MONTHLY PROGRESS REPORT
Hydrogen from Renewable Resources
University of Hawaii
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TASK 1. HYDROGEN PRODUCTION

A. Photobiological Production - D. Borthakur & K. Baker

Previously, we cloned the 334-bp Anabaena DNA fragment containing a part of the hupB gene into pBR322W. This new plasmid, called pUHA1 has been transferred to an E. coli strain containing a cloned Avai and AvaII methylases before transferring to Anabaena by methylases such that the Avai and AvaII restriction enzymes present in Anabaena cannot cleave the introduced DNA. Finally, we transferred this plasmid containing a part of Anabaena hupB gene into the wild-type Anabaena strain 7120. Many colonies that are resistant to Streptomycin (5µg/ml) appeared on the BG11 agar. We hope these are the expected mutants that arise through single recombination between the cloned fragment and the chromosome. These colonies are now being subcultured such that we can make DNA and analyze them by Southern hybridization.

Work continued on arrangements for transfer of the Mitsui Collection to the University of Hawaii Bioresources Laboratory. Items required to house the collection were ordered and facilities rearranged to accommodate the large number of organisms. During September, Kay Baker will travel to Miami to oversee final packing and shipment of the cultures. The new Marine Biotechnology Culture Collection

B. Photoelectrochemical Production - R. E. Rocheleau

Testing of our new epoxy-free Plexiglas electrolysis cell continued during August. Initial testing in July with metal substrate samples confirmed that the Teflon seals worked well to prevent leakage. During August, we successfully installed and tested the burettes for gas collection but subsequent efforts to test glass-substrate photoelectrodes resulted in damage to the photoelectrodes. The mounting
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system for the photoelectrodes, redesigned to reduce stress on the samples is currently being rebuilt in the shop.

A second Plexiglas electrolysis cell and electrochemical test station has been constructed to enhance our ability to conduct long-term testing of the catalyst samples and photoelectrodes. The second system is operational although an additional source measurement unit (current-voltage source) is being ordered (cost shared by UH) and the data acquisition system is being upgraded to allow automated data collection on the second system. A series of runs to sputter deposit NiOx catalyst samples of equal thickness at different growth rates and sputtering pressures (i.e. samples with different microstructure and initial behaviors) has been planned to complete the study initiated earlier. The depositions are expected to require approximately two weeks to complete. Experiments to monitor stability of selected anodic and cathodic catalyst samples in various electrolytes will begin as soon as these samples are available.

Failure of our emergency shut-off switch on the plasma-deposition system temporarily halted deposition of the a-SiC films. The failure was traced to a difficult to repair circuit board. A new safety system, which triggers on overpressure, overtemperature, and electrical or ventilation failure was designed, parts ordered and the system reconstructed. The new system has been installed and tested. SiC:H depositions will recommence in September. The initial set of experiments will be to produce films deposited under varying amounts of hydrogen dilution to determine its effect on hardness, adherence, and chemical corrosion resistance. In addition to our own corrosion measurements, Dr. Hihara of the Department of Mechanical Engineering (under other funding) will map the corrosion behavior of these samples in various electrolytes using a microprobe apparatus he has developed.

We continue, using student help, to develop our loss analysis models. Work continued on development of a graphical user interface (GUI) and modifications allowing assessment of graded bandgap i-layers. These advanced structures are being analyzed to determine catalyst requirements which would allow use of tandem devices which may yield higher hydrogen production rates than the triple junction devices now used for photoelectrode fabrication.
C. Thermochemical Production of Hydrogen from Wet Biomass - M. J. Antal

In the previous month, we improved heat transfer in the entrance region by using a coiled 1/16" annulus, resulting in complete gasification of 1.2 M glucose with no deactivation for the 6-hour operation. Gasification characteristics with this improved heat transfer were investigated this month.

Lower pressure gasification of 1.2 M glucose at 25.5 MPa, 600°C was conducted to determine the effect of pressure with this improved entrance region heat transfer. Unlike previous results conducted with a 1/8" annulus, complete conversion was attained with no deactivation in terms of carbon gasification efficiency. The hydrogen yield was low, however, with only 1.74 mol of hydrogen generated from 1 mol of glucose. Compared with the hydrogen yield of 2.15 under 34.5 MPa, gasification at 34.5 MPa is superior from the standpoint of hydrogen production, although lower pressure is desirable for industrial purposes and economic feasibility.

Glucose gasification without a carbonaceous catalyst was also conducted with the coiled 1/16" annulus in order to clarify the effect of the activated carbon. A 1.2 M glucose was sent into a reactor packed with only aluminum oxide at 34.5 MPa, 600°C. The gasification efficiency ranged between 75% and 85%, much lower than the 100% conversion achieved with gasification by the coconut activated carbon catalyst. Thus, the catalytic activity of the coconut activated carbon is essential for the complete gasification.

Gasification of whole biomass was also carried out using a 0.96 wt % dry banana stem slurry using the 1/16" coiled annulus. Sending the slurry into the reactor at 600°C, 34.5 MPa resulted in generation of hydrogen rich gas. TOC analysis of the liquid effluent indicated complete gasification. These results from the enhanced heat transfer in the entrance region will be utilized to publish a paper which proposes the supercritical gasification of wet biomass.

Improvement in operation procedure, as well as heat transfer in the entrance region, was attempted. The sudden increase in temperature as high as 90°C, which is observed when we switch from water to the glucose, was utilized in order to attain a desirable temperature profile more quickly. Switching to glucose when the water temperature is around 500°C resulted in quick attainment of temperature control at 600°C without overshooting. This operation was, however, unsuccessful after all because of the presence of colored liquid effluent, which indicates incomplete gasification. Perhaps switching to glucose while the temperature is below 600°C results in tarry material generation in the entrance region, which in turn hinders...
efficient heat transfer, causing more tarry material generation. Therefore, it is evident that we must attain a good temperature profile with water before switching to glucose.

The knowledge obtained from these experiments provides the operation for desirable gasification: first, attainment of 600°C, 34.5 MPa with water, followed by switching to the biomass feedstock for gasification with a carbonaceous catalyst. Further experiments will be conducted following this standard operation.

In September, we will concentrate on completing the paper, as well as on determining the characteristics of catalytic activity. Design of the large-scale reactor will also proceed, with the consideration of achieving a high heating rate at the entrance region.

TASK 2 - HYDROGEN STORAGE

A. Reversible Catalytic Dehydrogenation of Cycloalkanes by Polyhydride Complexes - C. Jensen

The cobalt complex, Co(η²-CH₂CHCH₂)(P(OMe)₃)₃ has been synthesized and purified through literature methods. This complex is known to be an active homogeneous catalyst for the hydrogenation of aromatic hydrocarbons. The catalytic reaction was reported in 1975 to be irreversible. Recently, advanced methods of reversing alkene hydrogenations which are catalyzed by complexes such as the well known Wilkinson's catalyst, RhCl(PPh₃)₃, have been discovered. We are presently preparing to examine the hydrogenation of arenes catalyzed by the cobalt complex and the reversal of the reaction under reflux conditions.

B. Polyhydride Systems Engineering - R. Rocheleau & R. Zidan

Uptake and release of gaseous hydrogen by and from solid iridium complex IrClH₂(H₂)(PPr₃)₂ was measured at two additional intermediate temperature, 30°C and 40°C, to verify behavior in this region of rapid uptake and release. The thermodynamic and kinetic characterization of this material are the focus of a technical paper under preparation. The draft in nearly complete and will be available in September. During September we will also initiate thermodynamic characterization of one of the promising Co complexes synthesized by C. Jensen's group.