CO_2-H_2O Synergy for Biomass Valorization into Useful Chemicals and Fuels

Armando T. Quitain,*[1,3], Taisei Nagamine,[2] Sumire Ichimaru,[2] Kota Nishimure,[2] Jonas Karl N. Agutaya,[3] Yusuke Inomata,[5] Maria Jose Cocero[6], Tetsuya Kida[5]

[1]*Center for International Education, Kumamoto University, Kumamoto, 860-8555, Japan*

[2]*Graduate School of Science and Technology, Kumamoto University, Kumamoto, 860-8555, Japan*

[3]*International Research Organization for Advanced Science and Technology, Kumamoto University, Kumamoto 860-8555, Japan*

[4]*Institute of Industrial Nanomaterials, Kumamoto University, Kumamoto 860-8555 Japan*

[5]*Faculty of Advanced Science and Technology, Kumamoto University, Kumamoto, 860-8555, Japan*

[6]*Department of Chemical Engineering and Environmental Technology, University of Valladolid, Valladolid, Spain*

**Corresponding author: quitain@kumamoto-u.ac.jp*

Highlights

- The proposed green approach using CO_2-H_2O can be utilized to valorize biomass.
- This is applied to conversion of sugars to HMF, selective removal of sugar moieties from bioflavonoids, deamination of bio-oil, etc.
- CO_2 pressurization aids catalysis with H_2O due to formation and dissociation of carbonic acid.

1. Introduction

The "Glasgow Climate Pact" agreed at the UN Climate Change Conference of the Parties (COP26) commits to accelerate global action this decade, by limiting global warming to 1.5°C over pre-industrial levels. To help achieve this ambitious goal, CO_2, the main contributor to the climate change, can be turned from a liability to an asset by mixing it with H_2O to produce an acidic condition suitable for many reactions. This opens new opportunities and challenges for researchers, process engineers and technologists.

In this regard, this talk will showcase the recent progress on our works on the CO_2-H_2O synergy under elevated temperatures and pressures as applied to many reactions involving biomass valorization and natural products of pharmaceutical interests. One good example is the removal of sugar moieties (rhamnose, glucose and rutinose) from hesperidin (HPD), a citrus bioflavonoid, to obtain a more bioactive and bioavailable aglycone – hesperetin (HPT) [1]. The concept of reactive separation, whereby HPT is simultaneously separated from the products will also be explained. Application to other natural products such as extraction of bioactive compounds from *Garcinia mangostana* pericarp, alkaloids from *Sophora flavescens* [2] and andrographolide from *Andrographis paniculate* [3]. Some of our unpublished works on the incorporation of the system in a microreactor for millisecond reactions, as well as the elucidation of the mechanism using Raman spectroscopy and quantum calculations will also be introduced. Furthermore, the positive effect of adding CO_2 to deamination to obtained high quality bio-oil by hydrothermal liquefaction of biomass will also be reported.

2. Methodology

As shown in Fig.1, the obtained sugar, like glucose, can be further converted into more useful chemicals such as 5-HMF taking advantage of the suitable balance of Bronsted base and acidities of the CO_2-H_2O mixture [4,5].

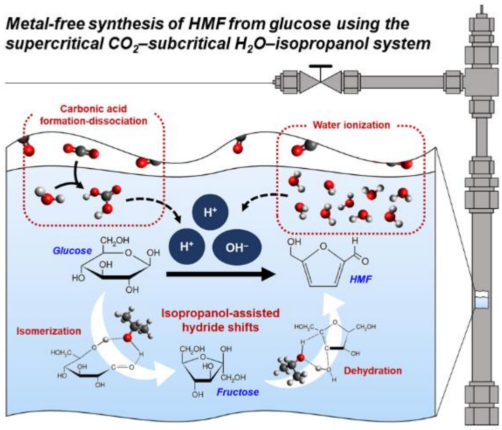

Figure 1. CO_2-H_2O system for glucose conversion to HMF

3. Results and discussion

Taking for example the conversion of glucose to 5-hydroxymethylfurfural (HMF). While HMF can be derived from biomass, specifically sugars, its synthesis typically requires the use of metal-based catalysts and ionic liquids. In this study, the supercritical CO_2-subcritical H_2O system was proposed as a green reaction medium for the conversion of glucose to HMF. The response surface methodology based on the Box-Behnken design was used to investigate the effect of temperature, pressure, and isopropanol concentration on the yield of HMF. From the quadratic models, the highest HMF yield was predicted to be 38.33% with a corresponding glucose conversion of 87.5% at 200 °C, 16 MPa, and 8 vol% IPA. A mechanistic study using DFT calculations was also performed and the results revealed that isopropanol can facilitate the various hydride shifts that occur in the conversion of glucose to HMF.

4. Conclusions

The proposed CO_2-H_2O synergy can be applied for the valorization of biomass into useful chemicals and fuels such as conversion of sugars to HMF, selective removal of sugar moieties from bioflavonoids, and deamination of bio-oil among many others.

References

[1] D Ruen-ngam, AT Quitain,* M Sasaki, M Goto, Ind. Eng. Chem. Res. **2012**, 51, 13545

[2] K Chhouk, AT Quitain*, et al. *J. Supercritical Fluids* **2016**, 110, 167

[3] RVC Rubi, AT Quitain*, et al. *J. Supercritical Fluids* **2019**, 152, 104546

[4] JKCN Agutaya, R Inoue, AT Quitain*, et al., *Ind. Eng. Chem. Res*. **2020**, 59, 16527

[5] R Inoue, JKCN Agutaya, AT Quitain*, et al. *J. Supercritical Fluids* **2021**, 168, 105079

Acknowledgement

The authors gratefully acknowledge the financial support from JSPS Grant-in-Aid for Scientific Research (Grant Numbers 17KK0118 and 18K05202), the Japan Science and Technology Agency via the e-ASIA joint research program in the field of Bioenergy (SICORP Grant Number JPMJSC18E2) and JSPS-NRCT Bilateral Joint Research Program with Chulalongkorn University (Thailand) and University of Valladolid (Spain).

Keywords

Supercritical carbon dioxide; subcritical water; HMF; isopropanol; bio-oil, bioflavonoids