneimine impregnation on microporous palm shell activated carbon. Sep. Purif. Technol. 62, 609-613.
- Benhouria, A., Islam, M. A., Zaghouane-Boudiaf, H., Boutahala, M., Hameed, B. H., 2015. Calcium alginate-bentonite-activated carbon composite beads as highly effective adsorbent for methylene blue. Chem. Eng. 270, 621-630.



- Boujibar, O., Ghamouss, F., Ghosh, A., Achak, O., Chafik, T., 2019. Activated carbon with exceptionally high surface area and tailored nanoporosity obtained from natural anthracite and its use in supercapacitors. J. Power Sources. 436, 226882.
- Cossutta, M., Vretenar, V., Centeno, T. A., Kotrusz, P., McKechnie, J., Pickering, S. J., 2020. A comparative life cycle assessment of graphene and activated carbon in a supercapacitor application. J. Clean. Prod. 242, 118468.
- Deng, H., Li, G., Yang, H., Tang, J., Tang, J., 2010. Preparation of activated carbons from cotton stalk by microwave assisted KOH and K<sub>2</sub>CO<sub>3</sub> activation. Chem. Eng. 163(3), 373-381.
- Erdoğan, S., Akmil Başar, C., Önal, Y., 2017. Particle size effect of raw material on the pore structure of carbon support and its adsorption capability. Particul. Sci. Technol. 35(3), 330-337.
- Foo, K. Y., Hameed, B. H., 2011. Utilization of rice husks as a feedstock for preparation of activated carbon by microwave induced KOH and K<sub>2</sub>CO<sub>3</sub> activation. Bioresour. Technol. 102(20), 9814-9817.
- Foo, K. Y., Hameed, B. H., 2012. Microwave-assisted regeneration of activated carbon. Bioresour. Technol. 119, 234-240.
- Habaki, H., Hayashi, T., Sinthupinyo, P., Egashira, R., 2019. Purification of glycerol from transesterification using activated carbon prepared from Jatropha Shell for biodiesel production. J. Environ. Chem. Eng. 7(5), 103303.
- He, B., Liu, J., Zhang, Y., Zhang, S., Wang, P., Xu, H., 2020. Comparison of Structured Activated Carbon and Traditional Adsorbents for Purification of H<sub>2</sub>. Sep. Purif. 116529.
- Huber, L., Hauser, S.B., Brendlé, E., Ruch, P., Ammann, J., Hauert, R., Widmer, R.N., Ubert, C.J., Matam, S.K., Yoon, S., Zhang, Y., 2019. The effect of activation time on water sorption behavior of nitrogen-doped, physically activated, monolithic carbon for adsorption cooling. Microporous Mesoporous Mater. 276, 239-250.
- Huo, E., Duan, D., Lei, H., Liu, C., Zhang, Y., Wu, J., Zhao, Y., Huang, Z., Qian, M., Zhang, Q., Lin, X., 2020. Phenols production form Douglas fir catalytic pyrolysis with MgO and biomass-derived activated carbon catalysts. Energy.117459.
- Inal, I. I. G., Aktas, Z., 2020. Enhancing the performance of activated carbon based scalable supercapacitors by heat treatment. Appl. Surf. 145895.
- Jiang, C., Yakaboylu, G. A., Yumak, T., Zondlo, J. W., Sabolsky, E. M., Wang, J., 2020. Activated carbons prepared by indirect and direct CO<sub>2</sub> activation of lignocellulosic biomass for supercapacitor electrodes. Renew. Energy. 155, 38-52.
- Koyuncu, F., Güzel, F., Sayğılı, H., 2018. Role of optimization parameters in the production of nanoporous carbon from mandarin shells by microwave-assisted chemical activation and utilization as dye adsorbent. Adv. Powder Technol. 29(9), 2108-2118.
- Kuptajit, P., Sano, N., 2019. Application of microwave-induced plasma for extremely fast synthesis of large surface-area activated carbon. Appl. Phys. Express. 12, 086001.



- Kuptajit, P., Nakagawa, K., Suzuki, T., Sano, N., 2021. Pseudo continuous reactor with microwave-plasma for preparation of high surface area activated carbon. J. Jpn. Inst. Energy, accepted for publication.
- Lam, S.S., Su, M.H., Nam, W.L., Thoo, D.S., Ng, C.M., Liew, R.K., Yuh Yek, P.N., Ma, N.L., Nguyen Vo, D.V., 2018. Microwave pyrolysis with steam activation in producing activated carbon for removal of herbicides in agricultural surface water. Ind. Eng. Chem. 58(2), 695-703.
- Li, K., Zhou, M., Liang, L., Jiang, L., Wang, W., 2019. Ultrahigh-surface-area activated carbon aerogels derived from glucose for high-performance organic pollutants adsorption. J. Colloid Interf. Sci. 546, 333-343.
- Liang, J., Qu, T., Kun, X., Zhang, Y., Chen, S., Cao, Y.C., Xie, M. Guo, X., 2018. Microwave assisted synthesis of camellia oleifera shell-derived porous carbon with rich oxygen functionalities and superior supercapacitor performance. Appl. Surf. 436, 934-940.
- Lippens, B., de Boer, J., 1965. Studies on Pore Systems in Catalysts V. The t Method. J. Catal. 4, 319-323.
- Liu, Q. S., Zheng, T., Wang, P., Guo, L., 2010. Preparation and characterization of activated carbon from bamboo by microwave-induced phosphoric acid activation. Ind. Crops Prod. 31(2), 233-238.
- Loya-González, D., Loredo-Cancino, M., Soto-Regalado, E., Rivas-García, P., de Jesús Cerino-Córdova, F., García-Reyes, R.B., Bustos-Martínez, D., Estrada-Baltazar, A., 2019. Optimal activated carbon production from corn pericarp: A life cycle assessment approach. J. Clean. Prod. 219, 316-325.
- Lozano-Castello, D., Alcaniz-Monge, J., De la Casa-Lillo, M. A., Cazorla-Amoros, D., Linares-Solano, A., 2002. Advances in the study of methane storage in porous carbonaceous materials. Fuel. 81, 1777-1803.
- Lv, Y., Zhang, F., Dou, Y., Zhai, Y., Wang, J., Liu, H., Xia, Y., Tu, B., Zhao, D., 2012. A comprehensive study on KOH activation of ordered mesoporous carbons and their supercapacitor application. J. Mater. Chem. 22, 93–99.
- Mukai, S. R., Tamitsuji, C., Nishihara, H., Tamon, H., 2005. Preparation of mesoporous carbon gels from an inexpensive combination of phenol and formaldehyde. Carbon. 12, 2628-2630.
- Njoku, V. O., Foo, K. Y., Asif, M., Hameed, B. H., 2014. Preparation of activated carbons from rambutan (Nephelium lappaceum) peel by microwave-induced KOH activation for acid yellow 17 dye adsorption. Chem. Eng. 250, 198-204.
- Morgan, M., 1971. Electrical conduction in amorphous carbon films. Thin Solid Films 7, 313-323.
- Nasrullah, A., Saad, B., Bhat, A. H., Khan, A. S., Danish, M., Isa, M. H., Naeem, A., 2019. Mangosteen peel waste as a sustainable precursor for high surface area mesoporous activated carbon: Characterization and application for methylene blue removal. J. Clean. Prod. 211, 1190-1200.



- Pena, J., Villot, A., Gerente, C., 2020. Pyrolysis chars and physically activated carbons prepared from buckwheat husks for catalytic purification of syngas. Biomass Bioenergy. 132, 105435.
- Rashidi, N. A., Yusup, S., 2017. Potential of palm kernel shell as activated carbon precursors through single stage activation technique for carbon dioxide adsorption. J. Clean. Prod. 168, 474-486.
- Rossi, G. E., Winfield, J. M., Mitchell, C. J., van der Borden, W., van der Velde, K., Carr, R. H., Lennon, D., 2020. Phosgene formation via carbon monoxide and dichlorine reaction over an activated carbon catalyst: Reaction testing arrangements. Appl. Catal A-Gen. 594, 117467.
- Sayğili, H., Güzel, F., Önal, Y., 2015. Conversion of grape industrial processing waste to activated carbon sorbent and its performance in cationic and anionic dyes adsorption. J. Clean. Prod. 93, 84-93.
- Selvaraju, G., Bakar, N. K. A., 2018. Process conditions for the manufacture of highly micro-mesoporous eco-friendly activated carbon from artocarpus integer bio-waste by steam activation. J. Taiwan Inst. Chem. Eng. 93, 414-426.
- Su, Y., Liu, L., Xu, D., Du, H., Xie, Y., Xiong, Y., Zhang, S., 2020. Syngas production at low temperature via the combination of hydrothermal pretreatment and activated carbon catalyst along with value-added utilization of tar and bio-char. Energy Convers. Manag. 205, 112382.
- Sulaiman, N. S., Hashim, R., Amini, M. H. M., Danish, M., Sulaiman, O., 2018. Optimization of activated carbon preparation from cassava stem using response surface methodology on surface area and yield. J. Clean. Prod. 198, 1422-1430.
- <u>Üner, O., Bayrak, Y., 2018. The effect of carbonization temperature, carbonization time</u> and impregnation ratio on the properties of activated carbon produced from *Arundo* <u>donax. Microporous Mesoporous Mater. 268, 225-234.</u>
- Xin-Hui, D., Srinivasakannan, C., Jin-Hui, P., Li-Bo, Z., Zheng-Yong, Z., 2011. Comparison of activated carbon prepared from Jatropha hull by conventional heating and microwave heating. Biomass Bioenergy. 35(9), 3920-3926.
- Yek, P. N. Y., Liew, R. K., Osman, M. S., Lee, C. L., Chuah, J. H., Park, Y. K., Lam, S. S., 2019. Microwave steam activation, an innovative pyrolysis approach to convert waste palm shell into highly microporous activated carbon. J. Environ. 236, 245-253.
- Yu, Y., Qiao, N., Wang, D., Zhu, Q., Fu, F., Cao, R., Wang, R., Liu, W., Xu, B., 2019. Fluffy honeycomb-like activated carbon from popcorn with high surface area and well-developed porosity for ultra-high efficiency adsorption of organic dyes. Bioresour. Technol. 285, 121340.
- Zabaniotou, A., Madau, P., Oudenne, P. D., Jung, C. G., Delplancke, M. P., Fontana, A., 2004. Active carbon production from used tire in two-stage procedure: industrial pyrolysis and bench scale activation with H<sub>2</sub>O–CO<sub>2</sub> mixture. J. Anal. Appl. Pyrolysis. 72, 289-297.



Zhang, Y., Song, X., Xu, Y., Shen, H., Kong, X., Xu, H., 2019. Utilization of wheat bran for producing activated carbon with high specific surface area via NaOH activation using industrial furnace. J. Clean. Prod. 210, 366-375.

Zhu, X., Gao, Y., Yue, Q., Kan, Y., Kong, W., Gao, B., 2017. Preparation of green algabased activated carbon with lower impregnation ratio and less activation time by potassium tartrate for adsorption of chloramphenicol. Ecotoxicol. Environ. 145, 289-294.

# 3.2 Rational Design of Metal-free Doped Carbon Nanohorns Catalysts for Efficient Electrosynthesis of H<sub>2</sub>O<sub>2</sub> from O<sub>2</sub> Reduction

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**ABSTRACT:** Electroreduction of O<sub>2</sub> is a promising method for decentralized H<sub>2</sub>O<sub>2</sub> production. Due to their high selectivity, low cost, and highly tunable properties, O and N doped carbon catalysts are appealing for this process. However, the relative effects of O and N dopants on the catalytic performances of carbon are not well understood. In this work, we present highly active and selective 2e<sup>-</sup> O<sub>2</sub> reduction catalysts based on doped carbon nanohorns (CNH), synthesized by gas-injected arc-in-water (GI-AIW) method. The effects of O and N dopants incorporated during the synthesis and the post-treatment are investigated. We discovered that the selectivity of CNH may be more sensitive to changes in N dopant than to changes in O dopant. Our doped CNH catalyst exhibits an early onset potential of 0.85 V vs. RHE, >80% selectivity, and excellent stability even after 5,000 cycles and 12 hours of flow electrolysis. Our gas diffusion device can generate H<sub>2</sub>O<sub>2</sub> at a practical concentration of 56 mM per hour, corresponding to a production rate of 0.74 mol h<sup>-1</sup> g<sup>-1</sup>. These results suggest that regulating both O and N dopants is an effective design strategy for an efficient carbon catalyst, which is essential in the electrosynthesis of H<sub>2</sub>O<sub>2</sub> from O<sub>2</sub>.

### INTRODUCTION

Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) is an important oxidizing agent used in the manufacture of numerous industrial and consumer products, including paper mills, textiles, pharmaceuticals, paints, polymers, and semiconductors.<sup>1</sup> H<sub>2</sub>O<sub>2</sub> is currently produced by the anthraquinone oxidation reaction, which is a highly energy-intensive process limited to large-scale facilities.<sup>2</sup> Due to the intricacy of the multi-step anthraquinone process and the instability of H<sub>2</sub>O<sub>2</sub>, the availability of H<sub>2</sub>O<sub>2</sub> in remote places has been limited. As a result, decentralized solutions for H<sub>2</sub>O<sub>2</sub> production are being investigated. One of the


processes that has received a lot of attention in recent years is the electrosynthesis of  $H_2O_2$  via the oxygen reduction reaction (ORR), which can operate at low temperature and atmospheric pressure under acid or alkaline conditions.<sup>3</sup> Despite the fact that  $H_2O_2$  is more stable in acid and can be produced at higher concentrations, alkaline hydrogen peroxide (AHP) is a very useful chemical, especially for biomass processing and biofuel production, due to its ability to selectively attack carbonyl and ethylene groups.<sup>4</sup> When combined with renewable electricity, the electrosynthesis of  $H_2O_2$  in alkaline can provide a decentralized method for producing green AHP on-site, which could be beneficial for biomass valorization applications.

As shown in Equation 1 and 2, the ORR in an alkaline electrolyte can proceed through the 2e<sup>-</sup> pathway to  $H_2O_2$  at the thermodynamic potential of 0.76 V vs. RHE; or reduce further via the 4e<sup>-</sup> pathway to a more thermodynamically stable product,  $H_2O$ , at 1.23 V vs. RHE. <sup>5,6</sup>

$O_2 + 2e^- + H_2O \rightarrow HO_2^- + OH^-$	E° = 0.76 V vs. RHE	(1)
$O_2 + 4e^- + 2H_2O \rightarrow 4OH^-$	$F^{\circ} = 1.23 \text{ V vs} \text{ RHF}$	(2)

The ability to fine-tune the binding strength between the electrocatalyst active sites and \*OOH. the first intermediate formed in the reaction, is vital to producing H<sub>2</sub>O<sub>2</sub> efficiently.<sup>7</sup> Strongly bound \*OOH would be reduced all the way to form the undesired  $H_2O$ . Weakly bound \*OOH, on the other hand, would result in a low ORR activity due to the inherent scaling relation between the \*OOH and \*OH adsorption energies.<sup>8–10</sup> Among the current H<sub>2</sub>O<sub>2</sub>-selective catalysts, which include noble metals, metal complexes, metal oxides, and single-atom catalysts,<sup>11</sup> metal-free carbon materials have gained the most interest due to their low cost, scalability, and high flexibility in structural and surface modifications.<sup>12</sup> Most notably, carbon materials doped with O and N atoms, such as commercial carbon blacks,<sup>3,13</sup> mesoporous carbon,<sup>14–18</sup> carbon dots,<sup>19</sup> carbon nanotubes,<sup>20–22</sup> graphenes,<sup>5,23–</sup> <sup>25</sup> and carbon nanohorns<sup>26</sup> have consistently demonstrated early current onset potentials and excellent selectivity towards the 2e<sup>-</sup> product. While a thorough understanding of the active sites has yet to be established, it is evident that both O and N dopants play a key role in directing the ORR activity and selectivity of carbon catalysts.<sup>11</sup> Multiple investigations have revealed that the H<sub>2</sub>O<sub>2</sub> selectivity is directly correlated to O content in the catalysts, and the active site is postulated to be the carbon atom adjacent to the carboxyl (-COOH), etheric (C-O-C), or quinone (C=O) functional groups.<sup>20,27,28</sup> Recently, Han et al. identified the active site to be the quinone functional group by experimentally and theoretically demonstrated that their carbon catalyst with guinone-functionalized edge sites achieved an onset potential of 0.83 V vs. RHE and >97% selectivity to H<sub>2</sub>O<sub>2</sub> in 0.1 M KOH (pH 13) due to having the most optimal  $\Delta G_{OOH^*}$ .<sup>29</sup> For N-doped carbon catalysts, there is substantial dispute on the nature of the ORR active sites since pyridinic N and pyrrolic N have all been proposed to be the origin of the catalytic activity towards H<sub>2</sub>O<sub>2</sub>. <sup>5,25,26,30</sup> Li et al., for example, reported a pyrrolic-N-rich carbon catalyst that achieved an onset of 0.76 V vs. RHE and >95% selectivity towards H<sub>2</sub>O<sub>2</sub> at pH 13.<sup>25</sup> Iglesias et al., on the other hand, demonstrated that their graphitized N-doped carbon nanohorns with the highest ratio of pyridinic N/pyrrolic N were the most active and selective for H<sub>2</sub>O<sub>2</sub> generation, with a moderate selectivity of 63% at pH 13 but a high selectivity of 98% at pH 1.<sup>26</sup> Despite the astounding benefits of N dopant towards the 2e<sup>-</sup> pathway of ORR, its effects cannot be decoupled from those of O dopant as the majority of N-doped carbons



reported in literature also contained O functional groups in their structures.<sup>31</sup> The lack of a complete understanding of the catalytic active sites, particularly the relative activity of O and N functional groups, inhibits a universal design strategy for an efficient ORR catalyst.

Herein, we investigate the highly active oxygen reduction electrocatalysts based on doped carbon nanohorns, synthesized by gas-injected arc-in-water (GI-AIW) method. This arc discharge method, which is conducted in water with an inert gas injected into the arc zone to rapidly guench the carbon vapor, is simple to set up and can produce high purity single wall carbon nanohorns with tunable properties at a scalable volume.<sup>32</sup> Since no metal catalyst is required, GI-AIW method yields completely metal-free carbon nanohorns, eliminating the effects of transition metal contamination on the ORR activity which is a typical concern for other graphitic carbon nanostructures.<sup>33</sup> We also demonstrate that the O and N contents of the nanohorns catalysts can be tuned by changing the type of carrier gases used during the GI-AIW technique, such as N<sub>2</sub> or Ar, or by performing post-treatment processes such as oxidation and nitridation. This variation in dopant species allows us to investigate the relative effects of O and N on the ORR activity and H<sub>2</sub>O<sub>2</sub> selectivity. The structural and reactivity relationships between four different carbon nanohorns catalysts are investigated by TEM, XRD, Raman spectroscopy, N<sub>2</sub> sorption, NEXAFS, XPS, RRDE measurements, capacitance determination, and Tafel analyses. We discovered that the selectivity of our catalysts is more sensitive to changes in the N dopants than to changes in O dopants, and we further demonstrate that our doped carbon nanohorns catalyst exhibits an early onset potential, good selectivity, and high stability even after 5,000 cycles of accelerated stability testing as well as 12 hours of continuous operation in a flow electrolysis cell. These findings demonstrate that doped carbon nanohorns are effective electrocatalysts for the electrosynthesis of H<sub>2</sub>O<sub>2</sub> from O<sub>2</sub> and further suggest a design strategy that can be applied to other carbon-based oxygen reduction catalysts.

### **EXPERIMENTAL SECTION**

CNH Catalyst Preparation. Single-wall carbon nanohorns (CNH) were synthesized by a previously reported gas-injected arc-in-water (GI-AIW) method.<sup>34</sup> As shown in Figure 1, a set of graphite electrodes consisted of an anode rod (99.9995% graphite SPK grade, Alfa Aesar) and a cathode tube, which also served as a reaction chamber, was submerged in de-ionized water. A direct electrical current of 100 A was supplied to generate an arc discharge between both electrodes. The anode was slowly raised toward the inner surface of the cathode hole by a step motor with a speed of 5.25 mm s<sup>-1</sup>. N<sub>2</sub> or Ar was employed as a carrier gas in the synthesis at the flow rate of 10 mL min<sup>-1</sup>, which resulted in carbon nanohorns with and without nitrogen content in the structure (CNH and CNH(Ar)). In this method, it is established that the fine powders that float on the water are carbon nanohorns, while the bulky deposits that sink are multiwall carbon nanotubes.<sup>34</sup> As a result, only the floating products were collected and dried in an oven set to 90 °C overnight. Oxygen-doped CNH catalyst (O-CNH) was synthesized by immersing a mixture of CNH and potassium hydroxide (1:4 by weight) in water for 8 hours. The mixture was dried in an oven at 80 °C overnight, followed by calcination in the air with a heating rate of 3 °C min<sup>-1</sup> and held at 600 °C for 1 hour.<sup>35</sup> The catalyst was thoroughly



washed with de-ionized water and dried at 90 °C overnight. Nitrogen-doped CNH catalyst (N-CNH) was synthesized by immersing a mixture of CNH and melamine (1:6 by weight) in 80 v% ethanol-water for 5 hours. The mixture was dried in an oven at 105 °C overnight, followed by calcination in a N<sub>2</sub> atmosphere with a heating rate of 10 °C min<sup>-1</sup> and held at 850 °C for 2 hours.<sup>36</sup>

**Physical and chemical characterizations.** Crystallographic identification of each catalyst was performed by X-ray diffractometry (XRD, Bruker, D8 advance) using CuKa radiation and operated at 40 kV and 40 mA with a scanning step of 0.02° s<sup>-1</sup> in the range of 10-80°. The defect density was assessed by Raman spectroscopy collected under a 532 nm-excitation (Horiba Scientific, LabRAM HR Revolution). The area ratio between the D and G bands (I<sub>D</sub>/I<sub>G</sub>) of the Raman spectra was determined in the OriginPro software. The morphologies of the catalysts were investigated by transmission electron microscopy (TEM, JEOL, JEM-2100Plus, operated at 200 keV). The specific surface area of each catalyst was assessed by N<sub>2</sub> physisorption at the liquid nitrogen temperature (Nova 2000e physisorption analyzer) using the Brunauer-Emmett-Teller (BET) method. Pore size and pore volume distribution were obtained by Barrett-Joyner-Halenda (BJH) analysis. The chemical compositions were analyzed by X-ray photoelectron spectroscopy (XPS, Shimadzu Kratos, AXIS Supra+) with AI Ka radiation and the high-resolution spectra were deconvoluted by the CasaXPS software in which the sp<sup>3</sup> C1s peak was calibrated to be 284.8 eV. The near-edge X-ray absorption fine structure spectroscopy (NEXAFS) was measured at BL3.2 of the Synchrotron Light Research Institute (SLRI), Thailand. The Kedge NEXAFS spectra of carbon, oxygen, and nitrogen were obtained using an energy resolution of 0.5 eV (FWHM) in the total electron yield (TEY) mode.<sup>37,38</sup> The C K edge spectra were normalized with standard gold and calibrated with a highly ordered pyrolytic graphite (HOPG) at 291.65 eV.

Electrochemical activity measurement. Glassy carbon disks (geometrical surface area of 0.196 cm<sup>2</sup>, Sigradur G HTW Hochtemperatur-Werkstoffe GmbH) were cleaned by ultrasonication in acetone, isopropanol, and water for an hour each. Catalyst inks were prepared by mixing 5 mg of the CNH catalyst, 980 µL of 200 proof ethanol, and 20 µL of 5 wt% Nafion<sup>™</sup> 117 ionomer. The mixture was dispersed by ultrasonication for at least an hour. 10 µL of the ink solution was added to the glassy carbon disk and spindried at 300 rpm for at least 2 hours. All electrochemical experiments were operated at ambient temperature and pressure and the measurements were conducted using a PARSTAT MC multichannel potentiostat (PMC1000). The electrochemical O<sub>2</sub> reduction reaction (ORR) activity of each catalyst was measured using a rotating ring-disk electrode setup (RRDE, Princeton Applied Research), which is a 4-electrode electrochemical system consisting of a carbon disk working electrode, a platinum ring working electrode, a platinum wire counter electrode, and a Ag/AgCl reference electrode. The ORR was performed in 0.1 M KOH (99.99%, Sigma-Aldrich), which was continuously purged with 99.99% O<sub>2</sub> gas at a flow rate of 50 mL min<sup>-1</sup>. The RRDE experiment was carried out by scanning the disk potential from 1.1 V to -0.6 V vs. the reversible hydrogen electrode (RHE) at 10 mV s<sup>-1</sup> while holding the Pt ring at 1.2 V vs. RHE to oxidize H<sub>2</sub>O<sub>2</sub> formed on the disk electrode. The rotating speed of the RRDE was 1600 rpm. The background capacitance was collected in an Ar (99.999%) saturated electrolyte. The cyclic



voltammograms (CVs) were corrected for 100% ohmic loss, determined by impedance spectroscopy (EIS) at the open circuit potential. The 3<sup>rd</sup> cycle of the CVs was reported. All potentials are reported with respect to the RHE scale, calculated by the following equation:

$$E_{RHE} = E_{Ag/AgCl} + 0.059 \times pH + 0.197 V$$

The system's ring collection efficiency (N) was determined using the reversible  $[Fe(CN)_6]^{4-}$ <sup>/3-</sup> redox couple. The RRDE measurement using Pt disk and Pt ring was performed in 10 mM K<sub>4</sub>Fe(CN)<sub>6</sub> (99.98%, Sigma Aldrich) in 0.1 M KOH at varying rotating speeds of 400, 900, 1600, 2500, and 3600 rpm. N was found to be 25.38% in our experiment.

The ORR and H<sub>2</sub>O<sub>2</sub> activities were reported after subtracting the current of the disk (*i*<sub>D</sub>) and the ring (*i*<sub>R</sub>) measured in an O<sub>2</sub>-purged electrolyte by the current measured in an Arsaturated electrolyte. The H<sub>2</sub>O<sub>2</sub> current density (*j*<sub>H<sub>2</sub>O<sub>2</sub>) was calculated from  $\frac{i_R}{N*A}$ , when N is the ring collection efficiency and A is the disk's geometric surface area. The selectivity of H<sub>2</sub>O<sub>2</sub> can be calculated as follow:</sub>

$$H_2O_2(\%) = 200 \frac{\frac{l_R}{N}}{i_D + \frac{i_R}{N}}$$

At least 3 data sets per catalyst were collected to calculate the averaged H<sub>2</sub>O<sub>2</sub> selectivity. The electrochemical active surface area (ECSA) was assessed by performing CVs in the non-Faradaic region, between -0.2 to 0.2 V vs. Ag/AgCl, at varying scan rates of 5, 10, 25, 50, and 100 mV s<sup>-1</sup> in an Ar-saturated electrolyte. The double-layer capacitance (C<sub>dl</sub>) was obtained from the slope of the averaged capacitive current densities  $(\frac{|j_{anodic}|+|j_{cathodic}|}{2})$  at 0 V vs. Ag/AgCl plotted against the scan rates. The stability of O-CNH (~0.5 mg cm<sup>-2</sup>) was assessed by performing 5,000 CVs between 1.0 to 0.25 V vs. RHE at the scan rate of 200 mV s<sup>-1</sup>. Slow CV scans at 10 mV s<sup>-1</sup> were collected at cycle number 1, 500, 1000, 2000, 3000, 4000, and 5000. The CVs and the C<sub>dl</sub> before and after stability testing were compared.

**Electrochemical device testing.** A gas diffusion electrode with the O-CNH catalyst layer was fabricated on a  $3.0 \times 3.0 \text{ cm}^2$  carbon paper, (Sigracet 39BB, Ion power, Inc.). The O-CNH ink was spray-coated on the carbon paper to obtain a carbon loading of ~0.5 mg cm<sup>-2</sup>. The H<sub>2</sub>O<sub>2</sub> synthesis was conducted in a 3-compartment Teflon compression cell, comprised of an O<sub>2</sub> gas compartment, a cathode compartment, and an anode compartment. The testing was done in a 3-electrode setup (Figure 6c, Figure S6d), consisting of the O-CNH gas diffusion as a working electrode, a miniature leakless Ag/AgCl (eDAQ) as a reference electrode, and a Pt wire (99.99%, Alfa Aesar) as a counter electrode. To prevent H<sub>2</sub>O<sub>2</sub> crossover, the anode and cathode compartments were separated by an anion exchange membrane (Selemion<sup>TM</sup> AMVN, AGC Engineering Co. Ltd.). O<sub>2</sub> was fed through the O<sub>2</sub> compartment with a flow rate of 40 mL min<sup>-1</sup> and 0.1 M KOH was fed to the cathode and anode compartment with a flow rate of 3 mL min<sup>-1</sup>. The



total electrolyte volume was 30 mL. The active area of the working electrode was 3.14 cm<sup>2</sup>. The ORR was conducted using a chronoamperometry method at 0.65 V vs. RHE. The catholyte was collected at 10, 20, 30, and 60 minutes. The concentration of the collected products was analyzed by a titration method by mixing the catholyte with a  $Ce(SO_4)_2$  solution (0.5 mM  $Ce(SO_4)_2$  solution (97%, Sigma Aldrich) in 0.1 M  $H_2SO_4$ ) at a volume ratio of 1:300. The reaction between  $Ce^{4+}$  and  $H_2O_2$  proceeds as follows:

 $2Ce^{4+} + H_2O_2 \rightarrow 2Ce^{3+} + 2H^+ + O_2$ 

The concentration of the remaining  $Ce^{4+}$  after reacting with  $H_2O_2$  was determined from the standard curve obtained from the absorbance at 315 nm by a UV-visible spectrophotometer (Thermoscientific, Evolution 350) (Figure S6a).



# **RESULTS AND DISCUSSION**

**Figure 1.** Diagram of the gas-injected arc-in-water (GI-AIW) setup for carbon nanohorns (CNH) synthesis.

### **Physical and Chemical Characterizations**

Single-wall carbon nanohorns were synthesized by the gas-injected arc-in-water (GI-AIW) method (diagram in Figure 1).<sup>32</sup> During the synthesis, only ultra-high purity graphites were consumed, eliminating transition metal contaminations that could affect the ORR activity.<sup>33</sup> Two types of carrier gas: N<sub>2</sub> and Ar, were employed in the synthesis of nanohorns catalysts, denoted as CNH and CNH(Ar), respectively. The as-synthesized CNH was oxidized further by annealing a mixture of CNH and KOH in air to generate O-CNH. Lastly, to make N-CNH, CNH was also subjected to a nitridation process employing melamine as a nitrogen source to produce N-CNH (see the Experimental Section). The transmission electron microscopy (TEM) image of CNH in Figure 2a reveals that the sample is comprised of 2 - 4 nm diameter nanotubes with conical tips, which is a signature morphology of carbon nanohorns. The single-wall carbon nanohorns were organized into a mixture of dahlia-like (protruding clusters) and bud-like aggregates (soft-edge clusters).<sup>39,40</sup> Unlike the CNH, the O-CNH shown in Figure 2b appears to have lost the



rigid and protruding structure of typical nanohorns. This is most likely due to the oxidation of the tips and sidewalls of CNH, which resulted in the formation of nanosized openings and defects on the structure, as previously shown in the carbon nanohorns literature.<sup>41–43</sup> As shown in Figure 2c and d, N-CNH and CNH(Ar) exhibit a similar morphology to CNH, confirming that the nanostructure features were preserved after the melamine treatment or when the sample was produced in a different gas environment.

Figure 2e shows that the X-ray diffraction (XRD) patterns of all samples contain a broad shoulder at  $2\theta = 25.9^{\circ}$  and a strong diffraction peak at 26.4°. The former is related to the (002) graphitic plane of carbon nanohorns, whereas the latter is associated with the (002) plane of micrometer-sized graphitic particles residue, which can be found up to 5% in the as-synthesized carbon nanohorns.<sup>44–46</sup> The graphitic residue has been demonstrated to be dense crystalline particles, resulting in a sharp XRD peak but a low surface area,<sup>44</sup> which would contribute minimally to catalytic activity. We assume that the residue was only present in a limited fraction of the samples because no graphitic particles were visible in the TEM images. Peak fitting shown in the inset of Figure 2e reveals that the peak intensity ratios of nanohorns and graphitic residue are similar in all samples, implying a similar residue content. Additionally, Scherrer analysis (Table S1) of the fitted full width at half maximum (FWHM) reveals that the crystallite size of the carbon nanohorns domain in each sample is within a tight range of 8.5-9 nm, with CNH being the largest and O-CNH being the smallest. The slightly smaller crystallite size of O-CNH proves that the oxidation process has introduced a significant defect density into the nanohorn structures, which is consistent with the TEM image in Figure 2b.

Figure 2f shows Raman spectra with two characteristic peaks: the defect band (Dband) at the lower wavenumber and the graphitic band (G-bands) at the higher wavenumber. The locations of these two peaks, as well as the intensity ratio between them, are correlated to the defect density of graphitic carbon. The D and G bands of CNH, N-CNH, and CNH(Ar) appear to have similar positions of roughly 1330 and 1590 cm<sup>-1</sup>, respectively. The D and G bands of O-CNH, on the other hand, are shifted to the higher wavenumbers of 1338 and 1595 cm<sup>-1</sup>. This blue shift could be attributed to a change in the electronic environment of the crystal boundary,<sup>47</sup> implying that the edges of O-CNH are chemically modified, most likely by C=O functional groups, as previously proposed.<sup>42</sup> The intensity ratios between the D and G bands (I<sub>D</sub>/I<sub>G</sub>) of CNH, O-CNH, N-CNH, and CNH(Ar) are 1.37, 1.74, 1.22, and 1.13, respectively. The locations and ratios of the peaks indicate that O-CNH has the highest defect density among the nanohorns samples. This observation is supported by the TEM and XRD analyses. The slightly lower ID/IG ratio of N-CNH could be attributed to the removal of non-crystalline carbon by N<sub>2</sub> annealing,<sup>48</sup> whereas the lower ID/IG ratio of CNH(Ar) coincided with the larger crystallite size of the graphitic impurity as suggested by the XRD (Table S1) or could arise from the lower dopant density, as will be discussed further.





**Figure 2.** TEM images of (a) CNH, (b) O-CNH, (c) N-CNH, and (d) CNH(Ar) catalysts; (e) X-ray diffraction patterns and the (002) peak fittings; (f) Raman spectra; and (g)  $N_2$  sorption isotherms of all CNH catalysts.



N<sub>2</sub> sorption isotherms, pore-volume, and pore-size analyses (Figure 2g and Table S2) reveal that both CNH and CNH(Ar) were predominantly mesoporous in nature, with average pore sizes of 19.7 and 17.1 nm, respectively, yielding Brunauer-Emmett-Teller (BET) surface areas of 303 and 385 m<sup>2</sup> g<sup>-1</sup>. These pore sizes arose from the interstitial pores between the exterior surfaces of nearest-neighbor nanohorns.<sup>49</sup> The surface area of CNH was greatly enlarged by the post-treatment methods. O-CNH and N-CNH exhibit higher BET surface areas of up to 872 and 469 m<sup>2</sup> g<sup>-1</sup>, respectively. According to the isotherm, O-CNH demonstrates a significant increase in micro- and mesoporosity, lowering the average pore size to 3.7 nm. This is most likely due to the nanosized windows opening on the wall, making the internal area of nanohorns accessible to N<sub>2</sub> gas (Table S1). <sup>41,42,50</sup> N-CNH exhibits a slight increase in the microporosity domain, but the majority of the pore diameters remained within the original range of 17.4 nm. As a consequence, surface defects in N-CNH were less prominent than in O-CNH. Nonetheless, the heat treatment of the nitridation process must have aided in the elimination of amorphous or defective carbon with irregular pore domains,<sup>41</sup> resulting in a greater surface area per mass and lower defect density, as suggested by Raman spectroscopy.



**Figure 3.** Normalized (a) C K-edge, (b) O K-edge, and (c) N K-edge NEXAFS spectra identify the types of O and N functional groups in all CNH catalysts.

The local chemical structures and functional groups of the catalysts were elucidated by near-edge X-ray absorption fine structure spectroscopy (NEXAFS) spectra as shown in Figure 3. The characteristic peaks of C K-edge presented in Figure 3a at 282 – 290 eV and 290.5 – 294.5 eV regions are primarily caused by 1s transitions to the unoccupied  $\pi^*$  and  $\sigma^*$  states, respectively. These characteristic peaks are followed by broad features of mixed symmetry transitions located at 297 – 310 eV. Specifically, the transitions at 284.2, 285.5, and 293.0 eV are analogous to graphite bands, indicating that the sp<sup>2</sup> hexagonal structures are present in all samples.<sup>51</sup> The major differences between two spectra appear at 287.6 and 288.3 eV, which correspond to the  $\pi^*$  states of C-O and



C-N functional groups, implying that each CNH sample contains varied O and N contents. The presence of oxygen-containing functional groups in the samples is confirmed by the O K-edge NEXAFS spectra (Figure 3b). The broad  $1s \rightarrow \pi^*$  transitions are correlated to quinone (530.0 eV) and ketone or carboxylic (530.5 eV) groups,<sup>29</sup> which appear to be the primary O-containing functional groups in all CNH catalysts. Interestingly, the 533.4 eV transition assigned to the  $\pi^*$  state of the epoxide or etheric structure is evident in the assynthesized CNH and CNH(Ar), but significantly weakens in the post-processed O-CNH and N-CNH. For the O-CNH, the oxidation process could have introduced high defects in the structure as well as converting the epoxides to more stable O-functional groups such as carboxylic and quinone, leading to the openings in the carbon nanohorns structure as suggested by TEM, XRD, Raman, and N<sub>2</sub> sorption results. This explanation is consistent with the presence of a peak at 528.6 eV, which is attributed to be the electronic transition from O1s to O2p holes associated with oxygen defects.<sup>52</sup> In the case of N-CNH, the epoxides were likely replaced by N functional groups during the nitridation process.53 Lastly, the N K-edge NEXAFS spectra (Figure 3c) show that both CNH and N-CNH contain a significant quantity of N species, while O-CNH contains only a trace and CNH(Ar) includes none. These results confirm that during the GI-AIW process, N from the N<sub>2</sub> gas carrier can be incorporated into the structure of CNH in the forms of pyrrolic-N (400 eV) and pyridinic-N (399 eV). The additional nitridation process can alter the type of N functional groups as shown in Figure 3c, resulting in a relatively higher amount of pyridinic-N and graphitic-N (401.5 eV) in N-CNH compared to the as-synthesized CNH. The oxidation process to produce O-CNH appears to remove some of the existing N species in the as-synthesized CNH, resulting in a substantially weaker N K-edge spectrum. Finally, due to the lack of N source, no N functional group is detected in CNH(Ar), confirming that the graphite source was N-free.







In addition to the qualitative chemical identification by NEXAFS spectra, the elemental quantifications of the O and N functional groups were performed by X-ray photoelectron spectroscopy (XPS) spectra as shown in Figure 4 and Figure S1-S2. Figure 4a and c reveal that the atomic concentrations of O species in CNH and CNH(Ar) are 4.37% and 6.51%, respectively. Approximately 30% of the O content in CNH and CNH(Ar) was O-C species, with the remainder being O=C for CNH and a mixture of O=C and quinone groups for CNH(Ar). N content is another variation between CNH and CNH(Ar), as shown in Figure 4b and d. 1.10% of N, predominantly the pyrrolic-N functional group, is found in CNH, whereas no N is detected in CNH(Ar). In comparison to CNH, the postoxidation O-CNH catalyst contains a higher O content of 5.58% and a lower N content of 0.36%. In addition to creating defects, the oxidation process also modified the surface functional groups of CNH; it converted most of the O-C and some of the O=C to the quinone functional groups, which are likely to be found at the new edge sites. Furthermore,



some of the N functional groups, especially the less stable pyrrolic-N, was oxidized off. N-CNH, on the other hand, contains a lower O content of 2.78% and a higher N content of 1.73%. As previously shown in the literature, a nitridation process typically eliminates O=C, which is the active site for C-N bond formation, while the high annealing temperature of the process is responsible for the volatilization of O-C groups to CO and CO<sub>2</sub>. <sup>[44–46]</sup> The newly introduced N functional group in N-CNH was predominantly pyridinic N, consistent with the type of N found in the melamine source.<sup>54,55</sup>



Electrochemical Activity, Selectivity, Stability, and Device Demonstration

**Figure 5.** (a) Current densities associated with  $H_2O_2$  production (anodic current) and overall oxygen reduction (cathodic current). (b) Selectivity towards  $H_2O_2$  production at varying potentials. (c) Double-layer capacitance (C<sub>dl</sub>) per geometric surface areas and the  $H_2O_2$  onset potentials measured at 0.1 mA cm<sup>-2</sup>. (d) Tafel plot of the oxygen reduction activities of CNH catalysts.

A suitable catalyst for the ORR to  $H_2O_2$  must have an early onset potential, a high selectivity towards the 2e<sup>-</sup> pathway, and a high stability under the relevant operating conditions. To assess the onset potential and selectivity of each nanohorns catalyst, a rotating ring-disk electrode (RRDE) measurements were conducted at 1600 rpm in  $O_2$  saturated 0.1 M KOH. Figure 5a show that the nanohorns catalysts are all active for the



ORR. Both as-synthesized samples: CNH and CNH(Ar) exhibit the onset potentials (defined here as the potential to achieve a  $H_2O_2$  current density of 0.1 mA cm<sup>-2</sup>)<sup>56</sup> of 0.76 V and 0.74 V vs. RHE, respectively. In terms of  $H_2O_2$  selectivity (Figure 5b), CNH exhibits the highest selectivity of 85% at 0.5 V vs. RHE, while CNH(Ar) achieves a slightly lower selectivity of 81% at 0.5 V vs. RHE. The post-processed catalysts, O-CNH and N-CNH, exhibit onset potentials as early as 0.85 and 0.82 V vs. RHE, respectively (Figure 5c). The maximum selectivity of O-CNH is 82% at 0.6 - 0.7 V vs. RHE, which is similar to that of the as-synthesized nanohorns. N-CNH, on the contrary, demonstrates a substantially lower selectivity of 54% at 0.6 V vs. RHE (Figure 5b).

To understand the trend in onset potentials of the catalysts, the double-layer capacitances (C<sub>dl</sub>), which are related to the electrochemically active surface area (ECSA), and to some extent, employed as a descriptor for active sites, were measured from the non-Faradaic region of each catalyst. The Cd of CNH, O-CNH, N-CNH, CNH(Ar) were determined to be 4.62, 6.84, 5.89, and 5.74 mF cm<sup>-2</sup>, respectively (Figure 5c and Figure S3), which is consistent with trend of the BET surface areas. However, the trend in C<sub>dl</sub> does not appear to correlate with the trend in onset potentials. CNH(Ar) exhibits a 24% larger ECSA and a 27% greater BET surface area than CNH (Figure S3f); nevertheless, the onset potential of CNH is better. Due to the structural similarities revealed by TEM and XRD, as well as the similar Tafel slope of 59 mV dec<sup>-1</sup> for CNH and 60 mV dec<sup>-1</sup> for CNH(Ar) (Figure 5d), differences in the defect density (confirmed by Raman) and surface functional groups (characterized by NEXAFS and XPS) may be the origin of the superior onset of CNH over CNH(Ar). For the post-processed nanohorns catalysts, the 48% and 27% increase in ECSA of O-CNH and N-CNH relative to as-synthesized CNH cannot account for the significant improvement in the onset potentials of both catalysts, as demonstrated by normalizing the current density with the double-layer capacitance (Figure S4). In the case of O-CNH, this result implies that the highly defective small porous structure and additional O functional groups generated by the oxidation process are more active than the as-synthesized surface, resulting in a smaller Tafel slope of 49 mV dec<sup>-1</sup> and a 70 mV shift in the ORR onset potential. At 0.85 V vs. RHE, the onset potential of O-CNH is among the earliest reported for carbon-based catalysts for the electrochemical production of H<sub>2</sub>O<sub>2</sub> from O<sub>2</sub>. <sup>24–26,29,57</sup> For N-CNH, the 60 mV improvement in onset potential, despite having a similar C<sub>dl</sub> to those of CNH and CNH(Ar), could arise from the inherent changes in the active sites caused by the increase in pyridinic N and graphitic N species. As a result of these variations, the Tafel slope was reduced to 54 mV dec<sup>-1</sup> and the selectivity towards the 2e<sup>-</sup> reduction pathway was significantly lower.

Except for N-CNH, all CNH catalysts exhibit similarly high selectivity (>80%) towards  $H_2O_2$ , on-par with the state-of-the-art carbon-based catalysts reported in the literature.<sup>17,23,58,59</sup> Unlike pristine carbon nanotubes, which required the O-doping process to improve the  $H_2O_2$  selectivity from ~60% to ~90% as shown by Lu et al.,<sup>20</sup> as-synthesized CNH catalysts exhibit high selectivity for  $H_2O_2$ , most likely due to the presence of intrinsic defects and functional groups introduced during the GI-AIW process. According to the NEXAFS results shown in Figure 4b-c, the most prominent functional groups in the CNH samples were quinone O and pyrrolic N, which have both been postulated as the O and N active sites for 2e<sup>-</sup> reduction pathway.<sup>11,25,29</sup> By comparing the current densities (Figure 5a), selectivity (Figure 5b), onset potentials (Figure 5c), and



normalized currents (Figure S4) of all CNH catalysts, the relative effects of O and N functional groups on the catalyst selectivity are realized. Due to the similar morphology and crystallinity of the as-synthesized catalysts, the ~1% N content may be the origin of the superior activity of CNH over CNH(Ar). When this N content, particularly the pyrrolic-N group, is eliminated by the oxidation process, the selectivity towards the 2e<sup>-</sup> pathway of O-CNH is slightly reduced (Figure 5b), despite containing a higher amount of O species, particularly the quinone functional group, than CNH. These results suggest that the selectivity of the carbon nanohorns catalyst is highly sensitive to the N functional group, much more so than the O functional group. This is further supported by the substantially lower selectivity of N-CNH, which has a high content of pyridinic-N and graphitic N that are likely the active sites towards the 4e<sup>-</sup> product.<sup>60</sup> While it has been established that tuning the O content is an effective design strategy,<sup>61</sup> our results suggest that incorporating the N dopant, particularly pyrrolic-N, on top of the O-dopant will distinctively further enhance the selectivity of carbon-based catalysts towards the 2e<sup>-</sup> ORR.

Among all catalysts, O-CNH demonstrates the earliest onset potential due to its high defect density and a good selectivity for the 2e<sup>-</sup> product due to the presence of pyrrolic N. Thus, the catalyst stability and scalability for the electrochemical  $H_2O_2$ production from O<sub>2</sub> were further examined. The O-CNH catalyst (~0.5 mg cm<sup>-2</sup> loading) was subjected to an accelerated durability testing between 1.0 V to 0.25 V vs. RHE in a 0.1 M KOH in a RRDE setup at 1600 rpm rotation rate. For the first few cycles, the activity of O-CNH drifted towards a lower ORR current density, possibly due to the surface transformation from hydrophobic to hydrophilic, consistent with the minor increase in Cdl after the stability testing (Figure S5b). This behavior is typically observed between the first and second CV scans from 1.1 V to 0.2 V vs. RHE. However, due to the narrow CV window chosen for stability testing, this transformation had taken place over multiple numbers of cycles. After establishing a steady CV, no significant change in both the current densities and the onset potentials was observed between the 500<sup>th</sup> to 5,000<sup>th</sup> cycle throughout the 10-hour testing (Figure 6a and Figure S5a). The selectivity measured at 0.65 V vs. RHE remains in the range of 82-85% (Figure 6a). After 5,000 cycles, no change in the shape of CVs measured in an Ar-saturated electrolyte was observed, indicating negligible chemical changes (Figure 6b).





**Figure 6** (a) Electrochemical performance of O-CNH during an accelerated stability testing by CV scans between 1.0 to 0.25 V vs. RHE at 200 mV s<sup>-1</sup> for 5,000 cycles and (b) the CV of O-CNH in an Ar-saturated electrolyte before and after the stability testing. (c) Electrochemical device setup for  $H_2O_2$  production from  $O_2$  and (d)  $H_2O_2$  production rate and concentration over an hour. (e) 12-hour continuous operation of O-CNH/GDE device at 0.65 V vs. RHE.

The efficacy of O-CNH catalyst as a gas diffusion electrode (GDE) was further evaluated in a 3-compartment compression cell, which included an  $O_2$  gas chamber, a catholyte chamber, and an anolyte chamber as shown in Figure 6c. ~0.5 mg cm<sup>-2</sup> of O-CNH was spray-coated on a commercial gas diffusion layer and assembled facing a catholyte chamber. 3 mL min<sup>-1</sup> of 0.1 M KOH was pumped to the catholyte chamber (total



volume of 30 mL), while 40 mL min<sup>-1</sup> of O<sub>2</sub> gas was delivered across the back of the electrode. The active area of the GDE was 3.14 cm<sup>2</sup>. The GDE was subjected to chronoamperometry at 0.65 V vs. RHE, and the H<sub>2</sub>O<sub>2</sub> concentration was detected using a Ce<sup>4+</sup> titration method (see the Experimental section). As shown in Figure 6d, the  $H_2O_2$ concentration in the electrolyte reaches 56 mM (0.2 wt%) over an hour of operation. The H<sub>2</sub>O<sub>2</sub> Faradaic efficiency (Figure 6d) and production rate (Figure S6b) are initially high in the first 10 minutes of reaction but level off due to the inherent instability of H<sub>2</sub>O<sub>2</sub> in an alkaline solution.<sup>62</sup> As a result, the average H<sub>2</sub>O<sub>2</sub> production rate of O-CNH/GDE has reduced drastically from 1.88 mol h<sup>-1</sup>  $g_{cat}^{-1}$  in the first 10 minutes to only 0.74 mol h<sup>-1</sup>  $g_{cat}^{-1}$ over an hour and achieved a maximum concentration of 73 mM (Figure S6c). Nevertheless, the device demonstrates superb stability as it can be operated continuously for at least 12 hours without any substantial decline in the current density, as shown in Figure 6e. To further improve the production rate, a stabilizer could be incorporated in the electrolyte to enhance the stability of the H<sub>2</sub>O<sub>2</sub> product.<sup>29</sup> The results demonstrated in our work have proven that the doped carbon nanohorns can be employed as an efficient and stable electrocatalyst to produce  $H_2O_2$  from  $O_2$  via an electrochemical route. Additionally, our results suggest that tailoring both O and N functional groups, particularly the pyrrolic-N, can be a viable design strategy for a highly active metal-free carbon electrocatalyst for the electroreduction of  $O_2$  to  $H_2O_2$ .

### CONCLUSION

In this study, four types of carbon nanohorns catalysts with varying degrees of O and N dopants: CNH, O-CNH, N-CNH, and CNH(Ar) have been investigated. All catalysts were active for the oxygen reduction reaction (ORR) in alkaline and CNH, O-CNH, and CNH(Ar) exhibited >80% selectivity towards H<sub>2</sub>O<sub>2</sub>. The as-synthesized CNH and CNH(Ar) catalysts were similar in morphologies and crystallinity, but CNH which contained pyrrolic N functional group exhibited an earlier onset potential and a higher selectivity than CNH(Ar) which was N-free. Oxidation of CNH produced O-CNH with more surface defects and quinone functional groups but fewer pyrrolic-N groups, resulting in an earliest onset potential albeit with slightly lower selectivity. Lastly, nitridation of CNH with a melamine source increased pyridinic N and graphitic N functional groups, resulting in N-CNH with a better onset potential but much decreased selectivity towards H<sub>2</sub>O<sub>2</sub>. These findings imply that the effect of N functional groups on the ORR selectivity may be more dominant than the O functional groups and that minor changes in N species, such as pyrrolic vs. pyridinic and graphitic N, can alter the selectivity of carbon nanohorns from the 2e<sup>-</sup> to 4e<sup>-</sup> pathway. Tuning both O and N contents, particularly the pyrrolic-N group, is thus an effective design strategy for a  $H_2O_2$ -selective carbon-based oxygen reduction catalyst. Finally, we demonstrated that O-CNH, which has the highest onset potential of 0.85 V vs. RHE and good H<sub>2</sub>O<sub>2</sub> selectivity of 82%, was highly stable even after 5,000 accelerated stability testing cycles or 12 hours continuous-flow operation at 0.65 V vs. RHE. Within an hour, the gas diffusion device based on O-CNH produced 56 mM of H<sub>2</sub>O<sub>2</sub>, corresponding to a  $H_2O_2$  production rate of 0.74 mol h<sup>-1</sup> g<sup>-1</sup><sub>cat</sub>. Our findings demonstrated that doped carbon nanohorns are an efficient and stable electrocatalyst for the electrochemical production of H<sub>2</sub>O<sub>2</sub> from O<sub>2</sub>.



# ASSOCIATED CONTENT

### **Supporting Information**

The Supporting Information is available free of charge.

Scherrer analysis, N<sub>2</sub> sorption analysis, XPS analysis, double-layer capacitance measurements, normalized current, cyclic voltammograms of the stability testing, UV absorbance calibration curve, device performance, and testing setup (PDF)

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### **Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

#### Notes

The authors declare no competing financial interest.

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### REFERENCES

- (1) Jones, C. W. *Applications of Hydrogen Peroxide and Derivatives*; Royal Society of Chemistry, 1999; Vol. 2.
- (2) Campos-Martin, J. M.; Blanco-Brieva, G.; Fierro, J. L. G. Hydrogen Peroxide Synthesis: An Outlook beyond the Anthraquinone Process. *Angew. Chemie Int. Ed.* **2006**, *45* (42), 6962–6984. https://doi.org/10.1002/anie.200503779.
- (3) Chen, Z.; Chen, S.; Siahrostami, S.; Chakthranont, P.; Hahn, C.; Nordlund, D.; Dimosthenis, S.; Norskov, J. K.; Bao, Z.; Jaramillo, T. F.; Nørskov, J. K.; Bao, Z.; Jaramillo, T. F.; Norskov, J. K.; Bao, Z.; Jaramillo, T. F. Development of a Reactor with Carbon Catalysts for Modular-Scale{,} Low-Cost Electrochemical Generation of H2O2. *React. Chem. Eng.* **2017**, 2 (2), 239–245. https://doi.org/10.1039/C6RE00195E.
- (4) Ho, M. C.; Ong, V. Z.; Wu, T. Y. Potential Use of Alkaline Hydrogen Peroxide in



Lignocellulosic Biomass Pretreatment and Valorization – A Review. *Renew. Sustain. Energy Rev.* **2019**, *112* (April), 75–86. https://doi.org/10.1016/j.rser.2019.04.082.

- (5) Kim, H. W.; Bukas, V. J.; Park, H.; Park, S.; Diederichsen, K. M.; Lim, J.; Cho, Y. H.; Kim, J.; Kim, W.; Han, T. H.; Voss, J.; Luntz, A. C.; McCloskey, B. D. Mechanisms of Two-Electron and Four-Electron Electrochemical Oxygen Reduction Reactions at Nitrogen-Doped Reduced Graphene Oxide. *ACS Catal.* **2020**, *10* (1), 852–863. https://doi.org/10.1021/acscatal.9b04106.
- (6) Vijapur, S. H.; Hall, T. D.; Snyder, S.; Inman, M.; Taylor, E. J.; Skinn, B. Electrochemical Peroxide Generation. *ECS Trans.* **2017**, 77 (11), 947–962. https://doi.org/10.1149/07711.0947ecst.
- (7) Jiang, K.; Zhao, J.; Wang, H. Catalyst Design for Electrochemical Oxygen Reduction toward Hydrogen Peroxide. *Adv. Funct. Mater.* **2020**, *30* (35), 2003321. https://doi.org/10.1002/adfm.202003321.
- (8) Man, I. C.; Su, H. Y.; Calle-Vallejo, F.; Hansen, H. A.; Martínez, J. I.; Inoglu, N. G.; Kitchin, J.; Jaramillo, T. F.; Nørskov, J. K.; Rossmeisl, J. Universality in Oxygen Evolution Electrocatalysis on Oxide Surfaces. *ChemCatChem* **2011**, *3* (7), 1159– 1165. https://doi.org/10.1002/cctc.201000397.
- Seh, Z. W.; Kibsgaard, J.; Dickens, C. F.; Chorkendorff, I.; Nørskov, J. K.; Jaramillo, T. F. Combining Theory and Experiment in Electrocatalysis: Insights into Materials Design. *Science (80-.).* 2017, 355 (6321), eaad4998. https://doi.org/10.1126/science.aad4998.
- (10) Montoya, J. H.; Seitz, L. C.; Chakthranont, P.; Vojvodic, A.; Jaramillo, T. F.; Nørskov, J. K. Materials for Solar Fuels and Chemicals. *Nat. Mater.* 2017, *16* (1), 70–81. https://doi.org/10.1038/nmat4778.
- (11) Jiang, Y.; Ni, P.; Chen, C.; Lu, Y.; Yang, P.; Kong, B.; Fisher, A.; Wang, X. Selective Electrochemical H2O2 Production through Two-Electron Oxygen Electrochemistry. *Adv. Energy Mater.* **2018**, *8* (31), 17–19. https://doi.org/10.1002/aenm.201801909.
- (12) Liu, X.; Dai, L. Carbon-Based Metal-Free Catalysts. *Nat. Rev. Mater.* **2016**, *1* (11). https://doi.org/10.1038/natrevmats.2016.64.
- (13) Xia, C.; Xia, Y.; Zhu, P.; Fan, L.; Wang, H. Direct Electrosynthesis of Pure Aqueous H2O2solutions up to 20% by Weight Using a Solid Electrolyte. *Science (80-. ).* 2019, 366 (6462), 226–231. https://doi.org/10.1126/science.aay1844.
- (14) Zhou, W.; Ding, Y.; Gao, J.; Kou, K.; Wang, Y.; Meng, X.; Wu, S.; Qin, Y. Green Electrochemical Modification of RVC Foam Electrode and Improved H2O2 Electrogeneration by Applying Pulsed Current for Pollutant Removal. *Environ. Sci. Pollut. Res.* **2018**, 25 (6), 6015–6025. https://doi.org/10.1007/s11356-017-0810-8.
- (15) Lee, Y. H.; Li, F.; Chang, K. H.; Hu, C. C.; Ohsaka, T. Novel Synthesis of N-Doped Porous Carbons from Collagen for Electrocatalytic Production of H 2O 2. *Appl. Catal. B Environ.* **2012**, *126*, 208–214. https://doi.org/10.1016/j.apcatb.2012.06.031.
- (16) Fellinger, T. P.; Hasché, F.; Strasser, P.; Antonietti, M. Mesoporous Nitrogen-



Doped Carbon for the Electrocatalytic Synthesis of Hydrogen Peroxide. *J. Am. Chem. Soc.* **2012**, *134* (9), 4072–4075. https://doi.org/10.1021/ja300038p.

- (17) Chen, S.; Chen, Z.; Siahrostami, S.; Kim, T. R.; Nordlund, D.; Sokaras, D.; Nowak, S.; To, J. W. F.; Higgins, D.; Sinclair, R.; Nørskov, J. K.; Jaramillo, T. F.; Bao, Z. Defective Carbon-Based Materials for the Electrochemical Synthesis of Hydrogen Peroxide. ACS Sustain. Chem. Eng. 2018, 6 (1), 311–317. https://doi.org/10.1021/acssuschemeng.7b02517.
- (18) Sun, Y.; Sinev, I.; Ju, W.; Bergmann, A.; Dresp, S.; Kühl, S.; Spöri, C.; Schmies, H.; Wang, H.; Bernsmeier, D.; Paul, B.; Schmack, R.; Kraehnert, R.; Roldan Cuenya, B.; Strasser, P. Efficient Electrochemical Hydrogen Peroxide Production from Molecular Oxygen on Nitrogen-Doped Mesoporous Carbon Catalysts. *ACS Catal.* **2018**, *8* (4), 2844–2856. https://doi.org/10.1021/acscatal.7b03464.
- (19) Pham-Truong, T. N.; Petenzi, T.; Ranjan, C.; Randriamahazaka, H.; Ghilane, J. Microwave Assisted Synthesis of Carbon Dots in Ionic Liquid as Metal Free Catalyst for Highly Selective Production of Hydrogen Peroxide. *Carbon N. Y.* **2018**, *130*, 544–552. https://doi.org/10.1016/j.carbon.2018.01.070.
- (20) Lu, Z.; Chen, G.; Siahrostami, S.; Chen, Z.; Liu, K.; Xie, J.; Liao, L.; Wu, T.; Lin, D.; Liu, Y.; Jaramillo, T. F.; Nørskov, J. K.; Cui, Y. High-Efficiency Oxygen Reduction to Hydrogen Peroxide Catalysed by Oxidized Carbon Materials. *Nat. Catal.* 2018, 1 (February), 156–162. https://doi.org/10.1038/s41929-017-0017-x.
- (21) Tuci, G.; Zafferoni, C.; D'Ambrosio, P.; Caporali, S.; Ceppatelli, M.; Rossin, A.; Tsoufis, T.; Innocenti, M.; Giambastiani, G. Tailoring Carbon Nanotube N-Dopants While Designing Metal-Free Electrocatalysts for the Oxygen Reduction Reaction in Alkaline Medium. ACS Catal. 2013, 3 (9), 2108–2111. https://doi.org/10.1021/cs400379h.
- (22) Sa, Y. J.; Kim, J. H.; Joo, S. H. Active Edge-Site-Rich Carbon Nanocatalysts with Enhanced Electron Transfer for Efficient Electrochemical Hydrogen Peroxide Production. *Angew. Chemie - Int. Ed.* **2019**, *58* (4), 1100–1105. https://doi.org/10.1002/anie.201812435.
- Han, L.; Sun, Y.; Li, S.; Cheng, C.; Halbig, C. E.; Feicht, P.; Hübner, J. L.; Strasser, P.; Eigler, S. In-Plane Carbon Lattice-Defect Regulating Electrochemical Oxygen Reduction to Hydrogen Peroxide Production over Nitrogen-Doped Graphene. ACS Catal. 2019, 9 (2), 1283–1288. https://doi.org/10.1021/acscatal.8b03734.
- (24) Kim, H. W.; Ross, M. B.; Kornienko, N.; Zhang, L.; Guo, J.; Yang, P.; McCloskey, B. D. Efficient Hydrogen Peroxide Generation Using Reduced Graphene Oxide-Based Oxygen Reduction Electrocatalysts. *Nat. Catal.* 2018, *1* (4), 282–290. https://doi.org/10.1038/s41929-018-0044-2.
- (25) Li, L.; Tang, C.; Zheng, Y.; Xia, B.; Zhou, X.; Xu, H.; Qiao, S. Z. Tailoring Selectivity of Electrochemical Hydrogen Peroxide Generation by Tunable Pyrrolic-Nitrogen-Carbon. Adv. Energy Mater. 2020, 10 (21), 1–10. https://doi.org/10.1002/aenm.202000789.
- (26) Iglesias, D.; Giuliani, A.; Melchionna, M.; Marchesan, S.; Criado, A.; Nasi, L.;



Bevilacqua, M.; Tavagnacco, C.; Vizza, F.; Prato, M.; Fornasiero, P. N-Doped Graphitized Carbon Nanohorns as a Forefront Electrocatalyst in Highly Selective O 2 Reduction to H 2 O 2. *Chem* **2018**, *4* (1), 106–123. https://doi.org/10.1016/j.chempr.2017.10.013.

- (27) Lu, X.; Wang, D.; Wu, K. H.; Guo, X.; Qi, W. Oxygen Reduction to Hydrogen Peroxide on Oxidized Nanocarbon: Identification and Quantification of Active Sites. *J. Colloid Interface Sci.* 2020, 573, 376–383. https://doi.org/10.1016/j.jcis.2020.04.030.
- (28) Miao, J.; Zhu, H.; Tang, Y.; Chen, Y.; Wan, P. Graphite Felt Electrochemically Modified in H2SO4 Solution Used as a Cathode to Produce H2O2 for Pre-Oxidation of Drinking Water. *Chem. Eng. J.* **2014**, 250, 312–318. https://doi.org/10.1016/j.cej.2014.03.043.
- (29) Han, G. F.; Li, F.; Zou, W.; Karamad, M.; Jeon, J. P.; Kim, S. W.; Kim, S. J.; Bu, Y.; Fu, Z.; Lu, Y.; Siahrostami, S.; Baek, J. B. Building and Identifying Highly Active Oxygenated Groups in Carbon Materials for Oxygen Reduction to H2O2. *Nat. Commun.* **2020**, *11* (1). https://doi.org/10.1038/s41467-020-15782-z.
- (30) Wang, T.; Chen, Z. X.; Chen, Y. G.; Yang, L. J.; Yang, X. D.; Ye, J. Y.; Xia, H. P.; Zhou, Z. Y.; Sun, S. G. Identifying the Active Site of N-Doped Graphene for Oxygen Reduction by Selective Chemical Modification. ACS Energy Lett. 2018, 3 (4), 986– 991. https://doi.org/10.1021/acsenergylett.8b00258.
- (31) Zhang, J.; Zhang, J.; He, F.; Chen, Y.; Zhu, J.; Wang, D.; Mu, S.; Yang, H. Y. Defect and Doping Co-Engineered Non-Metal Nanocarbon ORR Electrocatalyst. *Nano-Micro Lett.* **2021**, *13* (1). https://doi.org/10.1007/s40820-020-00579-y.
- (32) Sano, N.; Kimura, Y.; Suzuki, T. Synthesis of Carbon Nanohorns by a Gas-Injected Arc-in-Water Method and Application to Catalyst-Support for Polymer Electrolyte Fuel Cell Electrodes. *J. Mater. Chem.* **2008**, *18* (13), 1555. https://doi.org/10.1039/b717302d.
- (33) Kiciński, W.; Dyjak, S. Transition Metal Impurities in Carbon-Based Materials: Pitfalls, Artifacts and Deleterious Effects. *Carbon N. Y.* **2020**, *168*, 748–845. https://doi.org/10.1016/j.carbon.2020.06.004.
- (34) Sano, N. Low-Cost Synthesis of Single-Walled Carbon Nanohorns Using the Arc in Water Method with Gas Injection. J. Phys. D. Appl. Phys. 2004, 37 (8). https://doi.org/10.1088/0022-3727/37/8/L01.
- (35) Xiao, D.; Ma, J. J.; Chen, C.; Luo, Q.; Ma, J. J.; Zheng, L.; Zuo, X. Oxygen-Doped Carbonaceous Polypyrrole Nanotubes-Supported Ag Nanoparticle as Electrocatalyst for Oxygen Reduction Reaction in Alkaline Solution. *Mater. Res. Bull.* 2018, 105 (February 2017), 184–191. https://doi.org/10.1016/j.materresbull.2018.04.030.
- (36) Zhang, G.; Sun, Y.; Xu, Y.; Zhang, R. Catalytic Performance of N-Doped Activated Carbon Supported Cobalt Catalyst for Carbon Dioxide Reforming of Methane to Synthesis Gas. J. Taiwan Inst. Chem. Eng. 2018, 93, 234–244. https://doi.org/10.1016/j.jtice.2018.07.016.



- (37) Akasaka, H.; Tunmee, S.; Rittihong, U.; Tomidokoro, M.; Euaruksakul, C.; Norizuki, S.; Supruangnet, R.; Nakajima, H.; Hirata, Y.; Ohtake, N. Thermal Decomposition and Structural Variation by Heating on Hydrogenated Amorphous Carbon Films. *Diam. Relat. Mater.* 2020, 101, 107609. https://doi.org/10.1016/j.diamond.2019.107609.
- (38) Rittihong, U.; Akasaka, H.; Euaruksakul, C.; Tomidokoro, M.; Kamonsuttipaijit, N.; Nakajima, H.; Supruangnet, R.; Rojviriya, C.; Chingsungnoen, A.; Poolcharuansin, P.; Ohtake, N.; Tunmee, S. Synchrotron-Based Spectroscopic Analysis of Diamond-like Carbon Films from Different Source Gases. *Radiat. Phys. Chem.* 2020, 173, 108944. https://doi.org/10.1016/j.radphyschem.2020.108944.
- (39) Wang, H.; Chhowalla, M.; Sano, N.; Jia, S.; Amaratunga, G. A. J. Large-Scale Synthesis of Single-Walled Carbon Nanohorns by Submerged Arc. *Nanotechnology* 2004, 15 (5), 546–550. https://doi.org/10.1088/0957-4484/15/5/024.
- (40) Zhu, S.; Xu, G. Single-Walled Carbon Nanohorns and Their Applications. *Nanoscale* **2010**, *2* (12), 2538–2549. https://doi.org/10.1039/c0nr00387e.
- (41) Utsuini, S.; Miyawaki, J.; Tanaka, H.; Hattori, Y.; Itoi, T.; Ichikuni, N.; Kanoh, H.; Yudasaka, M.; Iijima, S.; Kaneko, K. Opening Mechanism of Internal Nanoporosity of Single-Wall Carbon Nanohorn. *J. Phys. Chem. B* **2005**, *109* (30), 14319–14324. https://doi.org/10.1021/jp0512661.
- (42) Fan, J.; Yudasaka, M.; Miyawaki, J.; Ajima, K.; Murata, K.; Iijima, S. Control of Hole Opening in Single-Wall Carbon Nanotubes and Single-Wall Carbon Nanohorns Using Oxygen. *J. Phys. Chem. B* 2006, *110* (4), 1587–1591. https://doi.org/10.1021/jp0538870.
- (43) Karousis, N.; Suarez-Martinez, I.; Ewels, C. P.; Tagmatarchis, N. Structure, Properties, Functionalization, and Applications of Carbon Nanohorns. *Chem. Rev.* 2016, *116* (8), 4850–4883. https://doi.org/10.1021/acs.chemrev.5b00611.
- (44) Fan, J.; Yudasaka, M.; Kasuya, D.; Azami, T.; Yuge, R. Micrometer-Sized Graphitic Balls Produced Together with Single-Wall Carbon Nanohorns. *J. Phys. Chem. B* 2005, 10756–10759. https://doi.org/10.1021/jp050548y.
- (45) Sun, L.; Wang, C.; Zhou, Y.; Zhang, X.; Cai, B.; Qiu, J. Flowing Nitrogen Assisted-Arc Discharge Synthesis of Nitrogen-Doped Single-Walled Carbon Nanohorns. *Appl. Surf. Sci.* **2013**, 277, 88–93. https://doi.org/10.1016/j.apsusc.2013.04.006.
- (46) Nakamura, M.; Kawai, T.; Irie, M.; Yuge, R.; Iijima, S.; Bandow, S.; Yudasaka, M. Graphite-like Thin Sheets with Even-Numbered Layers. *Carbon N. Y.* 2013, *61*, 644–647. https://doi.org/10.1016/j.carbon.2013.05.022.
- (47) Sze, S. K.; Siddique, N.; Sloan, J. J.; Escribano, R. Raman Spectroscopic Characterization of Carbonaceous Aerosols. *Atmos. Environ.* 2001, 35 (3), 561– 568. https://doi.org/10.1016/S1352-2310(00)00325-3.
- (48) Shamsudin, M. S.; Suriani, A. B.; Abdullah, S.; Yahya, S. Y. S.; Rusop, M. Impact of Thermal Annealing under Nitrogen Ambient on Structural, Micro-Raman, and Thermogravimetric Analyses of Camphoric-CNT. *J. Spectrosc.* **2013**, *2013* (1), 1– 6. https://doi.org/10.1155/2013/167357.



- (49) Utsumi, S.; Ohba, T.; Tanaka, H.; Urita, K.; Kaneko, K. Porosity and Adsorption Properties of Single-Wall Carbon Nanohorn. In *Novel Carbon Adsorbents*; Elsevier, 2012; pp 401–433. https://doi.org/10.1016/B978-0-08-097744-7.00013-2.
- (50) Hashimoto, A.; Yorimitsu, H.; Ajima, K.; Suenaga, K.; Isobe, H.; Miyawaki, J.; Yudasaka, M.; Iijima, S.; Nakamura, E. Selective Deposition of a Gadolinium(III) Cluster in a Hole Opening of Single-Wall Carbon Nanohorn. *Proc. Natl. Acad. Sci.* 2004, 101 (23), 8527–8530. https://doi.org/10.1073/pnas.0400596101.
- (51) Liang, X.; Zhong, J.; Shi, Y.; Guo, J.; Huang, G.; Hong, C. Hydrothermal Synthesis of Highly Nitrogen-Doped Few-Layer Graphene via Solid – Gas Reaction. *Mater. Res. Bull.* **2015**, *61*, 252–258. https://doi.org/10.1016/j.materresbull.2014.09.088.
- (52) Mizokawa, T.; Wakisaka, Y.; Sudayama, T.; Iwai, C.; Miyoshi, K.; Takeuchi, J.; Wadati, H.; Hawthorn, D. G.; Regier, T. Z.; Sawatzky, G. A. Role of Oxygen Holes in LixCoO2 Revealed by Soft X-Ray Spectroscopy. *Phys. Rev. Lett.* **2013**, *111* (5), 1–5. https://doi.org/10.1103/PhysRevLett.111.056404.
- (53) Meng, N.; Ren, J.; Liu, Y.; Huang, Y.; Petit, T.; Zhang, B. Engineering Oxygen-Containing and Amino Groups into Two-Dimensional Atomically-Thin Porous Polymeric Carbon Nitrogen for Enhanced Photocatalytic Hydrogen Production. *Energy Environ. Sci.* **2018**, *11* (3), 566–571. https://doi.org/10.1039/c7ee03592f.
- (54) Sheng, Z.; Shao, L.; Chen, J.; Bao, W.; Wang, F.; Xia, X. Catalyst-Free Synthesis of Nitrogen-Doped Graphene via Thermal Annealing Graphite Oxide with Melamine and Its Excellent Electrocatalysis. ACS Nano 2011, 5 (6), 4350–4358. https://doi.org/10.1021/nn103584t.
- (55) Duan, X.; Ao, Z.; Sun, H.; Indrawirawan, S.; Wang, Y.; Kang, J.; Liang, F.; Zhu, Z. H.; Wang, S. Nitrogen-Doped Graphene for Generation and Evolution of Reactive Radicals by Metal-Free Catalysis. ACS Appl. Mater. Interfaces 2015, 7 (7), 4169–4178. https://doi.org/10.1021/am508416n.
- Jiang, K.; Back, S.; Akey, A. J.; Xia, C.; Hu, Y.; Liang, W.; Schaak, D.; Stavitski, E.; Nørskov, J. K.; Siahrostami, S.; Wang, H. Highly Selective Oxygen Reduction to Hydrogen Peroxide on Transition Metal Single Atom Coordination. *Nat. Commun.* 2019, *10* (1). https://doi.org/10.1038/s41467-019-11992-2.
- (57) Kim, K.; Baek, S.; Kim, J. J.; Han, J. W. Catalytic Decomposition of N2O on PdxCuy Alloy Catalysts: A Density Functional Theory Study. *Appl. Surf. Sci.* 2020, *510* (September 2019). https://doi.org/10.1016/j.apsusc.2020.145349.
- (58) Jung, E.; Shin, H.; Hooch Antink, W.; Sung, Y. E.; Hyeon, T. Recent Advances in Electrochemical Oxygen Reduction to H2O2: Catalyst and Cell Design. ACS Energy Lett. 2020, 1881–1892. https://doi.org/10.1021/acsenergylett.0c00812.
- (59) Park, J.; Nabae, Y.; Hayakawa, T.; Kakimoto, M. A. Highly Selective Two-Electron Oxygen Reduction Catalyzed by Mesoporous Nitrogen-Doped Carbon. ACS Catal. 2014, 4 (10), 3749–3754. https://doi.org/10.1021/cs5008206.
- (60) Jia, Y.; Zhang, L.; Zhuang, L.; Liu, H.; Yan, X.; Wang, X.; Liu, J.; Wang, J.; Zheng, Y.; Xiao, Z.; Taran, E.; Chen, J.; Yang, D.; Zhu, Z.; Wang, S.; Dai, L.; Yao, X. Identification of Active Sites for Acidic Oxygen Reduction on Carbon Catalysts with



and without Nitrogen Doping. *Nat. Catal.* **2019**, *2* (8), 688–695. https://doi.org/10.1038/s41929-019-0297-4.

- (61) Zhou, W.; Xie, L.; Gao, J.; Nazari, R.; Zhao, H.; Meng, X.; Sun, F.; Zhao, G.; Ma, J. Selective H2O2 Electrosynthesis by O-Doped and Transition-Metal-O-Doped Carbon Cathodes via O2 Electroreduction: A Critical Review. *Chem. Eng. J.* 2021, 410 (October 2020), 128368. https://doi.org/10.1016/j.cej.2020.128368.
- (62) Wuorimaa, A.; Jokela, R.; Aksela, R. Recent Developments in the Stabilization of Hydrogen Peroxide Bleaching of Pulps: An Overview. *Nord. Pulp Pap. Res. J.* 2006, 21 (4), 435–443. https://doi.org/10.3183/npprj-2006-21-04-p435-443.

### 3.3 The Efficient Conversion of D-Fructose to 5-Hydroxymethylfurfural using Organic Acids as Catalytic Promoters

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## Abstract

5-Hydroxymethylfurfural (HMF) is one of the main chemical building blocks to generate other high value-added biofuels and biochemicals. This study aimed to produce HMF from fructose dehydration under a biphasic system using various organic acids as catalytic promoters, such as formic acid, acetic acid, lactic acid, succinic acid, and levulinic acid. Among these organic acids, the acetic acid was found to be the best promoter in this system. The experimental results showed a prominent correlation between the HMF formation and the  $pK_a$  – the higher  $pK_a$  gave rise to greater HMF yield and lower activity toward side reactions. Response surface methodology was performed to identify the optimum reaction temperature, time, and promoter concentration for fructose dehydration. Among the three variables, the reaction temperature played the most significant role in fructose conversion and HMF yield. The optimum condition to achieve the highest HMF yield at 72.5% from fructose dehydration was found at 195.8 °C under a mild concentration of acetic acid at 0.075 M for 3.2 min.

## Introduction



Fossil resources are still the primary sources of energy and chemicals, but fossil resources are fast depleted due to the growth of the world economy and the global population [1]. Therefore, it is essential to look for new resources to replace or slow down the consumption of limited fossil resources. Biomass becomes one of the most explored renewable resources for energy and chemical feedstocks to substitute fossil resources [2, 3]. Several biochemical and chemical platforms such as 5-Hydroxymethylfurfural (HMF), gamma-velerolactone (GVL), 2,5-Furandicarboxylic acid (FDCA), 2,5-Dimethylfuran (DMF), and 1,6-hexanediol can be produced from biomass [4, 5]. Among those chemicals, the production of HMF, one of the top-value bio-based chemical platforms for plastics, polymers, pharmaceuticals, and food improvement agents, has gained increasing interest nowadays [6].

HMF is an organic compound produced from the dehydration reaction of hexoses (mainly fructose) derived from cellulose [7-9]. Brønsted acid catalyst is favorable for the dehydration of fructose to HMF [10, 11]. The most common acid catalyst to convert fructose to HMF was mineral acid [12] such as hydrochloric acid [10, 13], sulfuric acid [14], and phosphoric acid [15, 16]. The conversion of fructose to HMF with these mineral acids at high temperatures (150 - 200 °C) was generally high, with HMF yield around 60 -80% [17, 18]. For example, the use of H<sub>3</sub>PO<sub>4</sub> catalyst for converting C6 sugar (glucose and fructose) to HMF at 200 °C for 5 min resulted in relatively high fructose conversion of 95% but low HMF yield since it remarkedly led to the undesired product [19]. In addition, microwave-assisted synthesis could promote the dehydration of fructose into HMF giving rise to higher fructose conversion and faster reaction time, compared to the conventional heating procedure. The fructose conversion using HCI as a catalyst under microwaveassited heating conditions exhibited the HMF selectivity of 63% with fructose conversion of 52% at 200 °C in only 1 s [9]. However, scaling-up the microwave process for industrial use is still a challenging task. It is clear that the use of the mineral acids has critical obstacles, such as high corrosiveness [11, 20], a requirement of neutralization step that results in the large generation of effluent and residues [20], high toxicity, and environmentally unfriendly compared to organic acids [12, 21].

Normally, the conversion of glucose to HMF takes two reaction steps, the isomerization of glucose to fructose and the dehydration of fructose to HMF. While the isomerization is catalyzed by Lewis acids, the dehydration is usually promoted by Brønsted acids. However, Lewis and Brønsted acids also catalyze undesirable side reactions, especially at high temperatures. For example, the dehydration of HMF with Brønsted acids markedly produced levulinic acid (LA) and formic acid (FA) as the undesired products [22]. The polymerization of sugars and the produced HMF can be further converted to humins [23]. Many studies reported that the undesired products are mostly organic acids such as carboxylic acids, which might be utilized in acid-catalyzing reactions [24]. Some research groups suggested the use of additives and organic promoters, such as formic acid [25], maleic acid [26, 27], and carbonic acid [28] for enhancement of HMF yield. These green organic acid promoters can be substitutes for mineral acids, metal catalysts, or organic solvents [22]. Previous studies reported that the addition of formic acid had led to the conversion of fructose to HMF with high yield by limiting the HMF rehydration side reaction [21, 25]. By adding formic acid into the biphasic system, 68% of HMF yield was achieved under the reaction at 170 °C for 70 min [25].



The organic acids can dissociate protons for catalyzing the dehydration of sugar to HMF. In comparison with strong mineral acids, the weak organic acids would cause less corrosion problem especially at high temperature [29].

Although some organic acids, such as formic acid, acetic acid, lactic acid, succinic acid, and levulinic acid, were considered as the undesired byproducts of the dehydration of C6 sugars [30], they can potentially act as a catalytic promoter in the sugar dehydration. In addition, the less corrosiveness and the more environmentally friendly nature of the organic acids compared to the strong mineral ones would be promising advantages for green production. This work aimed to investigate the potential of these organic acids as the promoter for HMF production. The reaction conditions with the presence of these organic acid promoters were also optimized by applying the statistic method, the surface response methodology.

#### Experimental Section

#### Materials

5-Hydroxymethyl-2-furaldehyde (>98% GC/HPLC), D-(-)-Fructose (≥99%), DL-Lactic acid (90% (T)), levulinic acid (98%), succinic acid (≥99%) and sodium chloride (NaCl, AR grade) were purchased from Sigma-Aldrich (Darmstadt, Germany). Toluene (AR grade) was supplied by RCI Labscan limited (Bangkok, Thailand). Acetic acid (>99%) was obtained from Duksan Pure Chemicals Co., Ltd (Gyeonggi-do, Korea). Formic acid (>98%) was purchased from Merck & Co., Inc (Darmstadt, Germany). All chemicals were used as received without an additional purification step. All solutions were prepared using deionized (DI) water with conductivity at less than 18 µs/cm.

### Fructose Dehydration to 5-HMF

Various organic acids, such as formic acid, acetic acid, lactic acid, succinic acid, and levulinic acid as the acid promoter for the dehydration of fructose were investigated. The reaction was performed in a 130-ml stainless steel autoclave with a magnetic stirrer. In a typical experiment, 300 mg of fructose was mixed with biphasic solvents, consisting of saturated NaCl aqueous solution (9 mL) and toluene (21 mL) (ratio of 3:7 v/v). Then, 1 ml of 0.1 M organic acid was added to the reaction. The autoclave was pressurized with nitrogen gas up to 15 bars and heated up to a set temperature (150 - 200 °C). After the reaction was carried out for 30 min, the reactor was cooled down to the ambient temperature, and the pressure inside the reactor was carefully released. The liquid product was poured into a funnel to separate the organic phase from the aqueous phase.

The chemical composition in both phases was analyzed by a high-performance liquid chromatography (HPLC, LC-20A Series, Shimadzu, Japan). BioRad Aminex HPX-87H column that was equipped with an ultraviolet (UV) detector at 210 nm and a refractive index detector was used for the chemical analysis for the aqueous phase at 45 °C.  $H_2SO_4$  solution (0.005 M) was used as the mobile phase at a flow rate of 0.6 ml/min. The concentration of products in the organic phase was analyzed with an Inertsil ODS-3 column at 30 °C with the mobile phase of methanol-water (5:95 v/v) at a flow rate of 1



ml/min and the UV detection at 278 nm. The conversion, and the product yield were calculated using the following equations (1) and (2):

Fructose conversion 
$$(X_F, \%) = (\frac{The number of mole of reacted D-fructose}{The number of mole of initial D-fructose}) \times 100$$
 (1)

 $HMF \ yield \ (Y_{HMF}, \%) = \frac{The \ number \ of \ mole \ of \ HMF}{The \ theoretical \ number \ of \ mole \ of \ HMF}) \times 100$ (2)

The best acid promoter found from these experiments was subjected to further process optimization using response surface methodology.

### **Experimental Design**

The response surface methodology (RSM) is widely used for designed experiments to achieve optimal conditions [31]. A central composite design (CCD) method was used for building a model for the response variables (the dependent variables), the fructose conversion ( $Y_1$ ) and HMF yield ( $Y_2$ ). Reaction temperature ( $x_1$ ), reaction time ( $x_2$ ), and concentration of acetic acid ( $x_3$ ) were set as the three independent variables, the key operating conditions to be optimized for the production of HMF. The CCD designed 20 experiments from 8 factorial points from the three variables, 6 axial points, and 6 centers. Each variable was investigated at three coded levels (-1,0,1), as listed in Table 2. The selection of this range was based on previous screen tests. The experimental design matrix and 5-HMF yields are shown in Table 3. The data obtained from the CCD were analyzed by applying Minitab software. It is worth mentioning that the center point was duplicated to check the experimental error and the reproducibility. The experimental models suggested a quadratic equation (Eq. (3)) for fructose conversion and HMF yield.

 $Y_{i} = \beta_{0} + \beta_{1}x_{1} + \beta_{2}x_{2} + \beta_{3}x_{3} + \beta_{11}x_{1}^{2} + \beta_{22}x_{2}^{2} + \beta_{33}x_{3}^{2} + \beta_{12}x_{1}x_{2} + \beta_{13}x_{1}x_{3} + \beta_{23}x_{2}x_{3}$ (3)

where,  $Y_i$  is the response term,  $\beta_0$  is intercept term,  $\beta_1$ ,  $\beta_2$ ,  $\beta_3$  are linear effects,  $\beta_{11}$ ,  $\beta_{22}$ ,  $\beta_{33}$  are quadratic effects, and  $\beta_{12}$ ,  $\beta_{13}$ ,  $\beta_{23}$  are the effect of interaction between factors.

### Results and Discussion

Screening for proper preliminary reaction temperature and time





**Figure 1.** Effect of reaction temperature on the dehydration of fructose to HMF in a biphasic system. Reaction condition: fructose 300 mg, solvent 30 mL (NaCl<sub>aq</sub> 9 mL and toluene 21 mL), time 15 min.

The screening test was carried out to scope the range of temperature and time for our experimental design. First, the effects of reaction temperature on fructose dehydration without catalyst/promoter or any additives were investigated as depicted in Figure 1. The experiments were carried out at 130, 150, and 170 °C for 30 min. The fructose conversion and HMF yield increased with the temperature, implying the endothermic reaction of the dehydration reaction. At 170 °C, fructose was almost completely converted and the highest HMF yield was obtained. At this temperature, the reaction was further explored in the time-dependent experiment. The results of time-dependent fructose conversion and HMF yield are illustrated in Figure 2.





**Figure 2.** Effect of reaction time on the dehydration of fructose to HMF in a biphasic system. Reaction condition: fructose 300 mg, solvent 30 mL (NaCl<sub>aq</sub> 9 mL and toluene 21 mL), temperature 170 °C.

While almost 100 % of fructose conversion was achieved right after 15 min of the reaction and remained constant, the HMF yield slightly increased from 42.1 % at 15 min to 67.4% at 30 min and then continuously dropped when the reaction was prolonged. Although at 170 °C the rate of chemical reaction was promoted and high fructose conversion was achieved, the side reactions were also pronounced, especially at longer reaction time. When the reaction duration was carried out for longer than 30 min, the HMF was further converted to other byproducts, such as formic acid, levulinic acid, and insoluble humins [32]. The amount of levulinic acid and formic acid increased with reaction time corresponding to the decrease of HMF as shown in Figure S1. Yu and coworkers [22] described that acid catalysts also expedite undesirable side reactions, especially under intensive heating. For example, the polymerization of sugars, intermediates, and HMF were converted to humins [23]. **Scheme 1** shows the reaction pathways for the HMF degradation.







### Screening for the proper catalyst promoter

Different organic acids were applied for the screening test of HMF production. The conversion was run at a controlled acid concentration at 0.1 mol/l (1 ml) at 170 °C for 15 min. The effect of various catalytic promoters on fructose conversion and HMF yield in the biphasic system is demonstrated in Figure 3. The fructose conversion was slightly enhanced by 15 - 25 % when the organic acids were added into the reaction, while the HMF yield was significantly improved. De Souza and coworkers [24] reported that the use of aqueous carboxylic acids as the reactive reaction media gave high conversion of fructose with 5-HMF yield up to 64%, indicating that these aqueous solutions provided the sufficient acidity to promote the reaction. The effect of the organic acids on the dehydration of fructose can be explained in term of  $pK_a$  and toluene-water partition coefficient ( $logP_{tw}$ ) following the equation (4) and (5).

$$pK_a = -logK_a \tag{4}$$

$$logP_{tw} = log\frac{C_{toluene}}{C_{water}} \tag{5}$$

where  $K_a$  is acid dissociation constant,  $C_{toluene}$  is concentration of organic acid in the toluene-rich phase,  $C_{water}$  is concentration of organic acid in the water-rich phase.[33]

The  $pK_a$  is used to describe acid dissociation – the higher  $pK_a$  value typically shows the weaker acidity. While the toluene-water partition coefficient can be used for estimating the extent to which the organic acid diffuses into the organic phase. The value is less than one if the organic acid is more soluble in water, and greater than one if it is more soluble in toluene. In this case the organic acids should prefereably appear in water phase since the reactive phase is water.

The acid promoter plays a significant role for producing HMF from fructose. The highest HMF yield is obtained when the weak acid and low  $logP_{tw}$  value are used in the acidic condition. Among the organic acids used, the acetic acid was found to be the most



favorable promoter, providing the highest fructose conversion and HMF yield. This might be because of the weak acidic nature of acetic acid ( $pK_a = 4.76$ ) compared among the organic acids shown in Table 1. Although formic acid, lactic acid, and succinic acid have lower  $logP_{tw}$  value than acetic acid, they are stronger acid than acetic acid, leading to the formation of formic acid as a by-product. Table 1 shows the yield of by-product (YFA) of 17.8%, 14.7%, and 8.0% from the reactions using formic acid, lactic acid, and succinic acid as promoters, respectively. Therefore acetic acid is preferred as an efficient promoter under the present condition.

It is considered that acetic acid could provide a suitable reaction environment for fructose dehydration while other acids with lower  $pK_a$  expedite more side reactions as suggested by the lower HMF yield. This happened when HMF was further converted to other chemicals, while fructose conversion remained high. Wang et al. previously reported the positive role of carboxylic acid synergized with sulfonic acid on surfaces of the solid catalysts in fructose [34]. In addition, Thananatthanachon and Rauchfuss [35] suggested that the rate of conversion qualitatively correlated with the  $pK_a$  of acid used. The application of acetic acid as the acid promoter for HMF production was further explored to find the optimized reaction condition.

organic acids	$pK_a$ a	logP <sub>tw</sub> <sup>b</sup>	Ү <sub>НМF</sub> <sup>с</sup> (%)	Y <sub>FA</sub> <sup>c</sup> (%)
Formic acid	3.75	-1.40	63.6	17.8
Acetic acid	4.76	-1.05	70.3	2.4
Lactic acid	3.83	-1.80	60.7	14.7
Succinic acid	4.21	-1.55	64.1	8.0
Levulinic acid	4.59	-0.81	54.7	4.7

### Table 1. Characteristic and effect of organic acid promoters on HMF production

<sup>a</sup>  $pK_a$  of organic acids at 25 °C 1 atm, <sup>b</sup> Simulated by Aspen plus at reaction condition: 170 °C 25 bar, and <sup>c</sup> Reaction condition: fructose 300 mg, solvent 30 mL (NaCl<sub>aq</sub> 9 mL and toluene 21 mL), organic acids (0.1 M) 1 mL, temperature 170 °C, and time 15 min.





Figure	3. Or	rganic a	acid :	screeni	ng ir	the	dehyd	Iratic	on o	f fru	ctose	to	HMF	in	a l	biphasic
system	. The	reactio	on wa	is carri	ed o	ut at	170°C	; for	15 I	min	with	1 m	L of	0.1	Μ	organic
acids.																

	Table 2.	The range a	and level of	independent	t variables
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factors	symbol	range and levels			
	Symbol -	-1	0	+1	
reaction temperature (°C)	<b>X</b> 1	150	175	200	
reaction time (min)	X2	10	20	30	
concentration of acetic acid (M)	<b>X</b> 3	0.05	0.10	0.15	

# Table 3. Experimental design matrix and results

run	temp (°C) <i>x</i> 1	time (min) <i>x</i> 2	acetic acid (M) <sub>X3</sub>	Xf (%) <i>Y</i> 1	Үнмг (%) <i>У</i> 2
1	200	30	0.05	99.1	33.4
2	150	10	0.15	40.4	26.0
3	175	20	0.1	94.4	58.3
4	175	20	0.18	100.0	18.2
5	175	20	0.1	94.4	58.3
6	175	3	0.1	99.6	58.8
7	175	20	0.1	100.0	60.6



run	temp (°C)	time	acetic acid (M)	X <sub>f</sub> (%)	Yhmf (%)
	X1	(min)	Хз	<b>y</b> 1	<b>y</b> 2
		X2			
8	217	20	0.1	100.0	16.3
9	200	10	0.05	100.0	53.4
10	175	20	0.016	100.0	44.5
11	150	30	0.15	100.0	59.4
12	133	20	0.1	38.6	22.1
13	150	30	0.05	67.6	38.5
14	175	20	0.1	100.0	60.6
15	175	20	0.1	100.0	55.9
16	150	10	0.05	51.1	30.4
17	200	10	0.15	99.8	53.7
18	175	37	0.1	100.0	60.6
19	200	30	0.15	100.0	20.6
20	175	20	0.1	100.0	55.9

### **Response surface analysis**

The effects of the three essential reaction variables, the concentration of acetic acid, reaction temperature, and reaction time, were investigated. Table 2 summarizes the independent variables and their range and level of experimental set. The selected variable range was based on our screen test. Fructose conversion and HMF yield in correspondent to the independent variables are tabulated in Table 3.

The Minitab was used to generate the correlation between the independent variables (reaction temperature  $(x_1)$ , reaction time  $(x_2)$ , and concentration of acetic acid  $(x_3)$ ) and the response variables (fructose conversion  $(Y_1)$  and HMF yield  $(Y_2)$ ) as expressed in Eq. (6) and (7).

 $Y_1 = -767 + 8.22 x_1 + 6.51 x_2 + 244 x_3 - 0.01865 x_1^2 - 0.0087 x_2^2 - 320 x_3^2$ 

- 0.0384 
$$x_1 x_2$$
 - 2.11  $x_1 x_3$  + 11.06  $x_2 x_3$   
(6)

 $Y_2 = -808 + 8.49 x_1 + 7.37 x_2 + 1080 x_3 - 0.02075 x_1^2 - 0.0134 x_2^2 - 3472 x_3^2$ 

- 0.0473 
$$x_1 x_2$$
 - 2.89  $x_1 x_3$  + 3.05  $x_2 x_3$  (7)

Table 4 represents the regression analysis for fructose conversion and HMF yield. The significance of second-order equations and the interaction between variables were proved by F-value in the ANOVA test. The F-value calculated from experimental data is larger than F critical value (F-table), suggesting that the variables were significant to the HMF production.

Figure 4 shows the observed and predicted values for fructose conversion and HMF yield. Both graphs indicated that the predicted and experimental values were relatively proximate to each other with the coefficient of determination ( $R^2$ ) larger than



0.75. This signified that the developed models were adequate and reliable. Furthermore, the variations, which were not described by the models, for fructose conversion and HMF yield were only 5.4% and 9.9%, respectively.

mode	SOS	DOF	MS	<b>F</b> value	$F_{table}$		
<u>Fructose</u> <u>conversion</u>							
Regression	7783.75	9	864.86	11.82	$F_{0.05} = 5.05$		
Residual	731.47	10	73.15				
Total	8515.21	19					
<u>HMF yield</u>							
Regression	4474.30	9	527.14	10.14	$F_{0.05} = 5.05$		
Residual	519.74	10	51.97				
Total	5264.04	19					
SOS: Sum of Squares, DOF: Degree of freedom, MS: Mean Squares							

## Table 4. Regression analysis (ANOVA)





**Figure 4.** Comparison of the observed and predicted values in fructose dehydration: (a) fructose conversion, and (b) HMF yield.





Figure 5. Pareto chart of HMF production for (a) fructose conversion and (b) HMF yield.



The Pareto chart in Figure 5 represents the effect magnitude of each variable. The Pareto chart indicated the significance of the interaction between reaction temperature, reaction time, and acid concentration with p-value < 0.05 for both fructose conversion and HMF yield. It appeared that the reaction temperature was the most influential factor ( $x_1$ ) among all three variables for both fructose conversion and HMF yield. In addition, it also indicated that the reaction duration ( $x_2$ ) showed the second most influential factor for the conversion (Figure 5(a)); however, it has no significant impact on the HMF yield (Figure 5(b)). On the other hand, the acetic acid concentration ( $x_s$ ) has no influence on the conversion but played a significant role in HMF yield. The relation between temperature and time ( $x_1x_2$ ) was also significant for the conversion and yield.

The models (Eq (6) and Eq (7)) generated the response surface (Figs. 6), showing a graphical relation between fructose conversion and HMF yield and the significant variables, respectively.






Figure 6 (a) demonstrates how fructose conversion increased with reaction temperature and time. Increasing temperature typically enhances the fructose. To ensure high conversion above 80%, the contour plot indicated that the reaction should be operated at above 160 °C for at least 15 min.

Figure 6 (b and c) illustrates the relationships among temperature, acid concentration, and reaction time on HMF yield. The mild temperature (140 to 175 °C) with the reaction duration longer than 27 min could provide high HMF yield. On the other hand, the higher temperature range above 175 °C requires shoter reaction time (less than 15 min) to gave an excellent yield. However, prolonging reaction time at this high temperature resulted in a decrease in HMF yield. At high temperature and longer reaction duration, the side reactions were promoted, reducing HMF yield. Figure 6 (c) illustrates the influence of acid concentration and temperature on the HMF yield. The suitable acid concentration for high yield (dark red) was found at around 0.05 - 0.14 M for the reaction at 160 – 190 °C. Zandvoort and coworkers [36] reported that the humin was formed under strong reaction conditions at above 180 °C and acid concentration at 0.1 M. In this work, the maximum 5-HMF yield of around 72.5% was obtained at 195.8 °C in 0.075 M.

#### Optimization of process parameters of 5-HMF yield

The RSM predicted the optimization conditions to achieve maximum HMF yield at 72.5 % from the dehydration reaction in a biphasic system with 0.075 M acetic acid promoter at 195.8 °C for 3.2 min. Additional tests were carried out at the predicted optimum conditions with 3 replicates for comparison (see Table 5). The predicted values were close to those obtained from the experiment with 4.3% deviation for HMF yield. These differences were less than 5% level of significance. Table 6 shows the comparison of the HMF production from different conditions over various acid catalysts. The use of mineral acids, such as H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub>, was previously studied for converting fructose into HMF in water system which leads 100% of fructose conversion but low HMF yield due to the formation of undesired product [37, 38]. The different metal salts (e.g. NH<sub>4</sub>Cl and MoCl<sub>3</sub>) were reported for catalyzing fructose to HMF in both alcohol and ionic liquid mediums, obtaining HMF selecitivity approximately 50% at low reaction temperature [39]. On the other hand, the organic acids are attractive Bronsted acid catalysts to promote the fructose dehydration [39, 40]. Lactic acid and formic acid were used in the conversion of fructose, achieving 70% of HMF selectivity at long reaction time above 70 min [24, 25]. The results from the present study suggested that the organic acid would be the good potential catalytic promoter for HMF production. The optimization study showed that acetic acid would work under milder reaction conditions providing a promising yield of HMF among reported catalytic systems.



Table 5. Fructose conversion and HMF yield at optimum condition (195.8 °C for 3.2min with the concentration of acetic acid of 0.075 M)

variables	pre	edicted valu (%)	es observe (%	d values %)	erro	or (%)
HMF yield		72.5	69	.4	4	.3
Table 6. Fructos	se conver	sion to HMF	using various	catalysts		
catalyst	Temp (°C)	Time (min)	Medium	X <sub>F</sub> (%)	Үнмғ (%)	Ref.
H <sub>2</sub> SO <sub>4</sub>	166	200	Water	100	56	[37]
H <sub>3</sub> PO <sub>4</sub>	240	2	Subcritical water	100	65	[38]
MoCl <sub>3</sub>	120	5	[BMIM]CI	64	31	[39]
NH4CI	120	1440	Isopropanol	100	65	[40]
Lactic acid	150	120	Water	95	64	[24]
Formic acid	170	70	Water/n- butanol	98	69	[25]
Acetic acid	195.8	3.2	NaCl <sub>aq</sub> /toluene	100	72.5	This work

#### 4. Conclusions

In this work, various organic acids as the alternative catalytic promoter to the mineral acids for fructose dehydration in the biphasic system between sodium chloride solution and toluene were investigated. The acetic acid showed the most promising catalyst among all investigated organic acids. RSM was used for predicting the optimum conditions for the HMF production. The optimized conditions were indicated to be with a mild concentration of acetic acid at about 0.075 M and the reaction temperature at 195.8°C for 3.2 min of reaction time. At these predicted conditions, around 72.5% of HMF yield was achieved experimentally, which was less than 5% error from the predicted values. This study is able to offer essencial knowledges for using less-corrosive homogeneous catalytic systems with the scaling-up ability combined with validated empirical model.



## Acknowledgment

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#### References

1. Wang, T., M.W. Nolte, and B.H. Shanks, Catalytic dehydration of C6carbohydrates for the production of hydroxymethylfurfural (HMF) as a versatile platform chemical. Green Chem., 2014. **16**(2): p. 548-572.

2. Wang, J., et al., Recent advances in heterogeneous catalytic conversion of glucose to 5-hydroxymethylfurfural via green routes. Science China Chemistry, 2017. **60**(7): p. 870-886.

3. Chen, W.-C., et al., Feasibility of enhancing production of 5-hydroxymethylfurfural using deep eutectic solvents as reaction media in a high-pressure reactor. Biochemical Engineering Journal, 2020. **154**.

4. Mika, L.T., E. Csefalvay, and A. Nemeth, Catalytic Conversion of Carbohydrates to Initial Platform Chemicals: Chemistry and Sustainability. Chem Rev, 2018. **118**(2): p. 505-613.

5. Gawade, A.B. and G.D. Yadav, Microwave assisted synthesis of 5ethoxymethylfurfural in one pot from d-fructose by using deep eutectic solvent as catalyst under mild condition. Biomass and Bioenergy, 2018. **117**: p. 38-43.

6. Mukherjee, A., M.-J. Dumont, and V. Raghavan, Review: Sustainable production of hydroxymethylfurfural and levulinic acid: Challenges and opportunities. Biomass and Bioenergy, 2015. **72**: p. 143-183.

7. A.D.Smith, et al., Chemical production from lignocellulosic biomass: thermochemical, sugar and carboxylate platforms, in Bioalcohol Production. 2010. p. 391-414.

8. Graham, B.J. and R.T. Raines, Efficient metal-free conversion of glucose to 5hydroxymethylfurfural using a boronic acid. Biomass Conversion and Biorefinery, 2018. **9**(2): p. 471-477.

9. Xu, C., et al., Recent catalytic routes for the preparation and the upgrading of biomass derived furfural and 5-hydroxymethylfurfural. Chem Soc Rev, 2020. **49**(13): p. 4273-4306.

10. Pagán-Torres, Y.J., et al., Production of 5-Hydroxymethylfurfural from Glucose Using a Combination of Lewis and Brønsted Acid Catalysts in Water in a Biphasic Reactor with an Alkylphenol Solvent. ACS Catalysis, 2012. **2**(6): p. 930-934.



11. Catrinck, M.N., et al., Direct conversion of glucose to 5-hydroxymethylfurfural using a mixture of niobic acid and niobium phosphate as a solid acid catalyst. Fuel, 2017. **210**: p. 67-74.

12. Wanninayake, P., et al., Conversion of rice straw into 5-hydroxymethylfurfural: review and comparative process evaluation. Biomass Conversion and Biorefinery, 2021.

13. Svenningsen, G.S., et al., Unifying Mechanistic Analysis of Factors Controlling Selectivity in Fructose Dehydration to 5-Hydroxymethylfurfural by Homogeneous Acid Catalysts in Aprotic Solvents. ACS Catalysis, 2018. **8**(6): p. 5591-5600.

14. Li, M., et al., High conversion of glucose to 5-hydroxymethylfurfural using hydrochloric acid as a catalyst and sodium chloride as a promoter in a water/ $\gamma$ -valerolactone system. RSC Advances, 2017. **7**(24): p. 14330-14336.

15. Daorattanachai, P., et al., Conversion of fructose, glucose, and cellulose to 5hydroxymethylfurfural by alkaline earth phosphate catalysts in hot compressed water. Carbohydr Res, 2012. **363**: p. 58-61.

16. Liu, Y., et al., One-Pot Catalytic Conversion of Raw Lignocellulosic Biomass into Gasoline Alkanes and Chemicals over LiTaMoO6 and Ru/C in Aqueous Phosphoric Acid. ACS Sustainable Chemistry & Engineering, 2015. **3**(8): p. 1745-1755.

17. Yang, F., et al., Conversion of biomass into 5-hydroxymethylfurfural using solid acid catalyst. Bioresour Technol, 2011. **102**(3): p. 3424-9.

18. Wrigstedt, P., J. Keskiväli, and T. Repo, Microwave-enhanced aqueous biphasic dehydration of carbohydrates to 5-hydroxymethylfurfural. RSC Advances, 2016. **6**(23): p. 18973-18979.

19. Daorattanachai, P., et al., 5-Hydroxymethylfurfural production from sugars and cellulose in acid- and base-catalyzed conditions under hot compressed water. Journal of Industrial and Engineering Chemistry, 2012. **18**(6): p. 1893-1901.

20. de Carvalho, E.G.L., et al., Experimental design and economic analysis of 5hydroxymethylfurfural synthesis from fructose in acetone-water system using niobium phosphate as catalyst. Biomass Conversion and Biorefinery, 2018. **8**(3): p. 635-646.

21. Sajid, M., et al., Organic acid catalyzed production of platform chemical 5-hydroxymethylfurfural from fructose: Process comparison and evaluation based on kinetic modeling. Arabian Journal of Chemistry, 2020. **13**(10): p. 7430-7444.

22. Yu, I.K.M., et al., Organic Acid-Regulated Lewis Acidity for Selective Catalytic Hydroxymethylfurfural Production from Rice Waste: An Experimental–Computational Study. ACS Sustainable Chemistry & Engineering, 2018. **7**(1): p. 1437-1446.

23. Jung, D., P. Körner, and A. Kruse, Kinetic study on the impact of acidity and acid concentration on the formation of 5-hydroxymethylfurfural (HMF), humins, and levulinic acid in the hydrothermal conversion of fructose. Biomass Conversion and Biorefinery, 2019.



24. de Souza, R.L., et al., 5-Hydroxymethylfurfural (5-HMF) Production from Hexoses: Limits of Heterogeneous Catalysis in Hydrothermal Conditions and Potential of Concentrated Aqueous Organic Acids as Reactive Solvent System. Challenges, 2012.  $\mathbf{3}(2)$ : p. 212-232.

25. Jiang, N., et al., Effect of Formic Acid on Conversion of Fructose to 5-Hydroxymethylfurfural in Aqueous/Butanol Media. BioEnergy Research, 2011. **5**(2): p. 380-386.

26. Zhang, X., et al., Maleic acid and aluminum chloride catalyzed conversion of glucose to 5-(hydroxymethyl) furfural and levulinic acid in aqueous media. Green Chemistry, 2016. **18**(19): p. 5219-5229.

27. Zhang, X., B.B. Hewetson, and N.S. Mosier, Kinetics of Maleic Acid and Aluminum Chloride Catalyzed Dehydration and Degradation of Glucose. Energy & Fuels, 2015. **29**(4): p. 2387-2393.

28. Jing, S., et al., In Situ Carbonic Acid from CO2: A Green Acid for Highly Effective Conversion of Cellulose in the Presence of Lewis acid. ACS Sustainable Chemistry & Engineering, 2016. **4**(8): p. 4146-4155.

29. Jung, Y.H. and K.H. Kim, Acidic Pretreatment, in Pretreatment of Biomass. 2015. p. 27-50.

30. Dessie, W., et al., Inhibitory effects of lignocellulose pretreatment degradation products (hydroxymethylfurfural and furfural) on succinic acid producing Actinobacillus succinogenes. Biochemical Engineering Journal, 2019. **150**.

31. Kshirsagar, M.P., V.R. Kalamkar, and R.R. Pande, Multi-response robust design optimization of natural draft biomass cook stove using response surface methodology and desirability function. Biomass and Bioenergy, 2020. **135**.

32. Li, X., et al., Production of 5-hydroxymethylfurfural and levulinic acid from lignocellulosic biomass and catalytic upgradation. Industrial Crops and Products, 2019. **130**: p. 184-197.

33. Bannan, C.C., et al., Calculating Partition Coefficients of Small Molecules in Octanol/Water and Cyclohexane/Water. J Chem Theory Comput, 2016. **12**(8): p. 4015-24.

34. Wang, J., et al., Efficient catalytic conversion of fructose into hydroxymethylfurfural by a novel carbon-based solid acid. Green Chemistry, 2011. **13**(10).

35. Thananatthanachon, T. and T.B. Rauchfuss, Efficient route to hydroxymethylfurans from sugars via transfer hydrogenation. ChemSusChem, 2010. 3(10): p. 1139-41.

36. van Zandvoort, I., et al., Formation, molecular structure, and morphology of humins in biomass conversion: influence of feedstock and processing conditions. ChemSusChem, 2013. **6**(9): p. 1745-58.



37. Fachri, B.A., et al., Experimental and Kinetic Modeling Studies on the Sulfuric Acid Catalyzed Conversion of d-Fructose to 5-Hydroxymethylfurfural and Levulinic Acid in Water. ACS Sustainable Chemistry & Engineering, 2015. **3**(12): p. 3024-3034.

38. Asghari, F.S. and H. Yoshida, Acid-catalyzed production of 5-hydroxymethyl furfural from D-fructose in subcritical water. Industrial & Engineering Chemistry Research, 2006. **45**(7): p. 2163-2173.

39. Yin, Y., et al., Rapid conversion of glucose to 5-hydroxymethylfurfural using a MoCl3 catalyst in an ionic liquid with microwave irradiation. Industrial Crops and Products, 2021. **160**.

40. Liu, J., et al., Conversion of fructose into 5-hydroxymethylfurfural (HMF) and its derivatives promoted by inorganic salt in alcohol. Carbohydr Res, 2012. **350**: p. 20-4.

## Outputs

## 4.1 Publications

- Chakthranont, P.; Nitrathorn, S.; Thongratkaew, S.; Khemthong, P.; Nakajima, H.; Supruangnet, R.; Butburee, T; Sano, N.; Faungnawakij, k. Rational Design of Metal-free Doped Carbon Nanohorn Catalysts for Efficient Electrosynthesis of H<sub>2</sub>O<sub>2</sub> from O<sub>2</sub> Reduction. ACS Appl. Energy Mater. 2021 <u>https://doi.org/10.1021/acsaem.1c02260</u>
- Songtawee, S.; Kraithong, W.; Klaysom, C.; Faungnawakij, K. The Efficient Conversion of D-Fructose to 5-Hydroxymethylfurfural Using Organic Acids as Catalytic Promoters. Biomass Convers. Biorefinery 2021. <u>https://doi.org/10.1007/s13399-021-01647-y</u>.
- Kuptajit, P.; Sano, N.; Nakagawa, K.; Suzuki, T. A study on pore formation of high surface area activated carbon prepared by microwave-induced plasma with KOH (MiWP-KOH) activation: Effect of temperature-elevation rate. Chem. Eng. Process. 2021, 167, 108511.
- Kuptajit, P.;Nakagawa, K.; Suzuki, T.; Sano, N. Pseudo Continuous Reactor with Microwave-plasma for Preparation of High Surface Area Activated Carbon. 2021, J. Jpn. Inst. Energy 100, 110-115.
- Vanavanichkul, T.; Le, GTT.; Lawagon, CP.; Sano, N.; Viriya-empikul, N.; Faungnawakij, K.; Charinpanitkul, T. Step-by-step conversion of water hyacinth waste to carbon nanohorns by a combination of hydrothermal treatment, carbonization and arc in water processes. 2021, Dia. Reat. Mater. 111, 108222.

## 4.2 Exchange and Visitation

• JASTIP seminar was held online on March 24, 2021 with 24 participants from both Kyoto and Thailand.



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## Catalytic pyrolysis process and hydrothermal liquefaction for bio-fuel production

Researchers (temporary from annual workshop: HO)

- 1. Prof. Armando T. Quitain
- 2. Prof. Suttichai Assabumrungrat
- 3. Dr. Bridgid Chin Lai Fui
- 4. Prof. Ir. Suzana Yusup
- 5. Ms. Elisabeth Rianawati
- 6. Dr. Yiin Chung Loong

Kumamoto University Chulalongkorn University Curtin University Malaysia Universiti Teknologi PETRONAS (UTP) Resilience Development Initiative Universiti Malaysia Sarawak

## Abstract

The ASEAN countries generate millions of cubic meters of agricultural waste products annually (e.g. palm kernel shells, rice husks, corn stover, coffee husks, sugarcane bagasse, etc.) that can potentially be tapped for bioenergy production. This large amount of residual biomass is widely available and can be converted to heat and power for agro-industrial processes. Studies have shown that lignocellulosic biomass can be converted to bioenergy using thermochemical, and biochemical processes such as fermentation, pyrolysis and gasification, among others.

Development of alternative technologies for the productions of renewable energy from biomass found in ASEAN geographical locations could help stimulate widespread use of biomass as fuel source for industrial and residential heating needs in the region. Consequently, this could lead to the introduction of biomass fed furnaces, boilers and stoves for industrial and residential heating applications.

In addition, the use of catalysts such as minerals can also enhance biomass conversion rate. To the best of our knowledge, most of the catalysts reported in previous studies of pyrolysis are commercial transition element, acid catalysts and mesoporous materials. Meanwhile, there are limited studies described and compared the effect of natural alkali catalysts on biomass pyrolysis.

This study focuses on the pyrolysis of rice husk in the presence of natural source of CaO catalyst i.e. limestone and eggshell. Also, this project aims to study the policy opportunities for drop-in sustainable aviation fuel (SAF) deployment in the ASEAN by considering the initiatives undertaken by Indonesia and Malaysia.

## **Research Summary**

This work showed the optimization of catalytic pyrolysis of oil palm empty fruit bunches and catalyst CaO/HZSM-5 via response surface methodology. Equipment used was lab scale drop type pyrolyser, and the experiments employed central composite rotatable design for obtaining a quadratic regression model. Three factors were studied: reaction temperature, catalyst loading, CaO loading. The quadratic model obtained has R<sup>2</sup> value of 0.8844, f-value of 8.5, and p-value of 0.0012, indicating the model was reliable,



significant, and fits well. Numerical optimization was performed and obtained an expected maximum bio-oil yield of 35.31 wt% at reaction temperature of 567.10 °C, catalyst loading of 3.22 wt%, and CaO loading of 1.25 wt%. Effect of particle size was studied at the optimum point and found that 250-350 µm provided an experimental yield of 37.59 wt% bio-oil, which did not differ significantly from the expected maximum yield. The catalyst with optimum CaO loading was characterized using XRD, FTIR, and FESEM coupled with EDX, and it was observed that CaO was successfully impregnated and evenly distributed on HZSM-5, with minimal influences on the overall catalyst structures due to its low loading of 1.25 wt% at the optimum condition determined. Biooil produced from the catalytic pyrolysis was analysed with CHNS and GC-MS, and the results showed the quality of bio-oil was detected to have increased higher heating value, H/C ratio, and aromatic content, as well as lower O/C ratio. The kinetic study via thermogravimetric analysis (TGA) and Coats-Redfern method had also indicated increased rate of reaction with addition of CaO/HZSM-5 catalyst. Besides that, this work also extended the kinetic and thermodynamic studies on oil palm fronds and oil palm trunks which had been conducted via pyrolysis process. The oil palm fronds (OPF) and oil palm trunk (OPT) were successfully investigated with the absence and presence of OPF ash, OPT ash, and OPF/OPT ash using TGA approach. It is found that the Coats-Redfern model gave the best prediction (regression coefficient >95%) for the noncatalytic and catalytic pyrolysis process using OPT and OPF, compared to Vyazovkin and Miura-Maki models. Based on activation energy (E<sub>A</sub>) calculated, the degradation results were found with the following conclusion: OPF-OPF/OPT ash > OPF-OPF ash > OPF > OPT-OPT ash > OPT-OPF/OPT ash > OPT. It is proven that OPF/OPT ash was suitable for OPF pyrolysis and OPT ash was suitable for OPT pyrolysis process for an effective energy-efficient bioenergy production.

In addition, utilizing four areas as coding framework, the current status, challenges, and policy opportunities, namely (1) policy, strategy, and reforms; (2) standards and certification system; (3) economic instruments; and (4) international integration were assessed. First, the current status and challenges within each country is assessed. Indonesia has shown a more command-and-control approach with an upfront SAF blending mandate. However, it needs to be supported by several compliance measures. Malaysia, on the other hand, has conducted country assessments but no SAF-specific policy has been issued yet. Both countries still lack the economic instruments, while international integration is still relatively under-explored with only limited inter-regional partnerships. As the biggest palm-oil producing countries, Indonesia and Malaysia possess enormous potentials to lead the region in deploying SAF, thus more initiatives are urged.

#### **Publications and Presentations**

 S.W. Hii, B. L. F. Chin, F.R.S.A. Majing, H.Y. Lim, A.C.M. Loy, C.L.Yiin, S. Yusup, A.T. Quitain, M.N. Acda, P. Unrean, E. Rianawati, Iso-conversional kinetic and thermodynamic analysis of catalytic pyrolysis for palm oil wastes, Chapter 12, Value-Chain of Biofuels, 2021.



Website:https://www.elsevier.com/books/value-chain-of-biofuels/yusup/978-0-12-824388-6

(Published date on 12<sup>th</sup> November 2021)

- 2) H.Y. Lim, S. Yusup, M. Komiyama, M. N. Acda, B. L.F. Chin, E. Rianawati, P. Unrean, A.T. Quitain, S. Assabumrungat. Optimization of catalytic pyrolysis of oil palm empty fruit bunches using CaO/HZSM-5 catalyst via central composite rotatable design (*Journal under preparation*).
- 3) Amelia Atmowidjojo\*, Elisabeth Rianawati, Bridgid Lai Fui Chin, Suzana Yusup, Armando T. Quitain, Suttichai Assabumrungrat, Yiin Chung Loong, Worapon Kiatkittipong, Atthapon Srifa, Apiluck Eiad-ua, "An assessment of the policy opportunities for driving sustainable aviation fuels in the ASEAN"
  - Presented on 2nd International Symposium of Earth, Energy, Environmental Science and Sustainable Development, 25 September 2021
  - Submitted to IOP Conference Series: Earth and Environmental Science

#### Group Workshops, meetings, and researcher exchange

The Online Workshop on ASEAN Biomass Conversion Technologies was held on 28<sup>th</sup> January 2021.

12:55~13:00 **Opening Remarks** 

Prof. Armando T. Quitain

Kumamoto University, Japan

#### JASTIP-Net 2019: Sustainable Production of High-quality Bio-oil from Different Agriculture

#### Wastes in the ASEAN Region through Catalytic Fast Pyrolysis

13:00~13:15 Thermal Degradation Behavior and Kinetic Analysis for Biomass in

#### **ASEAN** Countries

Dr. Bridgid Chin Lai Fui

Curtin University, Malaysia



13:15~13:30 Catalytic Pyrolysis of Oil Palm Wastes for Bio oil Production

Prof. Ir. Suzana Yusup

Universiti Teknologi PETRONAS (UTP), Malaysia

13:30~13:45 Potential and Challenges of Biofuel Implementation in ASEAN

Ms. Elisabeth Rianawati

Resilience Development Initiative (RDI), Indonesia

#### 13:45~14:00 Green Hydrogen Production from Low Transition-Temperature Mixtures

#### (LTTMs)-Deconstructed Oil Palm Biomass via Gasification

Dr. Yiin Chung Loong

Universiti Malaysia Sarawak (UNIMAS), Malaysia

#### 14:00~14:05 Break

#### 14:05~14:15 Introduction of the Japan-ASEAN Science, Technology and Innovation

#### Platform

Prof. Hideaki Ohgaki

Kyoto University, Japan

14:15~14:25 Technological Development on Biodiesel and Bio-hydrogenated

#### **Diesel Production**

Prof. Suttichai Assabumrungrat

Chulalongkorn University, Thailand



## 14:25~14:35 Recent Developments on Microwave Carbocatalysis for Biomass Conversion

Prof. Armando T. Quitain

Kumamoto University, Japan

#### 14:35~15:05 **Presentations from Students from Kumamoto University**

- Mechanistic Insights into the Acid-catalyzed Depolymerization of Cellulose and Fucoidan over Graphene Oxide under Microwave Irradiation (*Jonas Karl N. Agutaya*)
- 2. Conversion of Fructose into 5-Hydroxymethylfurfural, Formic Acid and Lactic Acid by Carbon-based Catalysts Activated by Microwave (*Miyu Nakamura*)
- Biodiesel Production from Microalgal Biomass via In-situ Transesterification using Carbon-based Catalyst under Microwave Irradiation (*Yik Lam Kam*)
- Immobilization of Enzyme on Carbon-based Catalyst for Depolymerization of Cellulose to Glucose (*Kisara Tsuruta*)
- Production of Third-generation Biodiesel from Microalgae via the Synergy of Supercritical CO2 and Subcritical H2O (*Daiki Fukushima*)
- 6. Deamination of Aspartic Acid using Supercritical CO2 and Graphene Oxide

(Shunsuke Kimura)

#### 15:05~ Open Forum





Figure 1: Screenshot of the group photo session during the Online Workshop on ASEAN Biomass Conversion Technologies held via Zoom online platform on 28<sup>th</sup> January 2021.

#### Other outcomes

Nil



# Efficient Conversion of Biomass Wastes to Carbon Materials, Fuels, and Electric Power Utilizing Degradative Solvent Extraction

#### Researchers

- 1. Jr. Assoc. Prof. Dr. Ryuichi Ashida
- 2. Assoc. Prof. Dr. Nakorn Worasuwannarak

3. Lecturer Dr. Xayalak Vilaida

4. Prof. Dr. Mya Thet Nwe

Kyoto University

Joint Graduate School of Energy and Environment (JGSEE) National University of Laos (NUOL) Technological University (Thanlyin), Yangon Division

#### Abstract

We have investigated possibilities of utilizing the products of the degradative solvent extraction of biomass wastes. Pelletized activated carbon fibers were prepared from the extracted product, soluble, and the electric and electrochemical properties of the fibers were examined. The results showed a good potential for producing supercapacitor from soluble produced from rice straw.

#### **Research Summary**

#### Carbon fiber preparation

Carbon fibers were produced from extracted soluble in 4 steps. In the first step called pretreatment of soluble, soluble was heated under nitrogen atmosphere at conditions 320 °C for 40 minutes with a heating of rate 10 °C/min. Then, the pretreatment soluble was spun to fibers at 280 – 320 °C by melt spinning method using a mono-hole continuous spinning machine at the winding speed 150 m/min under nitrogen atmosphere. The as-spun fibers were thus obtained from the pretreatment soluble, which are black and brittle. Then, the as-spun fibers were continuously stabilized at 300 °C for 60 min. with a heating rate of 0.5 °C/min. under air flow. Approximately 0.4 g. of thermal stabilized fibers were used to make tablet by using a hydraulic shop press machine at 400 °C with a heating rate 10 °C/min. and held under the applied pressure less than 16 bars for 10 minutes. The mold diameter used in tablet preparation was 13 mm. Finally, the fiber tablet (see Figure 1) was heated up from room temperature to 900, 1,200 and 1,400 °C, with a heating rate of 10 °C/min under nitrogen and held in a tube furnace. After that, we examined a composition of carbonized fiber and chose the best temperature of carbonization for activated carbon fiber.





Figure 1 Carbon fiber tablet.

#### Electrical conductivity of carbon fiber

Table 1 shows the electrical conductivity of carbon fiber tablets prepared from carbonized fiber at 900, 1,200, 1,400 °C respectively. The results showed that the electrical conductivity of the carbon fiber tablet decreased with increasing carbonization temperature. The carbon fiber tablet prepared from carbonized fiber at 900 °C had the highest electrical conductivity, which was 32.02 S/cm at electric current of 800  $\mu$ A. Alencherry, T *et al.* reported that the electrical conductivities of activated carbon were 0.84 – 1.19 S/cm. So, it was shown that our carbon fibers had larger electrical conductivity than those from the literature.

Carbonization Temperature (°C)	Thickness (cm.)	Electric current (µA.)	Conductivity (S/cm)
900	0.21	600	13.92
	-	800	32.02
1,200	0.27	600	7.55
	-	800	11.78
1,400	0.30	600	7.25
	-	800	8.61

Table 1 The electrical conductivity of carbon fiber tablet.

## **Electrochemical**

The specific capacitance values of activated carbon fibers (ACF) were measured from charge/discharge curve. The charge/discharge (GCD) test was conducted on batteries test system in a potential range -2 V to 2 V, and current density of 0.1 A/g by using 1M KCl and 1M KOH as an electrolyte. Table 2 shows the capacitance value of carbon fiber prepared at 900 °C by using 1M KCl and 1M KOH as an electrolyte. It was found that the specific capacitance measured by GCD method using 1M KCl as an electrolyte was higher than that using 1M KOH. The specific capacitance was 46.79 F/g for 1M KCl and 40.91 F/g for 1 M KOH. Comparing the specific capacitance from literatures, it was found that the carbon fiber prepared in this study showed greater



specific capacitance. So, these results showed a good potential for producing supercapacitor from soluble produced from rice straw.

Sample	Capacitance value (F/g) by using current density 0.1 A/g			
	1 M KCI	1 M KOH		
Carbon fiber at 900 °C	46.79	40.91		

Table 2 The capacitance of carbon fiber prepared at 900 °C.

#### **Publications and Presentations**

Tobuweang T., Aussawasathien D., and Worasuwannarak N. Preparation of supercapacitor from soluble produced from rice straw. Journal of Sustainable Energy & Environment, 11 (2020), 131-134.

Ashida R. Development of highly-efficient utilization methods of biomass/lignite based on their chemistry. SCEJ Regional Meeting in Akita (2021), B204.

#### Group Workshops, meetings, and researcher exchange

Online group workshop, Mar 16, 2021, Participants: Hideaki Ohgaki, Taro Sonobe, Ryuichi Ashida (Kyoto University), Worasuwannarak Nakorn (JGSEE), Xayalak Vilaida, Sengratry Kythavone (National University of Laos)

#### Other outcomes

NA



## Photocatalytic Study for Energy and Environment

## Researchers

- 1. Prof. Keiichi N Ishihara, Kyoto University
- 2. Prof. Wisanu Pecharapa, King Mongkut's Institute of Technology Ladkrabang
- 3. Prof. Sorapong Pavasupree, Rajamangala University of Technology Thanyaburi

#### Abstract

This research aims to study the effects of nanomaterials from leucoxene mineral addition in intumescent (fireproof) paint coating on thermal performance and char morphology with commercial titanium dioxide and nano-titanium dioxide comparison. The nanomaterials from leucoxene mineral were synthesized via hydrothermal process for steel structure fire protection. This is caused by the char formation after heating, which has the insulating effects. The thermal efficiency and char morphology of the char were influenced. The intumescent paint consists of acrylic thermoplastic resin, flame retardant agent, and organic fillers. The prepared samples were tested the physical properties before being used. The samples were evaluated the thermal performance and char formation. The fire test of the materials were investigated under ASTM E-119 standard with the temperature of 538, 704, 843, 927 and 1010 o C for 5, 10, 30, 60, 120 and 180 minutes, respectively. The foam structures of intumescent fireproof coating after combustion and surface with intumescent paint coating were observed by scanning electron microscope (SEM).

#### **Research Summary**

The results showed that the addition of 1.0% of nanomaterials from leucoxene mineral and commercial nano-titanium dioxide after burning, the formation of charcoal was porous, dense and expanded, which was porous, increased density and expansion of height. It can absorb heat from combustion, affecting the insulation of fireproof paints, which indicates that nanomaterials from leucoxene mineral can increase the fire retardant performance and the steel structure protection.

## **Publications and Presentations**

Chaisaenrith, P., Taksakulvith, P., Pavasupree, S., "Effect of nano titanium dioxide in intumescent fireproof coating on thermal performance and char morphology", Materials Today: Proceedings, 2021, 47, pp. 3462–3467

## Group Workshops, meetings, and researcher exchange

JASTIP-WP2 2020FY Annal Meeting was held on 2021 March 3, via on-line. 14 researchers are participated.



#### Other outcomes

This research also applied the nanomaterials from Thai minerals for commercial intumescent painting products with Thai Nakorn Paint Co., Ltd. under The Board of Investment of Thailand (BOI) commercial scale project.





## **Development of Bi-based Oxides photocatalysts**

#### Researchers

- 1. Prof. Keiichi N Ishihara, Kyoto University
- 2. Prof. Wisanu Pecharapa, King Mongkut's Institute of Technology Ladkrabang

### Abstract

In this group, we focus on the nano-materials produced by various methods to apply the commercial purpose.

#### **Research Summary**

Our group have studied the BiVO<sub>4</sub> photocatalysis made from hydro-thermal process and sono-chemical process. For the hydro-thermal process, it is found that the addition of KCI leads to the change of morphology and bandgap. Among the variation, the shuriken shape (cross chape) shows the highest performance. For sonochemical process, it is found that sonochemical reaction time and pH value are crucial process factors playing key role on crystalline phase, morphological structure, and photocatalytic properties of BiVO<sub>4</sub>. In addition, by doping with Mn, Fe element results to not only significant monoclinic-to-tetragonal phase change but also morphology and enhanced photocatalytic performance of BiVO<sub>4</sub>. Further study on the effects of others dopants is underway.

## **Publications and Presentations**

Sopheak Meng, Takaya Ogawa, Hideyuki Okumura, Keiichi N Ishihara, The effect of potassium chloride on BiVO<sub>4</sub> morphology and photocatalysis, Journal of Solid State Chemistry, 122291

Thanaphon Kansaard, Chatpong Bangbai, C. K. Jayasankar and Wisanu Pecharapa, "Effect of ultrasonic irradiation time on physical properties and photocatalytic performance of BiVO<sub>4</sub> nanoparticles prepared via sonochemical process", *Integrated Ferroelectrics*, Vol. 214 Issue 01 (2021) pp. 123-132

Tirapat Wechprasit, Thanaphon Kansaard, Atipong Bootchanont, Wisanu Pecharapa, "Structural and optical properties of Mn-incorporated BiVO<sub>4</sub> nanoparticles synthesized by sonochemical process", *Integrated Ferroelectrics,* accepted.

Group Workshops, meetings, and researcher exchange

JASTIP-WP2 2020FY Annal Meeting was held on 2021 March 3, via on-line. 14 researchers are participated.



## JASTIP-WP2 2020FY Annal Meeting (KU-KMITL team)

Date: 2021 March 3

#### Program

14:00 Opening remark

14:05 (Kyoto U)

--"The effect of KCI content on morphology and photocatalytic performance of BiVO<sub>4</sub>" Meng Sopheak

-- "The possibility of CuO and CeO<sub>2</sub> nano particles", Prof. Keiichi N. Ishihara 14:45 (KMITL)

-- "Progress work on BiVO 4 -based visible-driven photocatalyst" Assoc. Prof. Dr. Wisanu Pecharapa, KMITL

-- "Light scattering nanoparticles from glass cullet by mechanical milling process" Asst. Prof. Dr. Wanichaya Mekprasart,

15:25-15:40 Photo Session and Coffee Break

15:40 (JASTIP-net) "Nanochannel Surface Functionalized Cu-Cu<sub>2</sub>O/TiO<sub>2</sub> Nanorods Photoelectrode for Efficient Photoelectrocatalytic CO<sub>2</sub> Reduction to Hydrogen and Methanol", Prof. Nor Aishah Saidina Amin (UTM)

16:10 (JASTIP-net) "Fabrication of photocatalytically active fibers for water treatment application" Dr. Saepurahman (LIPI)

16:30 Discussion for 2021 activities in the team

16:55 Closing





#### Other outcomes

Poster presentation award in the 12<sup>th</sup> Asian Meeting on Ferroelectricity and the 12<sup>th</sup> Asian Meeting on Electroceramics Conference (AMF-AMEC 2021) in the title of "Sonochemical Synthesis, Characterization and Photocatalytic Activity of Fe-doped BiVO4 Nanoparticles".



## Transdisciplinary Study on Rural Electrification

#### Researchers

Kyoto University
Kyoto University
University of Malaya
University of Malaya
University of Malaya
LIPI
Institute of Technology of Cambodia
Institute of Technology of Cambodia

#### Abstract

In 2020-2021, the project has focused on analysing inequalities arising during electrification through their original assessment method based on Quality of Life (QoL) in South East Asia. Given the prolonged COVID-19 lockdowns in the region, the research team considered new sites with intermittent access in the area to conduct the analyses. We surveyed QoL levels in households from Occidental Mindoro and Tanay in the Philippines, who recently received a PV lighting system and could be briefly visited in September and October 2020 by our local collaborators. We found significant differences in how lighting reflects in the QoL subdomains through activities, use of time and perceptions about safety by gender, which could be associated with roles in the household and expectations from the new routines adopted. Also, with the help of local partners, we conducted a qualitative exploration in Blora, Indonesia, enquiring about the changes of roles inside the household for specific activities after electrification. We understood that based on various reasons, e.g. better proficiency for the task, a sense of duty, or perceived necessity, women were expected to be responsible for some household activities. In contrast, males were only expected to lead a handful of activities, namely fuelwood collection and water supply. This fact has implications on the potential benefit-receivers during electrification. In addition, we developed a framework to understand the connection between household roles and appliance-purchasing behaviour in urban settings as a starting point to assist in analysing appliance adoption in communities without electric power. The analysis relied on data from online surveys conducted in Oct 2020 and Mar 2021 in metropolitan cities of Indonesia and the Philippines. We found that, in general, more equitable roles in the household contribute to more energy-efficient appliance purchases. However, we also observed that the type of appliance and the domain of household relations are essential factors in cooking, cleaning and personal or entertainment-related appliances. These findings again have important implications on how household roles might determine unequal outcomes in the transition process of electrification. Finally, in addition to the empirical work above, we conducted a thorough review of gender-related studies in the region as another way to



understand inequalities during electrification in South East Asia. The review focused on articles from 1990 to 2021. We found that gender in the decision-making processes for the rural setting was one recurrent theme in the literature. As for the urban environment, gender-distinctive pro-sustainable behaviour took the most prominent place. Social outcomes of rural electrification projects through the lenses of gender differences were absent for the most part. This research project will continue targeting the changes in QoL dimensions in connection to unequal outcomes of electrification in SE Asia, where further details are needed for a more conclusive result. This is one part of the future research objectives for 2021-2022.

#### **Research Summary**

#### Transdisciplinary studies on rural electrification: perspectives from Quality of Life

Our objective for 2020-2021 was to understand inequalities arising during electrification in South East Asia through analysis of changes in diverse Quality of Life (QoL) measures, using our previously developed approach (2016-2020) based on the Wisconsin Quality of Life Index. Given the prolonged COVID-19 lockdowns in the region, data collection could only take place twice in 2020, from which we conducted the analyses of inequality.

In the case of Malaysia and Cambodia, the conditions were the most affected, suspending the access to rural villages during the time covered in this report. This led the research team to consider data collection in new sites with an intermittent but certain degree of access in the region. One of these was the Philippines, where we surveyed three communities in September and October 2020: Paluan (Occidental Mindoro), Rawang and Macantog (Tanay). A local non-profit organisation, Solar Hope, collaborated with our research team and was the main bridge with the local communities. Mark Napao and Joseph Quiñones from Solar Hope visited the locations, collected data and assisted with translation and interpretation. The communities received PV systems from Solar Hope to provide lighting and capabilities to charge electric devices. In the case of Indonesia, Yuka Asmara from the Indonesian Institute of Sciences (LIPI) had brief access to Blora (Java) to collect data in August 2020. The community was recently electrified.





#### QoL and sub-domains before and after Solar PV Lighting System

Figure 1 The effects of PV lighting systems on QoL in the Philippines

We centred on identifying inequalities using our QoL approach and on qualitative descriptions to explain the differences. First, through the analysis of the villages in the Philippines, we found that general QoL levels did not have a substantial change after introducing the PV solar lighting systems. This suggests that such a level of power might be insufficient for a distinguishable difference. However, we also found that by QoL sub-domains there were some increasing (how time is spent, satisfaction with housing and personal safety) and others reducing (how time is spent alone, satisfaction with main activity and with food & cooking, see figure 1). Yet, inequalities were more noticeable by some differences distinguished in the QoL outcomes by gender. There was a slight but detectable reduction in general QoL among men compared to women. Furthermore, the results were contrasting for levels of personal safety, which decreased among men but increased among women; satisfaction with time spent alone, which



decreased sharply among women compared to a slightly increase among men; and satisfaction with housing, which had a more substantial increase among males compared to women. In sum, there were important differences of how lighting reflects in the QoL subdomains through activities, use of time and perceptions about safety by gender, which could be associated with roles in the household and expectations from the new routines adopted. A more detailed discussion is available in document 5 of the research output list.

In Indonesia, on the other hand, a qualitative exploration was possible with a series of openended questions enquiring on the changes of roles inside the household for specific activities after electrification. These dimensions were laundering, cooking, fuelwood collection and water supply. We discovered that women were expected to take the responsible role in the household for laundering and cooking due to diverse reasons. Among these, we identified better proficiency for the task, a sense of duty, a primary role, and a perceived necessity as the main reasons. On the other hand, fuelwood collection and water supply were tasks for which males were expected to be responsible. Electrification did not change these results substantially. However, the analysis of changes in the QoL levels did find a significant difference between women and men on the satisfaction level of how they spent time and their main activity in the household, suggesting that electrification might have indirectly affected the levels in the subdomain. Nevertheless, we still need further details for a more conclusive outcome given that the samples of non-electrified households in the comparison were limited due to the recent electrification of the village.

#### Gender inequalities in renewable energy projects

In addition to the empirical work described above, and given the difficulties to access the field for data collection, another way to understand inequalities during electrification in South East Asia was by conducting a thorough review of gender-related studies in the region. We conducted a dedicated review focused on articles from 1990 to 2021. For the rural setting, we found studies on gender in the decision-making processes as the most recurrent theme in the literature. As for the urban environment, gender-distinctive pro-sustainable behaviour took the prominent place. However, social outcomes of rural electrification projects through the lenses of gender differences in the household was absent for the most part, whereas in the urban setting, no studies reported on the gender relations inside the household in connection to energy-efficient choices. These reviews formed the findings in document 6 of the research output list. The research was conducted in collaboration with Chansatya Meas, a doctoral candidate from the Graduate School of Energy Science (Kyoto University).

#### Household appliance purchasing behaviour

Finally, appliance purchasing behaviour literature reports that gender is an important determinant for acquiring more energy-efficient appliances. However, research on how gender roles influence sustainable behaviour is less common, particularly in the South-East Asian



region. Understanding the effect of gender roles could be central to clarifying residential practices that encourage reducing energy use in households and can ultimately affect QoL levels.

We developed a novel framework to understand the connection between household roles and appliance purchasing behaviour. First, we defined key roles in the household: the breadwinner, the decision-maker, the household manager and the primary appliance user. Then, we conducted an online survey of households in metropolitan cities of Indonesia and the Philippines twice in Oct 2020 and Mar 2021. We obtained a sample of 1210 households of cohabiting adults, nuclear and extended families. We found that, in general, more equitable roles in the household contribute to more energy-efficient appliance purchases. However, we also observed that the type of appliance and the domain of household relations are important factors in cooking, cleaning and personal or entertainment-related appliances. Our framework reveals important implications on energy policies for more equitable and efficient outcomes in residential energy consumption, which could also extend to rural settings and in connection to the observed differences in the QoL levels. The results are detailed in documents 2 and 3, and document 7. The research was conducted in collaboration with assistant professor Chen Qu from the Graduate School of Energy Science (Kyoto University), and three doctoral candidates from the same graduate school: Latifa Seniorita from Indonesia, Samuel Matthew Dumlao from the Philippines and Kiran Murthy from India.



### Publications and Presentations

2020

- Cravioto, J. Electrification in South East Asia: Agendas on the social dimensions. Data-oriented Area Study Unit 1<sup>st</sup> Research meeting, 2020. Center for Southeast Asian Studies, Kyoto University. Sep. 25, 2020. Kyoto Japan. (Oral presentation)
- 2. Seniorita, L., Dumlao, S.M., Kumar, K., Qu, C., Cravioto, J. and Ohgaki, H. A framework for understanding the influence of gender roles on appliance purchasing behaviour of urban middle class in developing nations. The 11th International Symposium of Advanced Energy Science Zero-Emission Energy. Sep. 15, 2020. (Poster)
- 3. Seniorita, L., Dumlao, S.M., Kumar, K., Qu, C., Cravioto, J. and Ohgaki, H. Study on the Influence of Gender Roles on Appliance Purchasing Behaviour in The Philippines, Indonesia and India. Zhejiang-Kyoto-Ajou Joint Online Symposium on Energy Science. Dec 2020. (Oral presentation)
- V. Vai, C. Chhith, S. Eng, C. Hel, O. Eth, L. Bun, H. Ohgaki "Improvement of the Small-scale Biogas Plant for a Household in a Rural Village", The 11th International Symposium of Advanced Energy Science, 2020.9.15 (Poster)
- 5. Nasrudin Abd Rahim, Hang Seng Che, Chia Kwang Tan, H. Ohgaki, J. Cravioto Caballero, "Study of the suitability of different types of battery for rural electrification and its impact to the quality of life of the communities ", The 11th International Symposium of Advanced Energy Science, 2020.9.15 (Poster)
- 6. H. Ohgaki, H.S. Che, J. Cravioto, S. Kobayashi, H. Toe, B. Long, E.O. Daya, V. Vannak, C. Kwang T., Nasrudin A. Rahim, H. Farzeneh, "Rural electrification and QoL: Lessons from Southeast Asia", The 3rd International Conference on Smart City Innovation (ICSCI), The 13th AUN/SEED-Net Regional Conference on Energy Engineering (RCEneE), and The 3rd International Conference on Dwelling Form (iDwell), UNIVERSITAS UDAYANA, 2020.10.28 (Invited)
- 7. V. Vai, L. Bun, H. Ohgaki, "Integrated Battery Energy Storage into an Optimal Low Voltage Distribution System with PV Production for an Urban Village", The 3rd International Conference on Smart City Innovation (ICSCI), The 13th AUN/SEED-Net Regional Conference on Energy Engineering (RCEneE), and The 3rd International Conference on Dwelling Form (iDwell), UNIVERSITAS UDAYANA, 2020.10.28 (Oral)
- 2021
  - 1. V. Vai, L. Bun, H. Ohgaki, "Integrated Battery Energy Storage into an Optimal Low Voltage Distribution System with PV Production for an Urban Village", International Journal on Advanced Science, Engineering and Information Technology, vol. 10, 6, pp2458-2464, 2021.1.29.
  - 2. Cravioto, J., "Innovations and challenges in the use of hard data in Energy-Related research from Social Science and humanities", International Workshop on Data-Oriented Approaches to the Social Sciences and Humanities. Center



for Southeast Asian Studies, Kyoto University, Feb 12, 2021. (Oral presentation)

- 3. Cravioto, J., Ohgaki, H., Napao, M., Quiñones, J., "Household lighting and quality of life in rural Philippines: the effect of PV lamps use in non-electrified communities of Tanay", 40<sup>th</sup> Annual Meeting of the Japanese Society of Energy and Resources. Aug. 3, 2021. (Oral presentation)
- 4. Meas, C., Cravioto, J., Ohgaki, H., "Gender Inequality in Renewable Energy Policy", 40<sup>th</sup> Annual Meeting of the Japanese Society of Energy and Resources. Aug. 3, 2021. (Oral presentation)
- 5. Hideaki Ohgaki, "Introduction to JASTIP Program Phase II", Mahidol-Kyoto Onsite Laboratory Workshop on Chemical Engineering on "Nanocarbon Materials for Sustainable Production and Storage of Green Fuels and Platform Chemicals", 2020.3.24 (Oral)

#### 2022

- Cravioto, J., Seniorita, L., Dumlao, S.M., Kumar, K., Qu, C., and Ohgaki, H. Household roles and efficient appliances purchasing in urban contexts of Indonesia and The Philippines. 38<sup>th</sup> Conference on Energy Systems, Economics and Environment. Japanese Society of Energy and Resources. Jan 25, 2022. (Oral presentation)
- 2. Anugerah Yuka Asmara, AR. Rohman Taufik Hidayat, Hideaki Ohgaki, Toshio Mitsufuji, Jordi Cravioto Caballero, "Utilisation of Solar and Wind Energy to Increase Quality of Life for Rural Communities in Blora Regency - Indonesia: From Triple Helix to Quadruple Helix", 5th International Conference on Planning in the Era of Uncertainty, "Rural Urban Connectivity", 2021.7.19 (Oral)

Group Workshops, meetings, and researcher exchange

## NA

## Other outcomes

**Best Paper**: Anugerah Yuka Asmara, AR. Rohman Taufik Hidayat, Hideaki Ohgaki, Toshio Mitsufuji, Jordi Cravioto Caballero, "Utilisation of Solar and Wind Energy to Increase Quality of Life for Rural Communities in Blora Regency -Indonesia: From Triple Helix to Quadruple Helix", 5th International Conference on Planning in the Era of Uncertainty, "Rural Urban Connectivity", 2021.7.19.