（様式４）

二国間交流事業 共同研究報告書

令和 4 年 4 月 26 日

独立行政法人日本学術振興会理事長 殿

［代表者所属機関・部局］
熊本大学・大学教育統括管理運営機構
［職・氏名］
教授・ QUITAIN Armando tibigin
［課題番号］
JPJSBP 120199962

1. 事 業 名 相手国:マレーシア (振興会対応機関:OP)との共同研究

2. 研究課題名

（和文） 油やし由来リグニンのバイオオイルへの転換技術開発

（英文） Bio-oil Conversion of Oil Palm-Derived Lignin

3. 共同研究全実施期間 2019 年 4 月 1 日 ～ 2022 年 3 月 31 日 (3 年 ヶ月)

4. 相手国代表者(所属機関・職・氏名【全て英文】)

Universiti Teknologi PETRONAS・Professor・Suzana YUSUP

5. 委託費総額(返還額を除く)

本事業により執行した委託費総額		3,770,000 円
内訳	1年度目執行経費	1,870,000 円
	2年度目執行経費	1,900,000 円
	3年度目執行経費	0 円

6. 共同研究全実施期間を通じた参加者数(代表者を含む)

日本側参加者等	30 名
相手国側参加者等	9 名

＊ 参加者リスト(様式 B1(1))に表示される合計数を転記してください(途中で不参加となった方も含め、全ての期間で参加した通算の参加者数となります)。

7. 派遣・受入実績

	派遣		受入
	相手国	第三国	
1 年度目	7	1	2(0)
2 年度目	-	-	-(-)
3 年度目	-	-	-(-)
4 年度目	-	-	-(-)

＊ 派遣・受入実績(様式 B1(3))に表示される合計数を転記してください。

派遣:本委託費を使用した日本側参加者等の相手国及び相手国以外への渡航実績(延べ人数)。

受入:相手国側参加者等の来日実績(延べ人数)。カッコ内は本委託費で滞在費等を負担した内数。

8. 研究交流実績の概要・成果等

(1)研究交流実績概要(全期間を通じた研究交流の目的・研究交流計画の実施状況等)

Malaysia provides huge biomass potential derived from its large agricultural resources. Oil palm is the most abundant, producing biomass close to about 84.7 million tons annually. This biomass consists of 56% empty fruit bunch (EFB), 32 % mesocarp fiber (PMF) and 12% kernel shell (PKS). This enormous oil palm biomass could be utilized in the production of bio-oil, a promising future renewable energy source. Other than oil palm, Malaysia has also plenty of fruits and plants such as cactus and herb, which contain high amount of malic acid. In our previous works on direct hydrothermal liquefaction of the biomass, we found that most of the compounds in bio-oil were derived from the lignin (30% of the biomass fraction). In this present bilateral joint research project, a two-step conversion of oil palm residues to bio-oil was proposed and was carried out as follows:

- extraction of the lignin from the oil palm wastes
- hydrothermal treatment to obtain high quality bio-oil

Based on the abovementioned general objectives, the following specific research plan and program of activities were carried out, and the results are also outlined below:

① Synthesis of solvent from natural malic acid and sucrose

Based on the optimum condition determined in our previous studies [CL Yiin, AT Quitain, *et al.*, Bioresource Technology, 199 (2016)], the low transition temperature mixture (LTTM) was synthesized from natural malic acid, and was successfully applied as a solvent to extract the lignin from the biomass samples.

② Delignification of oil palm biomass

The LTTM synthesized in ① was used to extract lignin from oil palm biomass feedstocks (EFB, MCF and PKS) at a temperature of 80℃. The lignin was then successfully separated from the LTTM, then further treated under hydrothermal conditions.

③ Hydrothermal conversion of lignin to bio-oil

The lignin obtained in ② was treated under hydrothermal conditions. The temperature (150~300℃) and pressure (25-40 MPa) of the reaction were varied and their effects on the composition of the bio-oil produced at various conditions were investigated.

The bio-oil were then analyzed and quantified using GC-MS, HPLC and GC-FID. Furthermore, the effects of additives such as ethanol (EtOH) and CO_2 and reaction time were also investigated.

Hydrothermal treatment of lignin at 250℃ with pure water solvent resulted in the most optimum conversion (48.93% bio-oil yield with 60.04% phenolic compounds). This is due to high ionization products and highest Kw value under this condition. Addition of EtOH and supercritical CO2 did not have significant effect on both bio-oil yield and quality in terms of phenolic compounds, but this will require detailed investigation in the future.

④ Comparison of the proposed method with our previous one-step hydrothermal liquefaction method

The proposed LTTM delignification followed by hydrothermal treatment method was then compared with our previously developed direct one-step hydrothermal treatment. The current method gave better bio-oil yield of 48.93% as compared to one-step approach of 37.39%, and composition in terms of phenolic compounds of 60.04% under milder conditions of 250 ℃.

This proposed two-step approach requires less energy due to milder extraction conditions at 80 ℃, and hydrothermal treatment conditions of 250 ℃. This also entails lower operating cost. Therefore, this technology is a cheaper yet greener approach to produce bio-oil as a new source of renewable energy in the near future.

Promotion of biomass-based research knowledge to young JAPAN-ASEAN students

To promote biomass-based research knowledge to Japanese young researchers, a total of 9 graduate students of the Japanese team were either dispatched to Malaysian counterpart university - Universiti Teknologi PETRONAS for short-term stay, or to attend international conferences both face-to-face and online. We also visited other partner universities such

as Curtin University (Sarawak), and their state-of-the-art supercritical fluid processing plants and laboratory.

Graduate students were also given opportunities to attend and present papers related to biomass utilization at international symposiums and conferences. Workshops were also held face-to-face at UTP during the first year, and online during the past 2 years due to COVID-19 pandemic. Prof. Dr. Suzana Yusup was also invited to give lectures in Kumamoto University about "Perspectives on Biomass Utilization" being offered as a "multidisciplinary studies" course both face-to-face and online.

A total of 3 researchers/top students from UTP have also been invited to join the JST Sakura Science Program face-to-face or online. In addition, 2 UTP undergraduate students have also been attached to Kumamoto University for a research internship related to the project theme. This encouraged interaction among Japanese and foreign students.

Lastly, a workshop entitled 'Workshop on ASEAN Biomass Conversion Technologies' was also held online during the past 2 years due to COVID-19 pandemic related travel restrictions. This was participated by the members of each team, and other external collaborators from ASEAN countries including graduate students from UTP and Kumamoto University.

As a result of this collaboration, numerous book chapters, journal articles have been published, and presented in local and international conferences either oral or poster. Related patents have also been applied and granted, numerous research awards/grants were also received to support further collaboration.

(2)学術的価値(本研究交流により得られた新たな知見や概念の展開等、学術的成果)

Our first attempt to investigate hydrothermal liquefaction of Malaysian oil palm residues to bio-oil under supercritical conditions proved to be promising, obtaining about 40% of bio-oil yield at around 390 ℃ and 25MPa, using only water as a solvent.

The current proposed LTTM delignification followed by hydrothermal treatment method was then compared with our previously developed direct one-step hydrothermal treatment. The current method gave better bio-oil yield of 48.93% as compared to one-step approach of 37.39%, and composition in terms of phenolic compounds of 60.04% under milder conditions of 250 ℃.

This proposed two-step approach requires lesser energy due to milder extraction conditions at 80 ℃, and hydrothermal treatment conditions of 250 ℃. This also entails lower operating cost. Therefore, this technology is a cheaper yet greener approach to produce bio-oil as a new source of renewable energy in the near future. Compared to conventional fast pyrolysis method, this approach has lesser (estimated to be less than half) global warming potential (GWP) impact. Other than that, the assessment on other environmental impacts indicated that hydrothermal liquefaction operation is more environmentally benign compared to fast pyrolysis due to the reduced energy consumption.

In addition, this novel two-step approach showed good prospects as solvents for delignification of oil palm biomass and lignin conversion to high-quality bio-oil.

(3)相手国との交流(両国の研究者が協力して学術交流することによって得られた成果)

This research project further strengthened the existing relationship between UTP and Kumamoto University towards a more active research collaboration on the development of green technologies for biomass utilization. Other than the main researchers involved in this project, a total of 3 faculty members/top students from UTP have also been invited to come to Kumamoto University for discussions regarding biomass utilization. In addition, 2 UTP undergraduate

students have also been attached to Kumamoto University for a research internship related to the project theme. As a result, new research topics for future collaboration have been developed, and participation of other universities in the region has been encouraged. Furthermore, an agreement for Double Degree PhD Program between UTP and Kumamoto University was signed. This is expected to further strengthen this active research collaboration and student exchanges in the future especially on topics related to development of green technologies for biomass utilization.

(4)社会的貢献(社会の基盤となる文化の継承と発展、社会生活の質の改善、現代的諸問題の克服と解決に資する等の社会的貢献はどのようにあったか)

The results of this bilateral exchange program will encourage regional "biomass-based recycling society" using environmental friendly solvent such as LTTM and water towards cleaner environment. The technology that will be developed based on vast Malaysian oil palm biomass resources could also serve as a model to other ASEAN countries, which will set them ready for the expected biomass boom in the region. In the future, it is expected that the world economy will shift to biomass-rich Asia, which is home to almost 1/3 of the world's biomass potential energy. The prototype of the process that will be developed based on the output of this collaboration will also be useful to the treatment of other biomass feedstocks including algal and marine biomass in the surrounding seawaters **to support the attainment of UN sustainable development goals and Carbon Neutral Society in the region**.

(5)若手研究者養成への貢献(若手研究者養成への取り組み、成果)

This bilateral exchange program had been beneficial to the young members of the Japanese team (consisting of 3 young professors below 50 years old and their graduate students) being involved in an international-based joint research project. This research collaboration also promoted biomass-based research knowledge to the young Japanese graduate students and the students from counterpart university. Taking part in this kind of international research collaboration gave them an opportunity to prepare for the 21st century challenge of becoming future global engineers or researchers, and to acquire the necessary cross-cultural communication skills. Participation in domestic and international conferences, related workshops also broadened their perspective on topics related to biomass utilization.

(6)将来発展可能性(本研究交流事業を実施したことにより、今後どの様な発展の可能性が認められるか)

The newly synthesized LTTMs from natural malic acids showed good prospects as solvents for delignification of oil palm biomass at low temperature of 80 ℃. Hydrothermal treatment can be further intensified by adding CO_2. Separation can also be carried out simultaneously, by simply passing CO_2 under supercritical conditions since most of the bio-oil components are soluble under these conditions. This will be further elucidated in the future, and extend the scope to cover other types of biomass in the region including algal or marine biomass. Participation of other universities will also be encouraged.

Furthermore, the newly signed Double Degree PhD Program between UTP and Kumamoto University will also sustain future collaboration.

(7)その他(上記(2)～(6)以外に得られた成果があれば記述してください)

例:大学間協定の締結、他事業への展開、受賞、産業財産権の出願・取得など

This research collaboration also led to research projects among universities in the Southeast Asian including UTP on biomass utilization for biochemical and biofuels, which are currently funded by JASTIP-Net and JST e-ASIA Joint Research Program in Japan.

A research grant from Malaysian government was also secured under Fundamental Research Grant Scheme(FRGS) of the Ministry of Higher Education (MoHE). Two related Malaysian patents have also been granted.

他事業への展開、受賞

1. JASTIP-Net Research Grant
2. Fundamental Research Grant Scheme under the Ministry of Higher Education (MoHE), Malaysia (1st November 2020 - 31st April 2023)

産業財産権の出願・取得

(a) Natural Low Transition Temperature Mixtures (LTTMs) and Processes for making the same. Filing under C/O Pyprus Sdn Bhd. Patent Grant No.: MY-178358-A.

(b) A Low Transition Temperature Mixtures (LTTM) and A Process of Preparation Thereof. Filing under Mirandah Asia (Malaysia) Sdn Bhd. Patent Grant No.: MY-184799-A