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Miniaturised Methanol Production as Hydrogen Carrier from Biomass Pyrolysis Syngas

End of Activity Report

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ARENA summary

Project Number	
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Project summary

This project seeks to develop and demonstrate a miniaturised process technology for renewable methanol synthesis from biomass pyrolysis syngas. While methanol is suitable as a liquid fuel in its own right for spark-ignition engines, methanol can also be used as a hydrogen carrier by conversion to dimethyl-ether (DME) suitable for compression-ignition engines. This project will reveal the reaction mechanisms of methanol synthesis and the limiting effect of heat-transport at very small scales. Building on our previous achievements in biomass pyrolysis, the technical development will focus on (1) developing robust catalysts and innovative reactors for methanol synthesis with high activity and durability; and (2) integrating biomass pyrolysis and methanol synthesis into a single, optimised process. The technology demonstration will be performed using a laboratory-scale process embracing biomass pyrolysis and methanol synthesis, proving the feasibility and flexibility of renewable methanol synthesis and allowing a techno-enviro-economic evaluation of renewable methanol production.

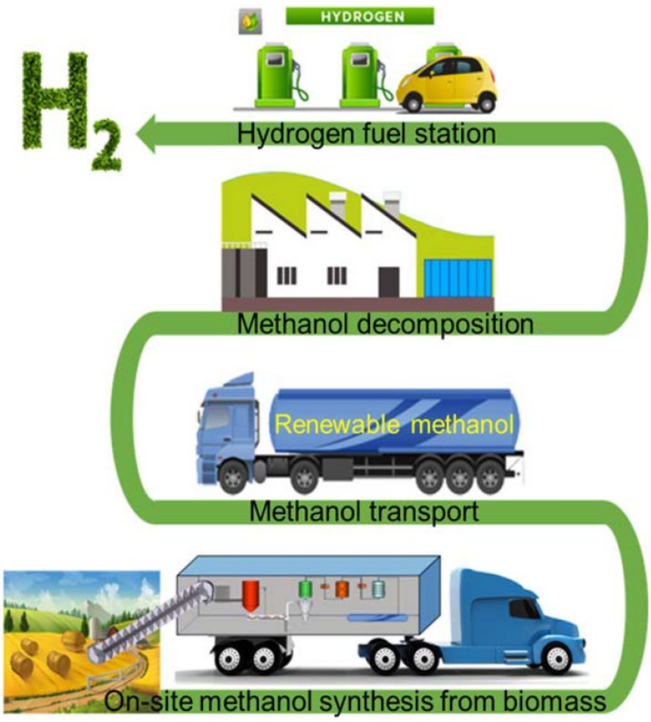

Figure 1 The concept of container-sized, miniaturised mobile platform for the production of methanol as a renewable hydrogen carrier using distributed biomass as the feedstock

Project summary and scope

Methanol synthesis is a well-developed, mature industrial process but is currently only economically viable at large-scale installations using syngas produced from coal gasification or reformed natural gas. Irrespective of the scale, methanol synthesis is typically conducted at 250 – 300°C and 5 – 10 MPa using a copper-containing catalyst (e.g. $CuO/ZnO/Al_2O_3$). Syngas can also be produced from biomass via pyrolysis, as opposed to gasification, paving the way for renewable methanol production at a small and flexible scale. Utilisation of biomass syngas for small-scale methanol synthesis faces several critical challenges, including the development of a robust catalyst that can handle the variable and less polished syngas, and an innovative miniaturised reactor that can dissipate intense reaction heat and effectively maintain optimum synthesis reaction conditions. With the aim of developing, demonstrating and optimising the methanol synthesis process from biomass pyrolysis syngas at small scale, four inter-related and sequential tasks have been designed:

- Catalyst design, preparation and evaluation: Although commercial Cu-Zn catalysts are a well-developed catalyst for methanol synthesis with high methanol selectivity and low cost, when used in an intensified process the heat generated from the exothermic reaction has been shown to sinter and deactivate the catalysts if the reaction heat cannot be properly managed and catalyst temperature exceeds 300°C. Furthermore, low H_2, high carbon oxides and high concentrations of impurities (e.g. methane and other small hydrocarbons) in biomass pyrolysis syngas, as well as variable load, frequent start-up and shutdown during operation, represent additional challenges in developing small-scale methanol synthesis catalysts. In this task, catalysts with a variety of metal oxides and molar ratios for methanol synthesis will be prepared by different methods using metal nitrates. The catalyst, including overall performance and the effect of properties on its performance in methanol synthesis, will be screened using artificial premixed syngas and a lab-scale fixed-bed reactor coupled with on-line gas chromatography.

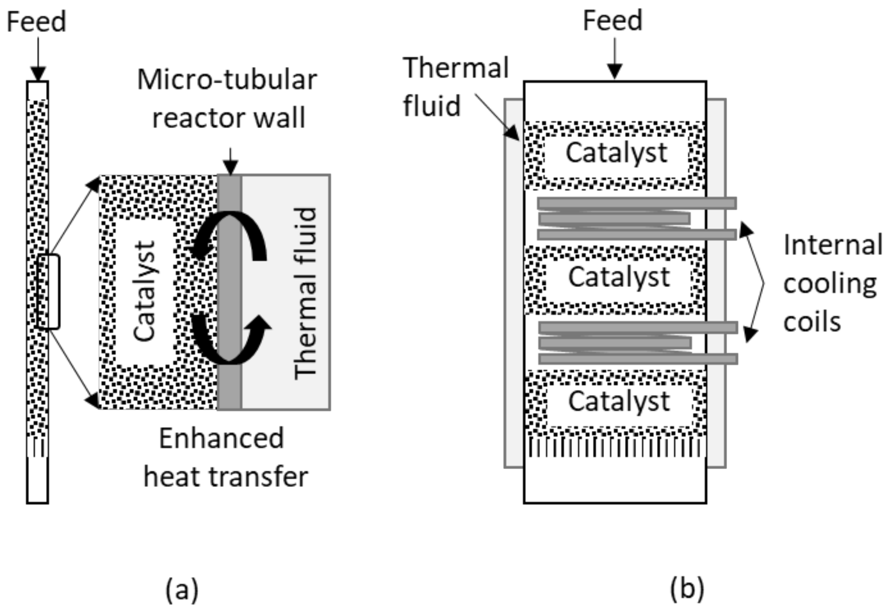

Figure 2 Schematic diagrams of (a) micro-tubular reactor and (b) internally cooled reactor

- Innovative reactor design and reactor performance evaluation: Two reactor designs are considered for heat management in a miniaturised methanol synthesis reactor system: (1) a micro-tubular reactor using thermal fluid/electrical heating (Fig. 2a) for catalyst screening, optimisation and operating conditions evaluation at laboratory scale, and (2) a structured reactor with internal cooling coils (Fig. 2b) for pilot scale process demonstration. The performance of the reactor system in methanol synthesis will be evaluated to obtain the optimal reaction conditions and reactor configurations.
- Process Integration of Biomass Pyrolysis and Methanol Synthesis: In the late stage of this project, process integration will take place by combining the biomass pyrolysis gas conditioning/upgrading unit and the methanol synthesis unit to form a complete system. Sufficient amounts of catalyst will be prepared following the aforementioned strategies and preparation methods.
- Techno-economic evaluation: To provide valuable and comprehensive analysis for commercialisation of the technology, a steady-state flowsheet for the process will be established using ASPEN HYSYS simulation software. The heat and mass balance data

obtained from the ASPEN HYSYS flowsheets will be used to predict the economics of production of methanol from biomass, with the cost of major pieces of equipment and the material of construction.

Project Outcomes met

The unprecedented coronavirus pandemic has caused dramatic impacts on all aspects of the research team's daily operation. However, we have utilised all the resources available and completed all milestone deliverables satisfactorily. Brief project outcomes we met are listed below:

Milestone 2.1: New catalysts developed and tested in laboratory bench reactors to demonstrate desirable methanol synthesis performance

Several Cu-based catalysts have been prepared using different metal combinations, supports and preparation methods and screened for their activity in methanol synthesis using a model biomass pyrolysis syngas. The preparation procedure of these methanol synthesis catalysts are documented in Deliverable 2.1.1 (Methanol synthesis catalyst preparation procedure and performance data set).

A $Cu/ZnO/Al_2O_3$ catalyst prepared using the co-precipitation method with a Cu/Zn/Al mass ratio of 60/30/10 demonstrated the highest activity for methanol synthesis. The activity of the best catalyst is stable under the test conditions over 8 heat up and cool down cycles with a total time on stream of 60 hours. The co-precipitation method is a low cost and suitable method for $Cu/ZnO/Al_2O_3$ catalyst production.

Milestone 2.2: Innovative reactor configurations (e.g. micro-multi-tubular reactor and/or structured catalytic monolith reactor) designed, constructed and evaluated in the laboratory to demonstrate desirable and optimum operation conditions

A fixed bed micro-tubular reactor was designed and constructed to operate at the following conditions:

- Reaction temperature from 200 to 340 °C
- Reaction pressure from 10 bar to 60 bar
- Feed flow rate from 60 mL min^{-1} to 200 mL min^{-1}
- Catalyst weight from 1 gram to 3 grams
- The feed and product gas at the reactor inlet and outlet can be analysed online during the test

The effect of temperature, pressure and Gas Hourly Space Velocity (GHSV) for methanol synthesis using the best candidate catalyst (Cu/Zn/Al:60/30/10 wt.%) was evaluated using the reactor system and the highest conversion of H_2 and CO, and methanol yield (31%, 31% and 16 %, respectively) were achieved at 260°C, 30 bar and 1800 h^{-1}. The activity of the best copper-based catalyst candidate (Cu/Zn/Al:60/30/10 wt.%) was stable even after 8 start-up and shut-down cycles, and total time on stream of 60 hours using the reactor system developed. The feed conversion and methanol yield significantly increased with increasing biomass pyrolysis syngas ratio R = (H_2 – CO_2)/(CO + CO_2).

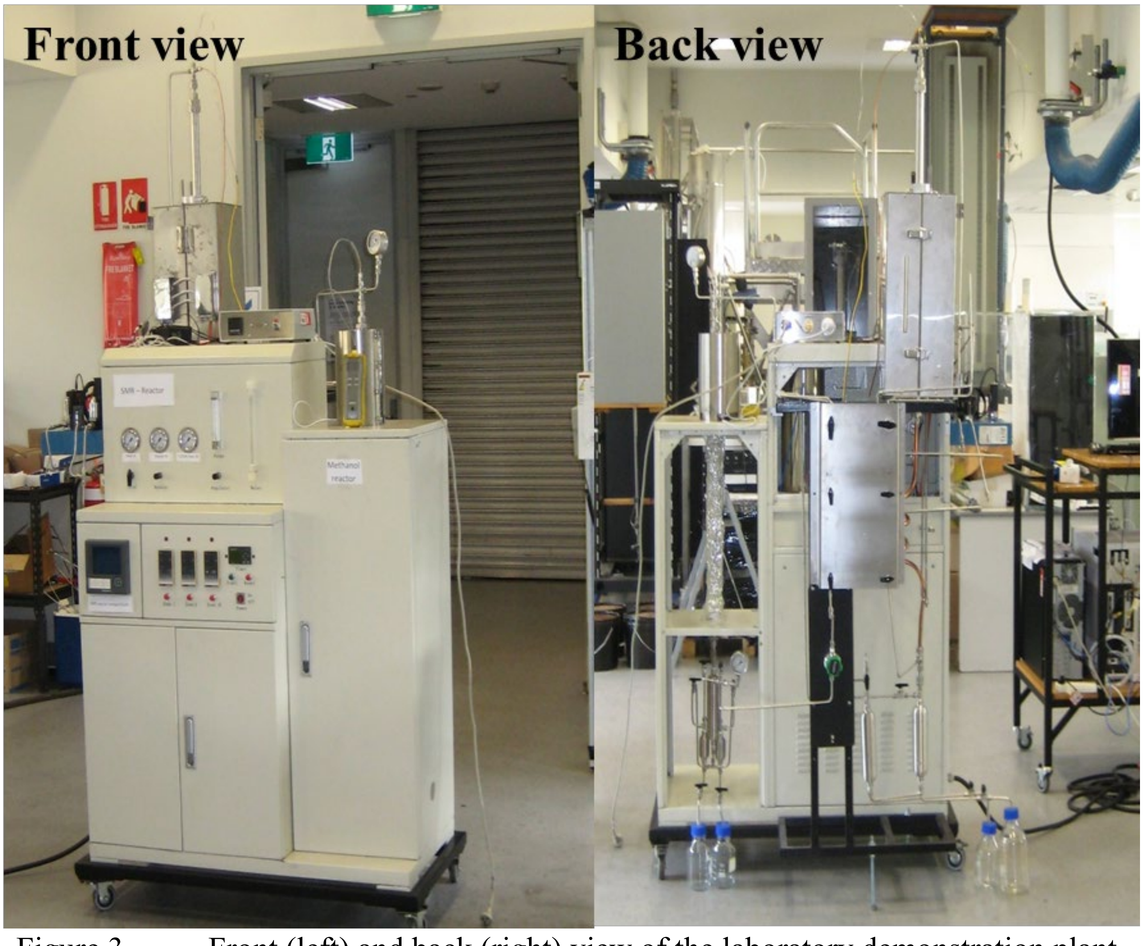

Figure 3 Front (left) and back (right) view of the laboratory demonstration plant

Milestone 3.1: A laboratory-scale pilot reactor system incorporating the catalyst and reactor developed, tested and demonstrated using both artificial syngas and real pyrolysis gas

By integrating the knowledge and technical know-hows we learnt from this project, an innovative laboratory demonstration plant was successfully designed and constructed to evaluate the biomass syngas treatment with steam methane reforming technique and methanol synthesis (Figure 3).

The laboratory demonstration plant consists 5 major parts: 1) Feed supply and pressure controller, 2) Steam methane reforming reactor, 3) SMR outlet gas cooling and water removal, 4) Methanol reactor and 5) Methanol product separation. Based on the catalysts performance results obtained from this project, the feed flow rate, operating conditions and required weight of catalysts for SMR and methanol production using raw biomass pyrolysis syngas are summarised below.

Feed flow rate (before SMR):	10 L/min
SMR catalyst:	100 g
SMR reaction temperature:	700 ^{o}C
SMR reaction pressure:	1 bar
Feed flow rate (after SMR):	17 L/min
Methanol reaction temperature:	220 ^{o}C
Methanol reaction pressure:	30 bar
Methanol catalyst:	510 gr

Milestone 3.2: The process feasibility fully assessed to identify technical boundaries and appraise the economic and environmental benefits of the novel renewable methanol technology quantitatively

A detailed techno-economic analysis of adding a miniaturised methanol production module to produce 3.48 ktonnes methanol per annum at 97.93% w/w purity that uses syngas from the pyrolysis of timber wastes in the Hazelmere Wood Waste to Energy Plant was conducted. The required CapEx and OpEx are $20.8M and 1.1 M per year, respectively. The economic evaluation shown a positive Net Present Value (NPV) of $3.57M and an Internal Rate of Return (IRR) of 9.4% based on a methanol selling price of 0.67 $/kg, a tax rate of 30% and an interest rate of 7%. The results showed that the economic performance of this project is sensitive to the interest rate, but flexible against changes in labour and maintenance costs. Finally, the fluctuation of price outlines that the minimum price in the market that could allow the business to keep operating without losing money is 0.51 $/kg. In conclusion, the miniaturised methanol production as hydrogen carrier from biomass pyrolysis syngas is technically feasible and economically viable under the current demand-supply-cost combination but vulnerable to external and market conditions. Therefore it is recommended that other hidden benefits, such as waste minimisation, utilisation and environmental benefits, should also be considered and included in a more comprehensive assessment.

In addition, a comprehensive handbook documenting the fundamental knowledge of methanol catalytic synthesis, technical know-how generated from this R&D project and a design toolkit with detailed methods, procedures and engineering data for the development, design, construction and operation of the miniaturised methanol synthesis plants was prepared (Please refer to the individual milestone deliverable reports for details).

Key highlights and difficulties experienced

- A micro-tubular reactor was built and commissioned for catalyst screening and reactor performance tests;
- A number of Cu-based catalysts have been prepared using different methods and screened for their activity in methanol synthesis using a model syngas and raw biomass pyrolysis gas and benchmarked against 3 commercial methanol catalysts. Co-precipitation method was the most suitable and low-cost method for $Cu/Zn/Al_2O_3$ catalyst production. A $Cu/ZnO/Al_2O_3$ catalyst prepared using the co-precipitation method with a Cu/Zn/Al mass ratio of 60/30/10 showed the highest activity for methanol synthesis using model syngas. However, the methanol yield was too low, when the real biomass syngas is used for all catalysts tested in this project, and leading to the difficulty to achieve the economic target;
- Steam methane reforming (SMR) using Ni-based catalyst can be readily deployed to improve the syngas quality, more specifically, the stoichiometric gas ratio R. Under the reforming condition of 695°C, constant pressure of 1 bar and GHSV of 13440 h^{-1}, the stoichiometric gas ratio R reaches 1.48, which is 11 times higher than that of the raw pyrolysis syngas;
- The effect of temperature, pressure and Gas Hourly Space Velocity (GHSV) for methanol synthesis using the best candidate catalyst (Cu/Zn/Al:60/30/10 wt.%) and the upgraded syngas was evaluated using the reactor system and the highest conversion of H_2 and CO, and methanol yield (25%, 57% and 57 %, respectively) were achieved at 220°C, 30 bar and 2000 h^{-1}. The activity of the best copper-based candidate catalyst (Cu/Zn/Al:60/30/10 wt.%) was stable after 8 start-up and shut-down cycles, and total time on stream of 60 hours during performance tests;
- Based on the knowledge and technical know-hows learnt from this project, an innovative laboratory demonstration plant was successfully designed and constructed;
- A detailed techno-economic analysis of adding a miniaturised methanol production module to produce 3.48 ktonnes methanol per annum at 97.9% w/w purity that uses syngas from the

pyrolysis of timber wastes in the Hazelmere Wood Waste to Energy Plant was conducted. The required CapEx and OpEx are \$20.8M and 1.1 M per year, respectively. The economic evaluation shown a positive Net Present Value (NPV) of \$3.57M and an Internal Rate of Return (IRR) of 9.41% based on a methanol selling price of 0.67 \$/kg, a tax rate of 30% and an interest rate of 7%;

- The results showed that the economic performance of this project is sensitive to the interest rate, but flexible against changes in labour and maintenance costs. Finally, the fluctuation of price outlines that the minimum price in the market that could allow the business to keep operating without losing money is 0.51 \$/kg;
- The miniaturised methanol production as hydrogen carrier from biomass pyrolysis syngas is technically feasible and economically viable under the current demand-supply-cost combination but vulnerable to external and market conditions.
- Since the beginning of coronavirus pandemic, we have experienced delays in getting materials and parts, prolonged turnaround time to get equipment/instruments serviced or repaired, social distancing in the workplace, restrictions in recruiting staff externally introduced by The University of Western Australia (as a mean to save existing jobs) etc. All of these have caused unprecedented impacts and difficulties in our execution of this project. Inevitably, our industry partner, Anergy, has also been hit hard and unfortunately went into administration in early 2022. Despite that, the research team at The UWA Centre for Energy has utilised all the resources available and completed all milestone deliverables satisfactorily.

Commercial status of project technology and commentary on commercialisation prospects

Based on the outcomes of this project, the project technology - miniaturised methanol production as hydrogen carrier from biomass pyrolysis syngas, is technically feasible and economically viable under the current demand-supply-cost combination but vulnerable to external and market conditions.

However, the commercialisation confidence level can be further boosted if other hidden benefits, such as waste minimisation, utilisation and environmental benefits are also considered and included in a more comprehensive assessment and reflected in the overall economic performance of the technology.

Summary of knowledge sharing activities completed

During the reporting period, the UWA Centre for Energy completed one ARENA R&D grantee survey and hosted three knowledge sharing workshops to engage relevant local and international industries and research institutes as per the agreed knowledge sharing plan. In addition, the knowledge sharing mid-term and end of activity reports and 2 lessons learnt reports were prepared for the duration of this project.

- ARENA R&D Grantee Survey – 13 Nov 2019
- Renewable Hydrogen Industry Engagement Workshop – 18 Jan 2019
- ARENA UWA Methanol from Syngas Project Knowledge Sharing Workshop – 17 Feb 2019
- International Workshop on Clean and Low-Carbon Energy – 9-11 Dec 2019
- Mid-term activity report – 21 Jul 2020
- Lessons learnt reports (1&2) – 21 Jul 2020
- End of Activity Report – 27 Jul 2022

Conclusions and next steps

In conclusion, the miniaturised methanol production as hydrogen carrier from biomass pyrolysis syngas proposed in this ARENA project is technically feasible and economically viable under the current demand-supply-cost combination but vulnerable to external and market conditions. A more comprehensive assessment which considers other hidden benefits, such as waste minimisation, utilisation and environmental benefits, should be considered in the future projects.