FURTHER DEVELOPMENT OF THE ISOPROPA
OL-ACETONE CHEMICAL HEAT ENGINE

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ABSTRACT

The performance and feasibility of a closed cycle chemical heat engine have been explored. This heat engine was
designed to convert moderate temperature solar thermal energy into electricity. The solar thermo-chemical cycle
comprises two processes: the dehydrogenation of isopropyl alcohol into hydrogen and acetone around 300 °C, a
temperature compatible with typical parabolic trough plants, and the hydrogenation of acetone in a fuel cell at 30 °C. To
evaluate the feasibility of this concept, the two processes were studied independently. First, the dehydrogenation of
isopropyl alcohol was studied at a temperature of 300 °C. Isopropyl alcohol was thermally decomposed into acetone
and hydrogen on a copper sponge catalyst. The products were measured using a gas chromatograph mass
spectrometer (GCMS) to determine catalyst activity and byproduct formation. Conversion percentages
of isopropyl alcohol to acetone were measured over an hour for each experiment. The main byproduct of the reaction was methyl
isobutyl ketone (MIBK), a product of two acetone molecules. Second, the hydrogenation of acetone was studied in a
Polymer Electrolyte Membrane Fuel Cell (PEMFC). At room temperature, the reaction of acetone and
hydrogen to isopropyl alcohol has a standard cell potential of 0.128 volts (for an equimolar mixture of acetone and
isopropyl alcohol). The fuel cell performed with an open circuit voltage of 0.12-0.14 volts for the various mixtures
and had a limiting current of 42 mA/cm² for a 4 molar acetone mixture in water. The process was found to be
feasible, but not optimal in practice due to its low cell potential.

1. INTRODUCTION

Sunlight is a renewable and plentiful source of thermal energy, but it has the inherent problem of only being available for less than half the day. Because of this, the capacity factors of many solar thermal plants are less than 31% without some sort of thermal storage. In order for solar thermal to be considered by industry, plants need to be able to generate electricity consistently throughout the day. A chemical heat engine that stores solar thermal energy as a chemical fuel could operate all day and at night allowing a solar power plant to operate with a higher capacity factor.

Furthermore, this system could be useful to power remote communities not currently connected to the electrical grid. This application requires an economical solar installation around the 1 MW scale. Generally, photovoltaic (PV) cells are favored over solar thermal at this scale despite their lower efficiency because of their modularity. Rankine cycles are most efficient and economical at a larger scale due to the mechanical turbine. A chemical heat engine uses a fuel cell to generate electricity in place of a turbine, with the fuel being regenerated in a high temperature process that takes the place of steam production in the Rankine cycle. As fuel cells are modular like PV cells, solar thermal installations using a chemical heat engine may be more competitive than traditional solar thermal at small scales.

The proposed chemical heat engine cycle employs a Solar Fuel Dehydrogenation Reaction (SFDR) and a Fuel Cell Hydrogenation Reaction (FCHR). This process is similar to the cycle proposed by Ando et al. except that the dehydrogenation process occurs chemically in a separate reactor. As shown in Fig. 1, the two processes operate in a closed loop with solar thermal energy as the only input, and electricity and waste heat as the outputs. The SFDR uses solar heat to create a fuel and oxidizer. In this case, isopropyl alcohol is being dehydrogenated into hydrogen and acetone using solar thermal energy from the sun. The second process, the FCHR, combines the acetone and hydrogen in a fuel cell to create isopropyl alcohol and electrical work with some heat rejected.
SFDR ($T \approx 300 - 380 \, ^\circ C$):

$$\left( \text{CH}_3 \right)_2 \text{CHOH} + Q_{\text{solar}} \rightarrow \left( \text{CH}_3 \right)_2 \text{CO} + H_2$$

FCHR ($T \approx 30 - 50 \, ^\circ C$):

$$\left( \text{CH}_3 \right)_2 \text{CO} + H_2 \rightarrow \left( \text{CH}_3 \right)_2 \text{CHOH} + W_{\text{electric}} + Q_{\text{reaction}}$$

Solar thermal energy is used to heat the isopropyl alcohol to temperatures around 300°C. At these temperatures isopropyl alcohol is converted into acetone and hydrogen. The acetone and H$_2$ are stored for use in the fuel cell. The fuel cell reverses the reaction. Acetone and H$_2$ are combined near room temperature in a fuel cell to create electricity and renew the original supply of isopropyl alcohol.

![Diagram of chemical heat engine process](image)

Fig. 1: Schematic of chemical heat engine process

The chemical heat engine operates using changes in the Gibbs free energy with temperature. The Gibbs free energy of the reaction ($\Delta G_R$) is a measure of the potential work of the system. $\Delta G_R$ is defined as the Gibbs free energy of the dehydrogenation process:

$$\Delta G_R = G_{\text{Acetone}} + G_{\text{Hydrogen}} - G_{\text{Isopropyl Alcohol}}$$

As thermal energy from the sun is used to heat the isopropyl alcohol, $\Delta G_R$ decreases. At a high temperature (300-400 °C), $\Delta G_R$ is slightly negative, so the dehydrogenation reaction is thermodynamically favored and the isopropyl alcohol thermally decomposes into acetone and hydrogen. Near room temperature (298 K), $\Delta G_R$ is near a positive 24 kJ/mol, meaning the hydrogenation reaction is favored, and the combination of the acetone and hydrogen in a fuel cell can produce 24 kJ/mol of electrical work using an electrochemical process. This system allows heat energy from the sun to be converted into electrical energy in a decoupled two-step process. Further, since the acetone and hydrogen can easily be stored, the fuel cell can run continuously. This process is similar to other higher temperature chemical engine processes that use zinc or magnesium instead of isopropyl alcohol.\(^3\)

### 2. SOLAR FUEL PROCESS – DEHYDROGENATION OF ISOPROPYL ALCOHOL

#### 2.1 Experimental Method

The SFDR experimentation was performed in heated, airtight Swagelok tubing. Inside the tubing, a packed bed reactor was positioned in a tube furnace to control temperature. Mass flow controllers and a syringe pump were used to introduce regulated flows of nitrogen, hydrogen, and isopropyl alcohol into the reactor. The isopropyl alcohol was introduced into the gas flow in a heated vaporizer tube packed with glass wool prior to entering the reactor. The products exiting the reactor were diluted with helium gas sufficient to prevent condensation of the vapor products. The product gas composition was measured by the GCMS. Prior to the start of each experiment, the catalyst was weighed and inserted into the tubing to create the packed bed. The packed bed was heated to 300 or 350 °C with pure nitrogen flowing before being reduced in pure hydrogen (48 standard cubic cm per minute, sccm). Experiments were performed at flow rates of 237 sccm for the nitrogen carrier gas and 0.5 ml/min (147 sccm as a vapor) for isopropyl alcohol. The reaction products were diluted with 3400 sccm helium. The vaporizer tube was heated to between 150 and 200 °C, with the reactor held at 200 or 300 °C.

Sponge copper was used as the catalyst. The copper sponge catalyst was mixed with granular high purity silicon dioxide (40 mesh) to expand the bed and reduce catalyst loading to the desired level. A batch of catalyst with 1.00 wt% copper loading was prepared by mixing silicon dioxide and sponge copper in DI water using ultrasonication. The mixture was dried in an oven at 110 °C. After drying, the catalyst took on a greenish-gray hue, presumably due to the presence of surface oxides and hydroxides. For each experiment, 0.5 g of fresh catalyst was loaded into the reactor and held in place with glass wool.

#### 2.2 Results and Discussion

The main objective of the solar fuel tests was to see if the dehydrogenation of isopropyl alcohol could occur at 200-300 °C with a copper sponge catalyst, quantify the percentage of isopropyl alcohol that was converted to acetone, identify the activity and decay of the reaction, and identify any problems inhibiting future commercialization. Using the setup described above, the GCMS measured a conversion percentage of isopropyl alcohol into acetone as high as 54% indicating a successful reaction, but the conversion percentage decayed rapidly over time. Several combinations of reduction and reaction conditions were considered. Generally, the conversion decreased with time as the catalyst became less active. In most cases, the
conversion decayed roughly exponentially with time. For each experiment, the initial conversion was noted, and the time constant of decay was calculated by fitting the data to an exponential function. This data is summarized in TABLE 1. Ranges given represent standard deviations. For reduction times ranging from 15 to 90 minutes, the reduction time did not affect the overall conversion, so experiments are grouped only by reduction and reaction temperature.

TABLE 1: CONVERSION PERCENTAGE AND TIME CONSTANT OF DECAY FOR VARIOUS REACTION CONDITIONS:

<table>
<thead>
<tr>
<th>$T_{\text{red}}$ (°C)</th>
<th>$T_{\text{rxn}}$ (°C)</th>
<th># of Trials</th>
<th>Initial Conversion (%)</th>
<th>Time constant of decay (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>300</td>
<td>5</td>
<td>37 ± 16</td>
<td>59 ± 55</td>
</tr>
<tr>
<td>350</td>
<td>300</td>
<td>7</td>
<td>32 ± 12</td>
<td>89 ± 40</td>
</tr>
<tr>
<td>350</td>
<td>200</td>
<td>9</td>
<td>7.2 ± 2.3</td>
<td>406 ± 415</td>
</tr>
</tbody>
</table>

The copper sponge catalyst showed good activity at both 200 °C and 300 °C. The variability of the conversion was higher than expected for identical experimental conditions. This could be due to settling of the catalyst bed, which was oriented horizontally in the tube furnace. At 200 °C, the conversion is low enough to neglect the unknown rate law of the reaction and calculate the catalyst activity. For 200 °C and an isopropyl alcohol partial pressure of 38 kPa, the activity is $1.6 \pm 0.5 \times 10^{-3}$ mol/(s·g$_{\text{Cu}}$). An accurate estimate of activation energy cannot be made because the conversion at 300 °C is too high to neglect the rate law.

Because deactivation could be a serious problem, two strategies for reactivating the catalyst were investigated: a second reduction cycle, and an oxidation reduction cycle. After a 75 minute experiment, the reduction procedure was repeated before starting a second experiment. In this experiment, conversion was very low indicating that the catalyst activity was not restored by reduction alone. Next, an oxidation-reduction cycle was performed by passing air, then hydrogen over the catalyst at the reduction temperature. The oxidation-reduction cycle regenerated the catalyst activity after experiments that were performed at 300 °C. A typical result of this procedure is shown in Fig. 2, which shows the results of four consecutive experiments on the same catalyst bed at a reaction temperature of 300 °C. These experiments were split over two days with the reactor cooled to room temperature under nitrogen overnight between the second and third experiments. In another reaction at 200 °C, the decay in conversion was much slower, and the oxidation-reduction procedure did not restore the catalyst activity despite being performed at 350 °C as in Fig. 2.

The large decay in the activity, resulting in decaying conversion, was unexpected. Previous literature studies of similar copper catalysts showed the conversion at lower temperatures to be stable over several hours. For reaction temperatures of 300°C, the most likely explanation is that heavy organic byproducts accumulate on the catalyst surface. These byproducts block active sites which would reduce catalyst activity. When these byproducts are oxidized by air, the catalyst activity was restored. The drop in activity at 200 °C may have been caused by another slower but irreversible mechanism as the oxidation-reduction cycle had little effect on catalyst activity. During preliminary experiments at 300 °C with much higher catalyst loadings, methyl isobutyl ketone (MIBK), a chemical formed by two acetone molecules, along with small quantities of larger compounds formed by three and four acetone molecules were detected as the main byproducts. These heavy byproducts are hypothesized to be the cause of the activity decay. The experiments with 5.0 mg copper loading (all shown in TABLE 1) produced only trace amounts of MIBK. MIBK production is much higher with high catalyst loadings because of two reasons. First, the additional catalyst surface area allows for more reactions to occur. Second, because the acetone production is increased by the surface area, more acetone is available to produce MIBK. In large scale reactors, the catalyst loading would have to be optimized for the tradeoff between acetone conversion and MIBK production.

Fig. 2: Four consecutive experiments on the same catalyst bed showing catalyst regeneration by passing air then hydrogen over the bed. The reaction temperature was 300 °C, and regeneration took place at 350 °C with 30 minutes each of air and hydrogen. The time shown is the cumulative reaction time, which counts only the time that isopropyl alcohol was reacting in the catalyst bed.

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3. FUEL CELL PROCESS – HYDROGENATION OF ACETONE

3.1 Experimental Method

The FCHR was tested in a polymer electrolyte fuel cell (PEMFC). Normally, a PEMFC operates with H₂ on the anode electrode and O₂ on the cathode electrode with water being produced on the cathode side. At the anode catalyst, H₂ is ionized into H⁺. The H⁺ travels through the electrolyte to the cathode catalyst while the resulting electrons travel through a load. At the cathode, H⁺, oxygen, and electrons combine to produce water. In this modified fuel cell, the O₂ was replaced with an acetone solution. At the cathode, instead of O₂ combining with H⁺ and an electron to produce water, the H⁺ and electrons combine with acetone to make isopropyl alcohol.

The fuel cell experiments were performed using a commercial 3-layer membrane electrode assembly with a Nafion® 115 membrane and catalyst loading of 0.3 mg Pt/cm². On each side of the catalyst layer was a Toray® carbon paper gas diffusion layer (200 μm thickness), a PTFE seal, a graphite bi-polar plate, a gold plated electron conduction plate and an aluminum shell for gas inputs. A potentiostat controlled cell current and measured voltage using two pairs of leads connected to the gold plated electron conduction plate. H₂ gas flow rates and humidity levels were controlled through the fuel cell test stand. The acetone was mixed with water to keep the cathode side of the electrolyte from becoming dehydrated.

Various mixtures of acetone and isopropyl alcohol and water were tested to discover what effect different conversion percentages from the Solar Fuel process would have on the Fuel Cell process. In the experiments, the liquid mixture was pumped with a peristaltic pump through the fuel inlet. Since the fuel cell consumes very small amounts of acetone, but the pump has a relatively high flow rate, the acetone mixture was recirculated back into a beaker. This avoided the need for large amounts of fuel mixtures and reduced the amount of chemicals being used. It was assumed that the acetone concentration would not be changed significantly by recirculation. Multiple verification tests show consistent results between recirculation and non-recirculation techniques, verifying the assumption that recirculating the fluid does not significantly change the acetone concentration or the final result.

3.2 Results and Discussion

The main objective of the fuel cell test was to see if the hydrogenation of acetone into isopropyl alcohol could occur in a standard PEMFC, quantify the basic performance of the PEMFC, and identify any problems inhibiting future commercialization. Using the setup described above, the fuel cell was successful in producing power from the fuel inputs of H₂ and acetone. This was verified with two results: a GCMS scan showing isopropyl alcohol in the fuel cell products and the voltage versus current graph. First, samples were injected into the GCMS and the result showed acetone, water, and isopropyl alcohol. These are the products that would be expected from the proposed system. Water was used to dilute the acetone and keep the membrane hydrated. Second, the voltage versus current graph shows results matching the theoretical expectations for an isopropyl alcohol-acetone reaction. This proves it is possible for this reaction to occur with standard industrial fuel cell technology.

The effect of acetone concentration on fuel cell performance was evaluated. Several solutions with varying acetone and isopropyl alcohol concentrations were used and polarization curves were recorded for each solution, as seen in Fig. 3. The solutions tested were: 4M acetone, 3M acetone + 1M isopropyl alcohol, 2M acetone + 2M isopropyl alcohol, 1M acetone + 3M isopropyl alcohol, and 4M isopropyl alcohol. The polarization curves were recorded by scanning current from open circuit to the limiting (short circuit) current at a rate of 1 mA/s. The cell temperature was 30 °C, and the hydrogen gas flow rate was 0.2 L/min with a relative humidity of 100%. As expected, the isopropyl alcohol only solution produced very little current. The small current that is seen is likely due to a combination of double-layer capacitance and hydrogen adsorption on the catalyst surface. The voltage at zero current (the open circuit potential) was seen to be about 0.12-0.14 volts for all of the remaining acetone-isopropyl alcohol solutions. The measured open circuit potential for the 2+2 mixture (0.129 V) corresponds well with the Nernst potential of 0.128 V for acetone and isopropyl alcohol in an ideal equimolar mixture. The Nernst potential was calculated for a simplified thermodynamic model in Engineering Equation Solver® using thermodynamic data from the NASA database. The open circuit voltage and limiting current increased with increasing acetone concentration as expected. However, in the intermediate current density range where ohmic resistance normally dominates, the 1M acetone solution produced a higher potential than the 3M acetone solution. This unexpected result may be an effect caused by the interaction of isopropyl alcohol and acetone, but further exploration is required. The curves then diverge at the higher current levels as mass transport effects begin to dominate. The limiting current was higher with higher concentrations of acetone. This result corresponds to what is expected as the limiting current is based on mass transport limitations. Since mass transport is concentration driven, higher concentrations of acetone should yield higher mass transport and thus higher limiting currents.
Oxygen dissolving in the acetone fuel posed a potential problem to the performance results. Oxygen dissolving in the acetone would have caused hydrogen and oxygen to react and create water. If this oxygen reaction was occurring, at least some of the current produced could have been a result of the $\text{H}_2$-$\text{O}_2$ reaction instead of the acetone-isopropyl alcohol reaction. Since this current is not from the acetone reaction, it would cause the current trace to indicate a higher performance than was actually occurring. In initial tests without any oxygen removal techniques employed, abnormally high open circuit voltages were occurring most likely as a result of the oxygen reduction reaction. In subsequent experiments, $\text{N}_2$ was bubbled through the acetone fuel mixtures to remove the oxygen. The same technique was followed for all of the mixtures shown in Fig. 3. Fig. 3 proves the new technique removed the oxygen from the mixture. The lowest curve (the 4 M isopropyl alcohol mixture) drops off immediately with very little current flow. This is expected since there is no acetone in the mixture and thus should be no reaction. However, if oxygen had been dissolved in the mixture, at least some low current level would be sustained. Since the current plummeted immediately, this indicates that the dissolved oxygen had been removed from the mixture. Since the same de-oxygenation procedure was followed for all of the different mixtures, this indicates that all of the mixtures should have been oxygen free.

Another issue with the fuel cell performance was the deactivation of the catalyst. For several mixtures, the fuel cell was cycled from the open circuit voltage to the limiting current and then back several times. This test showed decreasing performance with time. It was hypothesized that the catalyst layer was becoming deactivated. Upon further exploration, a process was devised to reactivate the fuel cell. It was found that holding the potential of the fuel cell at 1.00 V for 2 minutes would renew the fuel cell to its original performance. This process is believed to oxidize any catalyst poisons that may accumulate during the experiment. However, before running this process to reactivate the cell, it was necessary to purge with water to prevent excessive oxidation of isopropyl alcohol at 1.0 V. The length of time and voltage necessary to reactivate the fuel cell could be much lower than these values as they were not optimized to minimize parasitic power usage.

4. CONCLUSIONS

The isopropyl alcohol-acetone chemical heat engine has several advantages. First, the Solar Fuel Dehydrogenation Process operates at low temperatures of 300 °C. This eliminates any materials challenges and allows the process to operate with relatively low temperature solar inputs consistent with current parabolic trough technology. Second, this system uses an inexpensive chemical fluid (isopropyl alcohol) that is recycled in a closed loop system. Unlike fossil fuel systems, the process uses a chemical fuel that can be restored and reused, eliminating any adverse environmental effects. The low cost chemical fluid makes the Solar Fuel Dehydrogenation Process inexpensive and simplistic without chemical hazards, or expensive chemical handling needed. Third, the system is decoupled. The decoupled system allows for the storage of solar energy and much higher capacity factors for the power plant. Acetone could be accumulated during the day and used to power the fuel cell 24 hours a day.

Despite the several promising advantages and earlier theoretical studies that promised 29-32% ideal efficiencies, this chemical heat engine process has several problems that appear to make it uneconomical. First, the catalysts in both the Solar Fuel Reactor and the Fuel Cell become deactivated in a short period of time. Methods to reactivate the catalysts were found, but long and/or expensive reduction procedures make these methods unviable in an industrial system. Although this problem could be solved with further catalyst studies and optimization, the low Nernst potential of 0.128 volts in the Fuel Cell cannot be improved since it is dictated by the first and second laws of thermodynamics. Ironically, this low Nernst potential is mainly due to the low temperature difference between the solar fuel reactor and the fuel cell that was advantageous because of the low temperature heat source and lack of high temperature materials required. With such a low output, any system
would require a large number of fuel cells (about 100 times as many as a hydrogen-air fuel cell) and without extremely inexpensive fuel cells, this system would require large capital investment for relatively low power output. Because of this low Nernst potential, systems that have a higher temperature solar fuel reactor should be considered. This would allow for a much larger temperature differential, and a much higher power output.

5. REFERENCES


(4) Vannice, M.A., Kinetics of catalytic reactions, Springer, 2005


