Hawaiʻi Natural Energy Institute Research Highlights

Alternative Fuels

Liquid Fuels from Synthesis Gas

OBJECTIVE AND SIGNIFICANCE: The purpose of this project was to develop technologies to produce high-grade liquid fuel from synthesis gas derived from agricultural wastes. The drop-in liquid fuel can be directly used in modern engines of vehicles and ships without sacrifice of engine performance.

BACKGROUND: Agricultural wastes are underutilized renewable resource with low heating values (HHV 15-18 MJ/kg) and high oxygen contents (40-50 wt%). The composition of raw biomass varies depending on plant species and farming conditions. It is a technical challenge to convert agriculture wastes into high-grade liquid fuels that meet the fuel standards of modern engines. The biomass wastes, however, can be gasified into a synthesis gas (syngas) that contains primarily carbon monoxide (CO), hydrogen (H_2) and carbon dioxide (CO_2). The new technologies in development produce polyhydroxybutyrate (PHB) from the syngas by using microbial organisms and then reform the PHB polyester into gasoline-grade liquid fuel.

PROJECT STATUS/RESULTS: Two core technologies were investigated and developed: (a) microbial gas fermentation and (b) thermal catalytic reforming of PHB. Because of the poor solubility of gas in aqueous solution, a novel bioreactor was invented to enhance the mass transfer of gas substrates in aqueous solution by 40-200% in comparison with conventional aerated bioreactors. In addition, a continuous liquid flow operation mode of the bioreactor further increased the productivity up to 2 g/L.h, the benchmark of fuel ethanol fermentation. Under controlled conditions, the microbial cells formed a large amount of PHB (60% of cell mass) as an energy storage material. The novel bioreactor was scaled up to 200 liters for a pilot project that is in negotiation with potential industrial partners and investors.

PHB was recovered and reformed on a solid acid catalyst under mild conditions (<240 ºC) to form a hydrocarbon oil. The major compounds of the PHB oil were alkanes, alkenes, and aromatics, the same compounds found in fossil gasoline and diesel. Depending on boiling points, the PHB oil was divided into a light oil (77 wt%) and a heavy oil (23 wt%). Their elemental compositions and heating values were determined and compared with commercial gasoline and biodiesel as shown in Table 1. The light oil has the same elemental composition and heating value of the gasoline obtained from a local gas station and the heavy oil is very close to a commercial biodiesel.

PHB is a polyester of 3-hydroxybutyrate ($C_4H_5O_2$) and contains a substantial amount of oxygen (38% wt). Oxygen removal is essential to make hydrocarbon compounds for high heating value and desired fuel performance. The research identified the main reactions and key intermediates in the catalytic reforming of PHB. It was revealed that oxygen was removed as CO_2 without hydrogen consumption, a techno-economic advantage in comparing with other biofuel technologies that consume large amounts of hydrogen.

The project, now completed, has generated four reports and twelve research articles in peer-reviewed scientific journals. One invention of novel bioreactor has been disclosed and filed for global patents.

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Table 1. Comparison of PHB oils with commercial gasoline and biodiesel

Liquid Fuels	Gasoline	Light PHB oil	Heavy PHB oil	Biodiesel
Boiling Points (ºC)	40-200	40-240	240-310	180-330
C (wt %)	80.4	81.4	79.4	77
H (wt %)	12.3	11.3	9.7	11.8
N (wt %)	0.1	0.1	0.2	-
O (wt %)	7.2	7.2	10.7	11.2
Heating Value (HHV MJ/kg)	41.8	41.4	38.4	39.7

ADDITIONAL PROJECT RELATED LINKS

TECHNICAL REPORTS:

1. 2019, J. Yu, **Liquid Fuels from Syngas**, Task 3.3, in ***APRISES 14 Final Technical Report***, Office of Naval Research Grant Award Number N00014-15-1-0028.
2. 2018, J. Yu, **Liquid Fuels from Synthesis Gas**, Task 3.2d, in ***APRISES 12 Final Technical Report***, Office of Naval Research Grant Award Number N00014-13-1-0463.
3. 2018, J. Yu, **Liquid fuels from Synthesis Gas**, Task 3.2d, in ***APRISES 13 Final Technical Report***, Office of Naval Research Grant Award Number N00014-14-1-0054.
4. 2017, J. Yu, **Biochemical Conversion of Synthesis Gas into Liquid Fuels**, Task 3.2d, in ***APRISES 11 Final Technical Report***, Office of Naval Research Grant Award Number N00014-12-1-0496.

PAPERS AND PROCEEDINGS:

1. 2019, J. Yu, Y. Lu, **Carbon dioxide fixation by a hydrogen-oxidizing bacterium: Biomass yield, reversal respiratory quotient, stoichiometric equations and bioenergetics**, Biochemical Engineering Journal, Vol. 152, Article 107369.
2. 2018, J. Yu, P. Munasinghe, **Gas Fermentation Enhancement for Chemolithotrophic Growth of Cupriavidus necator on Carbon Dioxide**, Fermentation, Vol. 4, Issue 3, Paper 63. (Open Access: **PDF**)
3. 2018, J. Yu, **Fixation of carbon dioxide by a hydrogen-oxidizing bacterium for value-added products**, World Journal of Microbiology and Biotechnology, Vol. 34, Issue 7, Article 89.
4. 2017, Y. Lu, J. Yu, **Comparison analysis on the energy efficiencies and biomass yields in microbial CO2 fixation**, Process Biochemistry, Vol. 62, pp. 151-160.
5. 2017, Y. Lu, J. Yu, **Gas mass transfer with microbial CO2 fixation and poly(3-hydroxybutyrate) synthesis in a packed bed bioreactor**, Biochemical Engineering Journal, Vol. 122, pp. 13-21.
6. 2015, S. Kang, J. Yu, **A gasoline-grade biofuel formed from renewable polyhydroxybutyrate on solid phosphoric acid**, Fuel, Vol. 160, pp. 282-290.
7. 2015, S. Kang, J. Yu, **Reaction routes in catalytic reforming of poly(3-hydroxybutyrate) into renewable hydrocarbon oil**, RSC Advances, Vol. 5, Issue 38, pp. 30005-30013.
8. 2014, S. Kang, J. Yu, **One-pot production of hydrocarbon oil from poly(3-hydroxybutyrate)**, RSC Advances, Vol. 4, Issue 28, pp. 14320-14327.
9. 2013, J. Yu, A. Dow, S. Pingali, **The energy efficiency of carbon dioxide fixation by a hydrogen-oxidizing bacterium**, International Journal of Hydrogen Energy, Vol. 38, Issue 21, pp. 8683-8690.
10. 2011, M.M. Porter, J. Yu, **Crystallization kinetics of poly(3-hdyroxybutyrate) granules in different environmental conditions**, Journal of Biomaterials and Nanobiotechnology, Vol. 2011, Issue 2, pp. 301-310. (Open Access: **PDF**)
11. 2011, M. Porter, J. Yu, **Monitoring in situ crystallization of biopolyester granules in Ralstonia eutropha via infrared spectroscopy**, Journal of Microbiological Methods, Vol. 87, Issue 1, pp. 49-55.
12. 2008, Z. Xu, J. Yu, **Hydrodynamics and mass transfer in a novel multi-airlifting bioreactor**, Chemical Engineering Science, Vol. 63, Issue 7, pp. 1941-1949.

PRESENTATIONS:

1. 2019, J. Yu, **Drop-in Transportation Fuels from Renewable Hydrogen and Carbon Dioxide**, Presented at the Would Hydrogen Technologies Convention, Tokyo, Japan, June 2-7.
2. 2018, J. Yu, **A Green Plastic and Drop-in Transportation Fuels from Carbon Dioxide and Renewable Energy**, Proceeding of the TechConnect World Innovation Conference & Expo, TechConnect Briefs, Vol. 2 Materials for Energy, Efficiency and Sustainability: TechConnect Briefs, pp. 187-190.
3. 2017, J. Yu, **Drop-in Transportation Fuels from Carbon Dioxide and Solar Hydrogen**, Presented at the Environmental and Energy Resource Management Summit, Washington, DC, November 9-11.
4. 2015, J. Yu, **Direct Production of Bioplastics and Chemicals from Carbon Dioxide and Solar Energy**, Presented at the European Meeting on Chemical Industry and Environment, Tarragona, Spain, June 10-12.
5. 2014, P. Munasinghe, S. Kang, J. Yu, **Renewable Hydrocarbon Oils and Chemicals from Solar Energy and Carbon Dioxide**, Presented at the Asia Pacific Clean Energy Summit and Expo, Honolulu, Hawaii, September 15-17.
6. 2013, J. Yu, **Direct Conversion of CO2 into Biopolyester with Solar Energy and Water**, Presented at the American Chemical Society National Meeting, Indianapolis, Indiana September 8-12.
7. 2012, J. Yu, **Clean Production of Bioplastics and Bio-Oil from Solar Energy and Carbon Dioxide**, Presented at the CleanTech Conference & Showcase, Santa Clara, California, June 18-21, 2012.

STUDENT THESES:

1. 2012, A.R. Dow, **Novel method for determination of gas consumption in Cupriavidus necator : assessing feasibility of CO2 fixation from biomass-derived syngas**, Master of Science Thesis, Department of Molecular Bioscience & Bioengineering, University of Hawaii at Manoa, Honolulu, HI.
2. 2010, M.M. Porter, **In situ crystallization of native poly(3-hydroxybutyrate) granules in varying environmental conditions**, Master of Science Thesis, Department of Bioengineering, University of Hawaii at Manoa, Honolulu, HI.
3. 2007, Z. Xu, **Hydrodynamics and mass transfer in a novel multi-airlifting membrane bioreactor**, Master of Science Thesis, Department of Bioengineering, University of Hawaii at Manoa, Honolulu, HI.

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