Centre for Energy

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Miniaturised Methanol Production as Hydrogen Carrier from Biomass Pyrolysis Syngas

Mid-term Activity Report

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ARENA summary

Project Title	Miniaturised Methanol Production as Hydrogen Carrier from Biomass Pyrolysis Syngas
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ARENA Disclaimer

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Contents

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 liquid fuel 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.

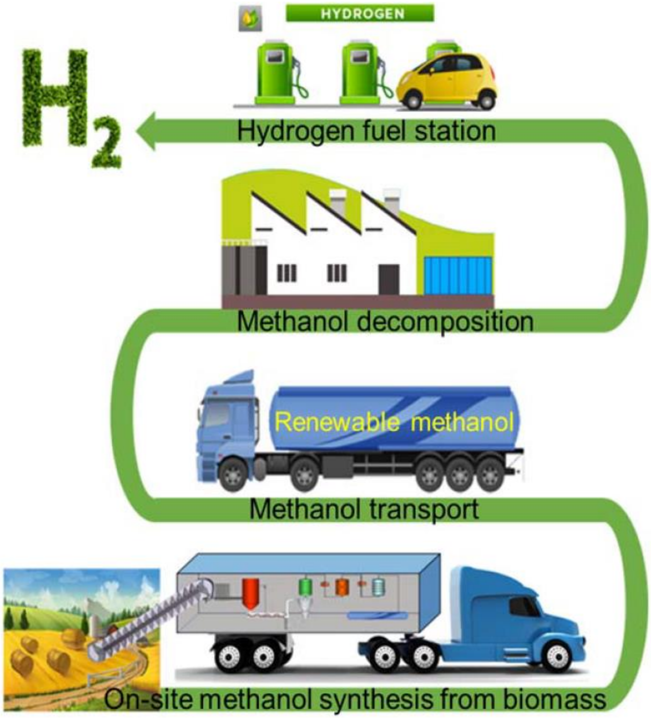

Figure 1 The concept of container-sized, miniaturised mobile platform for the production of methanol as a renewable hydrogen carrier using distributed biomass as the feedstock

Project 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:

- <u>Catalyst design, preparation and evaluation</u>: 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.

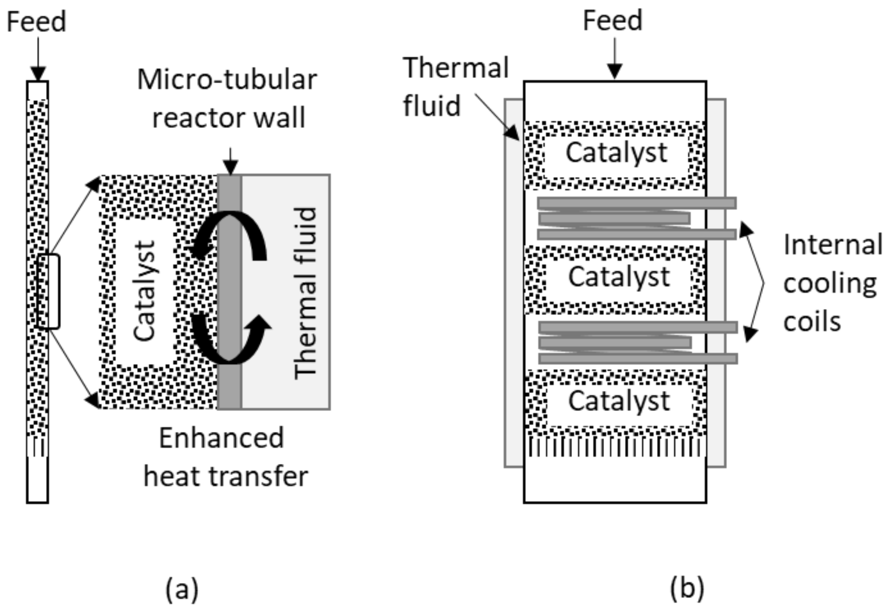

Figure 2 Schematic diagrams of (a) micro-tubular reactor and (b) internally cooled reactor

- 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 at our project partner's biomass pyrolysis plant at Hazelmere, WA. The demonstration reactor will be integrated with the biomass pyrolysis using real syngas produced on site. Sufficient amounts of catalyst will be prepared following the aforementioned strategies and preparation methods. A platform of biomass to renewable methanol production in real operation will thus be demonstrated.
- 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 Plus simulation software, and Gibbs or equilibrium reactors will be used to model the flowsheet reactors. The heat and mass balance data obtained from the ASPEN Plus 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.

Progress update

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 have made appropriate progress. Brief project milestones updates 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).

Milestone 3.2: The process feasibility assessment to identify technical boundaries and appraise the economic and environmental benefits of the novel renewable methanol technology quantitatively. Several master process flowsheets were prepared to represent different scenarios of interests, and process model simulation was started using the Aspen Hysys software package.

Key highlights and difficulties experienced

- A number of Cu-based catalysts have been prepared using different methods and screened for their activity in methanol synthesis using a model syngas;
- 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;
- Co-precipitation method was the most suitable and low-cost method for $Cu/Zn/Al_2O_3$ catalyst production;
- A micro-tubular reactor was built and commissioned for catalyst screening and reactor performance tests;
- 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 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 using the reactor developed;
- The feed conversion and methanol yield significantly increased with increasing biomass pyrolysis syngas ratio $R = (H_2 – CO_2)/(CO + CO_2)$;

Since the beginning of coronavirus pandemic, we have experienced and still experiencing 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 like many other companies around the world. But they are still committed to participate in and make their contributions to this project.

Commentary on commercialisation prospects

This ARENA funded UWA Centre for Energy project has attracted some significant interests from local and international industry partners including:

1. South West Agroforestry Network, WA
2. Forico Pty Ltd, Tasmania
3. Anshan District Heating Company, Liaoning, China
4. Shangren Group, Malaysia, and
5. Yongneng, Shandong, China

Many of the above parties attended the International Workshop on Clean and Low-Carbon Energy hosted by Centre for Energy, either directly or via representatives. Negotiations are in progress to develop joint venture arrangements for demonstration and commercialisation of the outcomes of ARENA funded UWA Centre for Energy project.

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 activity report and 2 lessons learnt reports were prepared.

- 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 – 21 Jul 2020

Lessons Learnt Report 1

Knowledge Category:	Technical
Knowledge Type:	Technology
Technology Type:	Hydrogen energy
State/Territory:	WA

Key learning

In milestone 3 of this project, a miniaturised methanol synthesis reactor system will be designed, constructed and taken to our project partner's biomass pyrolysis plant in Hazelmere WA to be integrated with and use the actual syngas produced from the biomass pyrolysis plant on site. However, while the catalytic methanol synthesis reaction requires high pressure, the pyrolysis syngas produced from our project partner's biomass pyrolysis plant can only reach a level slightly higher than atmospheric pressure. The safety of pressure boosting combustible gas has been a significant factor in deciding the means of feed gas supply for the pilot-scale trials.

Implications for future projects

n/a

Knowledge gap

The potential safety issues involved in boosting combustible gas should not be underestimated.

Background

Objectives or project requirements

The methanol synthesis reactor requires 50 – 100L min^{-1} feed gas flow rate and 30 – 50 bar pressure.

Process undertaken

After consulting various gas compression equipment suppliers, multi-stage pneumatic-driven gas booster was identified to meet our project requirement.

Lessons Learnt Report 2

Knowledge Category:	Pandemic
Knowledge Type:	Pandemic
Technology Type:	Hydrogen energy
State/Territory:	WA

Key learning

The unprecedented coronavirus pandemic has caused dramatic impacts on all aspects of the research team's daily operation. Since the beginning of coronavirus pandemic, we have experienced and still experiencing 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.

Implications for future projects

The lessons learnt today from this pandemic hopefully will provide guidance for any future projects.

Knowledge gap

The unprecedented impacts caused by the COVID-19 pandemic is unforeseeable. There are so many knowledge gaps in almost every aspects of our life.

Background

Objectives or project requirements

n/a

Process undertaken

The research team have utilised all the resources available to execute the project.