#### e-ASIA Joint Research Program Progress Report

1. Project Title: Development of Functional Nanocarbon-Based Catalysts for Biomass Conversion Processes

- 2. Joint Research Period: November 2014~ (for 3 years)
- 3. Principal Investigators:
- Japan : Tetsuya Kida, Professor, Department of Applied Chemistry and Biochemistry, Faculty of Engineering, Kumamoto University, Kumamoto 860-8555, Japan Planned Funding Period: April 1, 2015 – May 31, 2016
- Thailand : Artiwan Shotipruk, Professor, Chemical Engineering Research Unit for Value Adding of Bioresources, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Phayathai Road, Bangkok 10330, Thailand Planned Funding Period: June 1, 2015 – May 31, 2016
- Philippines: Joseph Auresenia, Professor, Department of Chemical Engineering, De La Salle University, Manila, Metro Manila, Philippine Planned Funding Period: June 1, 2015 – May 31, 2016

4. Summary of the Progress of the Joint Research:

This collaborative research aims to synthesize nanocarbon materials such as graphene oxide, carbon nanotube and hydrothermal carbon, and utilize them for efficient conversion of vast biomass resources into useful compounds under special reaction field of supercritical fluid and microwave irradiation.

**Japan:** The Japan team had successfully utilized the synergy of graphene oxide (GO) and microwave (MW) irradiation for cellulose depolymerization and biodiesel production, including glycerol conversion into fuel additives. The use of sub- and supercritical fluid as a solvent has also been investigated. Results indicated that microcrystalline cellulose can be effectively depolymerized into glucose, generating yields as high as 73% in 1 h. GO can effectively convert free fatty acid to biodiesel with 99.2 % yield in 3 min, but would require functionalization with sodium silicate to obtain 99.6% conversion of the triglyceride in 30 min. Other related works that have been carried out include nitrogen-functionalization of GO obtaining 11% N-doping level (the highest reported so far) and its application to CO<sub>2</sub> capture, liquefaction of oil palm biomass into bio-oil obtaining higher yield compared to metal oxide-based catalysts and hydrolysis of polyphenols to remove the sugar moieties.

**Thailand:** The Thai team had successfully synthesized and characterized sulfonated hydrothermal carbon-based acid catalyst from glucose, and applied

this to cellulose hydrolysis and fructose dehydration reaction obtaining 43.63±1.62 wt.% of glucose yield, and 87.56±0.37 wt.% of fructose conversion, respectively. The yield is better compared to conventionally synthesized hydrothermal carbon acid catalyst via incomplete carbonization in sulfuric acid, obtaining highest sugar yield of 40.7% from the hydrothermal hydrolysis of eucalyptus chips in 5 min. The possibility of enhancing the biomass conversion yield by the application of the catalyst with the addition of chromium chloride was also evaluated for the production of HMF and levulinic acid from cellulose in single and biphasic systems.

**Philippines:** The Philippine team has successfully synthesized carbon nanotubes from indigenous materials such as coconut shell, and applied this to the synthesis of biodiesel production from microalgae, kenaf and kakawate seeds using microwave irradiation. Determination of mechanism pertaining to the reaction and estimation of the parameters have also been started and on-going. Supercritical carbon dioxide extraction apparatus has also been built and applied to extraction of oil feedstock for biodiesel production. The research outputs have been disseminated by journal publication and in various conferences around the region, some of which have been organized by the research team.

5. Outstanding Results and Achievements (Training, Workshop, Publication, etc, if any):

5-1. Training

### Philippines

- A training on "Molecular Spectroscopic Techniques for Materials Research" by Dynalab and ThermoFischer held last October 25, 2016 in Quezon City, Philippines was attended by Engr. Alva Durian of DOST East Asia. (Philippines)
- 2. A lecture and training on chemostat, bioreactor and esterification reactor modelling was attended by members of the DOST East Asia Research Team held at DLSU last March 3, 2017. This activity also includes training in process simulation using Matlab. (Philippines)

#### 5-2. Workshop

# Japan

- Joint International Symposium on 「Regional Revitalization and Innovation for Social Contribution」 and 「e-Asia Functional Materials and Biomass Utilization」 2015, October 1, 2015. (Fukuoka, Japan)
- 2. Joint International Symposium on 「Regional Revitalization and Innovation for Social Contribution」 and 「e-Asia Functional Materials and Biomass Utilization」 2016, December 7, 2016. (Fukuoka, Japan)

# Thailand

1. Development of Functional Nanocarbon-Based Catalyst for Biomass Conversion Processes, the e-ASIA Joint Research Program (e-ASIA JRP), September 19-20, 2016, Thailand

#### Philippines

 DOST East Asia organized the Asian Federation of Biotechnology (AFOB) Regional Symposium 2017 held last February 9-11, 2017 at DLSU, Manila, Philippines

## 5-3. Publication

## Japan

- 1. Baldovino et al., "Synthesis and characterization of nitrogen-functionalized graphene oxide in high-temperature and high-pressure ammonia," RSC Advances 6 (115), 113924-113932 (2016)
- 2. Sumigawa et al., "Graphene Oxide and Microwave Synergism for Efficient Synthesis of Biodiesel" ACS Energy and Fuels (under revision)
- 3. Mission et al., "Synergizing graphene oxide with microwave irradiation for efficient cellulose depolymerization into glucose," Green Chemistry (under revision)
- 4. Uchikado et al., "Microwave-Assisted Solvothermal Conversion of Glycerin to Biofuel Additives," Biomass and Bioenergy (under revision)

### Thailand

 Nopparat Suriyachai, Verawat Champreda, Chularat Sakdaronnarong, Artiwan Shotipruk, Navadol Laosiripojana, Sequential organosolv fractionation/ hydrolysis of sugarcane bagasse: The coupling use of heterogeneous H<sub>3</sub>PO<sub>4</sub>-Activated carbon as acid promoter and hydrolysis catalyst, Renewable Energy (under revision)

#### Philippines

- 1. Torres et al, (2016). Production of Carbon Nanotubes from Coconut Biomass using Microwave Assisted Processes. In Proceedings: Regional Symposium in Chemical Engineering 2016.
- 2. Macawile et al., (2007). Extraction of Kenaf Seed Oil and Kakawate Seed Oil using Supercritical Carbon Dioxide, In Proceedings of the AFOB 2017.
- 3. Alva Durian et al. (2017) Microalgal Lipid Extraction Supercritical Carbon Dioxide and its Conversion to Fatty Acid Methyl Ester, In Proceedings of the AFOB 2017.
- 4. Torres and Auresenia (2017). Production of Carbon Nanotubes from Coconut Biomass using Microwave Assisted Processes. In Proceedings of the AFOB 2017.
- 5. Durian et al. Extraction of Micro-Algal Fatty Acid from the Philippine Coastline and Conversion to FAME, In Proceedings of the PICHE Convention 2017.

7. Recommendations and Comments to the Program (if any):

(ex. Any support to request from the Program in order to achieve item 6.)