2018 NDIA GROUND VEHICLE SYSTEMS ENGINEERING AND TECHNOLOGY SYMPOSIUM
POWER & MOBILITY (P&M) TECHNICAL SESSION
AUGUST 7-9, 2018 - NOVI, MICHIGAN

Rapid Production of Hydrogen-Rich Syngas Using a Non-Thermal Plasma Fuel Reformer

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ABSTRACT

Non-thermal plasma-assisted partial oxidation of hydrocarbon fuels (including military logistic fuels) is considered with the intent to rapidly produce hydrogen-rich syngas with the least amount of electrical power. The syngas produced can be used to fuel quiet solid oxide fuel cell (SOFC) auxiliary generators, be added to engines or combustors to extend lean operation (decrease NO_x *and increase efficiency) or be further reformed to increase hydrogen yield (via water-gas shift and gas cleanup) for low-temperature fuel cells. Unlike catalytic fuel reformers that suffer from adverse issues involving catalyst deactivation (coking and tolerance to sulfur) and require a warmup period dependent on the thermal mass of the catalyst, plasma reforming offers a non-catalytic approach for rapid "on-demand" hydrogen-rich syngas production (quick startup). Plasma fuel reforming is also fuel flexible and can be applied to applications needing dynamic control of a varying amount of syngas such as those having a time-dependent load (e.g., engine acceleration/ deceleration). It can also be used to rapidly produced hydrogen for fuel cell powered robots used in place of batteries. In this study, experimental results using a non-thermal 'warm' plasma reformer are presented with a focus on the hydrogen and carbon monoxide yields, their selectivities, the efficiency of the reformer and the specific energy density (SED) - a measure of the amount of electricity needed to produce a kilogram of hydrogen or syngas. In terms of fuel feedstocks, much of our work to date has focused on plasma reforming of natural gas with recent efforts to extend the work to JP fuels.*

INTRODUCTION

Fuel cells and other applications require hydrogen. In commercial systems, hydrogen is traditionally produced in large-scale steam reforming plants and transported to the point of use, which is not practical for most military operations. Instead, fuel reformers are needed to convert jet fuel (a complex blend of heavy hydrocarbons with sulfur impurities) to hydrogen or hydrogen-rich syngas at the point of use. A practical approach is to partially oxidize the available fuel to hydrogen-rich syngas, which is a mixture of hydrogen and carbon monoxide. For SOFC's, the entire reformate containing mostly hydrogen, carbon dioxide, and small hydrocarbons can potentially be used provided the sulfur levels and aromatic content are sufficiently low. For low-temperature proton-exchange membrane (PEM) fuel cells, the water gas shift reaction can be used to convert the carbon monoxide in the reformate to additional hydrogen with the use of steam followed by gas cleanup; the steam can also potentially be recovered from the output of the fuel cell.

For partial oxidation, catalytic, thermal, and plasma-based approaches exist. Catalytic reforming has been shown to work at least for a limited time [1] yet is sensitive to the high aromatic content and sulfur in the fuel. Also, the catalyst must be initially heated which can slow the startup time depending on its thermal mass. Thermal partial oxidation (TPOX) is also an option, conveniently avoids the need for catalysts, yet does require high reaction temperatures (~1200^{o}C or higher) to achieve high hydrogen concentrations; the high temperatures limit the choice of materials to high temperature metals, metal alloys or ceramics; TPOX reformers also require a startup period dependent on the thermal mass of the reformer.

In this work, our focus is on non-thermal plasma-assisted partial oxidation. No catalysts are needed and the reformer can rapidly produce hydrogen from a cold start. It is also fuel flexible and sulfur tolerant. It does, however, require electricity to generate a high voltage, low current electric discharge (arc) with which the reactants interact, producing radicals and charged species that promote reforming reactions. Stainless-steel electrodes are used in our reformer and can handle typical operating temperatures of 800-1000^{o}C. Also, in our system, the arc discharge continuously translates between two opposed electrodes; this avoids the formation of local hot spots on the electrodes that are undesirable. In effect, by continuously translating the arc discharge, a 'volumetric' discharge is generated that then is used to reform a continuous reactant flow.

A key focus of our current work (now funded through the Department of Energy) is also on developing effective ways to lower the electricity needed for plasma-assisted fuel reforming; this is important since the cost of electricity is the primary operating cost [4]. To do so, our approach has been to efficiently preheat the reactants using heat from the hot reformate exiting the reformer; this raises the temperature of the reactants, which increases the reaction rates resulting in higher syngas yields for the same electrical power. Prior work showing the benefit of preheating is available in references 6 and 7.

THERMAL VS. NON-THERMAL PLASMA FUEL REFORMING

There are two fundamental types of plasmas, thermal and non-thermal, both of which have application for fuel reforming. Both plasmas consist of electrons, ionized species and neutral species that promote fuel reforming. For conditions where the all constituents are very energetic (high electron, ion and gas temperatures), the plasma is referred to as a thermal plasma. High electrical power is, however, needed to generate thermal plasmas and is used for bulk heating of the entire gas mixture. With that said, however, thermal plasma fuel reformers are very efficient at producing hydrogen-rich syngas from a variety of different hydrocarbon fuels (natural gas, gasoline, diesel, oil, biomass, and jet fuel), have a fast response time, and can be compact (owed to their high-power density) [9].

In comparison, non-thermal plasmas require less electrical power as they do not provide for bulk heating of the gas. Rather, the gas temperatures are comparatively low (neutral and ionized species temperatures are ~300-1,500K), while the electron temperatures are very high (10,000-100,000K). With lower gas temperatures, the need for expensive, high-temperature materials is avoided and electrode stability/lifetime is extended. In essence, in non-thermal plasmas, high-grade electricity is used to create a strong non-equilibrium between the electron temperature and the temperature of the gas molecules and ions; the electrons subsequently participate in dissociation and ionization reactions that promote syngas production without substantial heating of the gas mixture. In our system, heating of the gas mixture is largely provided from the exothermicity of the partial oxidation process together with heat recuperation from the hot reformate with a limited amount of heating provided from the electrical discharge.

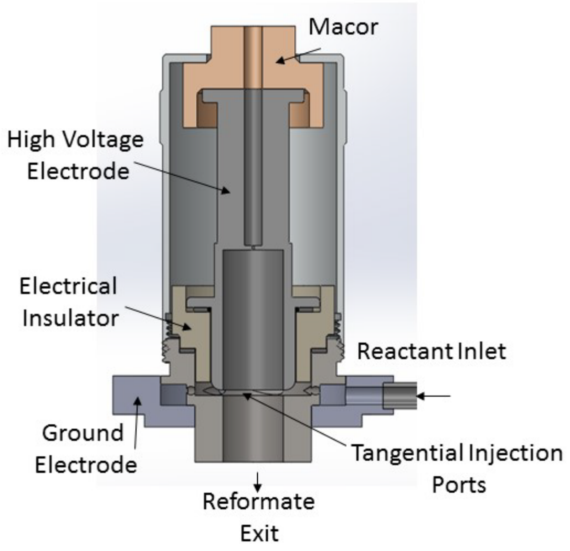
Non-thermal plasmas can further be divided into two classes: "cold" and "warm." Both classes generate a pool of active species that serve a similar role as a catalyst. Cold plasmas, including dielectric barrier discharges (DBD), coronas, and pulsed coronas, do not provide heating of the gas, and are usually used in applications requiring low process temperature and low power density, such as surface treatment, ozone production, and disinfection [12]. "Warm" discharges are intermediate between cold and thermal plasmas and include low-current arcs, glow discharges [13], microwave discharges [10,11], and gliding arc discharges [5]. Gliding arc discharges are especially well-suited for fuel reforming since their temperatures are in the 800-1000^oC range, which is similar to that needed for traditional reforming. In terms of prior studies on plasma reforming, notable contributions include work by the Drexel Plasma Institute who used a gliding arc plasma reactor for steam or dry reforming of JP8 with H_2O and CO_2; here, the H_2O and CO_2 represent the products of an SOFC exhaust stream [2]. Also, Ceramatec has developed a plasma reformer for reforming diesel and JP8 [3].

EXPERIMENTAL APPARATUS

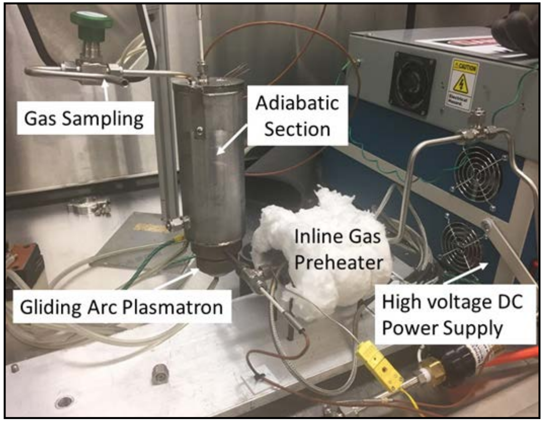
A gliding arc plasma reactor that accepts a premixed fuel-air reactant flow was designed, fabricated and tested (Figure 1). For gaseous reactants, mass flow controllers were used to meter the gases. For liquid fuels and steam addition, a vaporizer was also developed. The liquid fuels and/or water were metered using a positive displacement pump sometimes in conjunction with a low flow of nitrogen to sweep the vaporized species into a separate air flow upstream of the entrance to the reformer. Provisions for preheating the fuel-air mixture were also incorporated into the design to prevent condensation of the vaporized fuel and/or water (steam) upstream of the reactor entrance.

Internal to the plasma reactor are multiple tangential injection ports through which the reactants are introduced; these gas injection ports generate internal swirl and form of a reverse vortex where the reactants swirl upwardly along the internal walls of the plasma reactor and subsequently circulate back down through the reactor core. This reverse vortex flow was inspired many years ago by the flow in 'vortex tubes' used for temperature separation [10,11] and has been shown to be an effective way to create a volumetric plasma discharge. At the exit from the plasma reformer, a cylindrical stainless steel tube having a length of 30-90cm with internal alumina lining is attached. This volume is referred to as an 'adiabatic' volume and allows reforming reactions to continue after the hot reformate exists the plasma reactor. Temperatures in this section are typically 800-1100^oC as the gases enter this volume and decrease by a few hundred degrees prior to exiting into a fume hood where the reformate is flared before venting for safety.

Regarding the electrode design, the housing serves as the ground (low potential) electrode and an opposed cylindrical high voltage electrode is used. The discharge is ignited with a high voltage DC power supply (3-5kV). Once ignited, the discharge is sustained at lower voltage (1-2kV) with a low current ranging from 100-500 mA such that the average output power is controlled from 100-850W. Support hardware for gas control and metering, mixing, preheating, gas sampling and temperature measurements was also used. A GRI gas chromatograph was used to analyze the reactants and reformate composition and was calibrated using available standards.



(a)



(b)

Figure 1: (a) Cross-section of gliding arc plasma reformer, (b) Reactor assembly.

TEST PROTOCOL

Laboratory tests have been performed using the plasma fuel reformer with methane-air (with and without the addition of steam) and JP-24-air. The gases are metered using mass flow controllers and the liquid feeds are vaporized using a custom temperature-controlled vaporizer. The jet fuel was provided and analyzed courtesy of Wright Patterson Air Force Base. Noteworthy is that the JP-24 fuel sample contained 13.9% hydrogen (by mass) and 0.02% sulfur (by mass).

RESULTS AND DISCUSSION

Partial oxidation experiments were performed using rich fuel-air premixtures at flowrates ranging from 35-75 SLPM and equivalence ratios (Φ) ranging from 1.8 to 4.0. Our focus here is on quantifying the reformate composition as a function of the equivalence ratio, reactant flowrate, applied electrical power, and the extent of heat recuperation/ preheating of the reactants.

Plasma Assisted Partial Oxidation of Methane-Air - Reformate Concentration vs. Power

Figure 2 shows representative experimental results for rich methane-air premixtures without reactant preheating at a fixed total flowrate (35 SLPM) and reactant composition (Φ=4, O/C=1) for a range of electrical powers (400-817W). For this mixture, the thermodynamic equilibrium hydrogen and carbon monoxide concentrations (computed using a thermodynamic equilibrium code GASEQ [14]) are 31.9% and 14.8%, respectively. As shown, the hydrogen concentration nearly doubles with increasing power (over the range considered) while the carbon monoxide concentration also increases, albeit to a lesser extent with near equilibrium concentrations of both hydrogen and carbon monoxide achieved at the highest power.

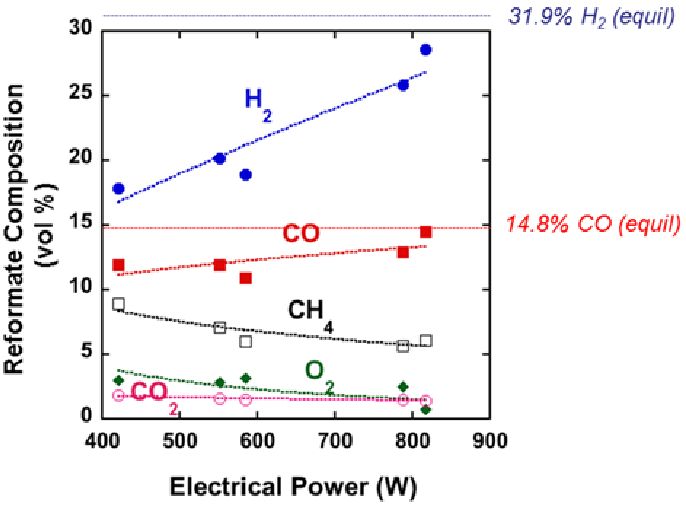
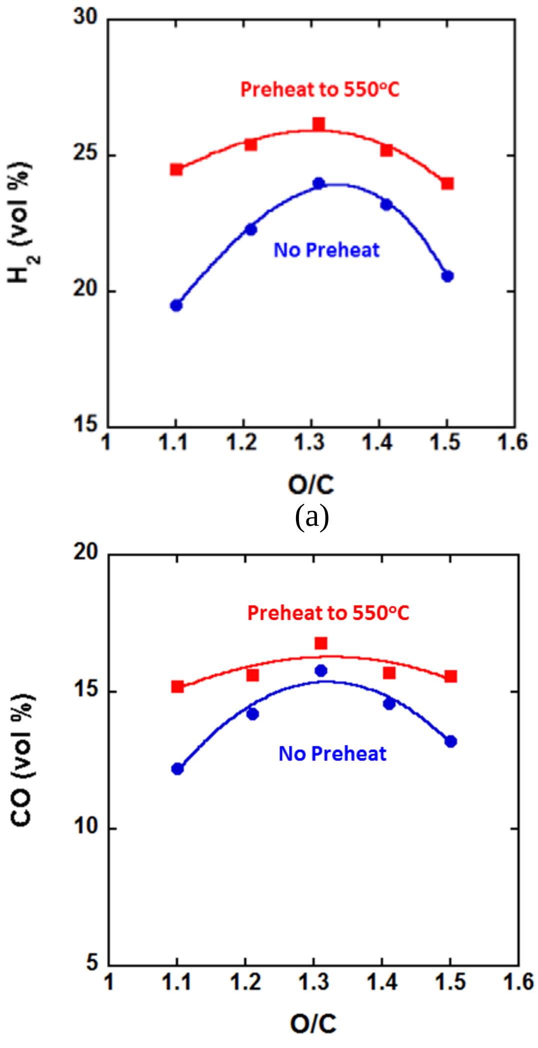


Figure 2: Reformate concentration as a function of electrical power for rich CH_4-air, Φ=4.0, O/C = 1, 35 SLPM total flowrate, 400-817W.

Plasma Assisted Partial Oxidation of Methane-Air - Preheating Improves Syngas Yield

Similar tests were performed with preheating of the methane-air premixture to 550°C. Results were then baselined against those without reactant preheat. Figures 3a and 3b show the hydrogen and carbon monoxide concentrations in the reformate for oxygen-to-carbon (O/C) ratios ranging from 1.1 to 1.5; the corresponding equivalence ratios are 3.6 to 2.6. In these tests, the applied power was nominally 600W (ranged from 601-624W). As shown, the hydrogen concentration in the reformate is higher with preheating than without preheating; specifically, the average hydrogen concentration for these test conditions over the O/C ratio considered, with preheat, was 25.0% compared to 21.8% without preheat. Similarly, the CO concentration in the reformate for these same test conditions shows preheating also increases CO yield.



(a)

(b)

Figure 3: (a) Hydrogen concentration, (b) Carbon monoxide concentration in the reformate using CH_4-air at O/C ratios from 1.1 to 1.5 for fixed power (600W) and total flowrate of 72 SLPM. Higher hydrogen and carbon monoxide concentrations are achieved with preheating.

Plasma Assisted Partial Oxidation of Methane-Air - Steam Addition (Autothermal Reforming)

The addition of steam to rich CH_4-air premixtures was also considered. This is autothermal reforming (ATR); ATR conveniently uses the heat released from exothermic partial oxidation to offset the endothermicity of the steam reforming reactions. Representative data from preliminary tests is shown in Table 1. In all cases, the inlet temperature ranged from 269-300°C.

CH_4 (SLPM)	Air (SLPM)	H_2O (SLPM)	Pwr (W)	H_2 (%)	CO (%)
22.5	10.2	6.9	336	17.1	10.3
22.5	10.2	6.9	483	17.1	10.3
22.5	10.2	3.4	474	16.6	9.9
22.5	10.2	3.4	485	18.8	11.3

Table 1: Initial data for plasma-assisted autothermal reforming of CH_4-air-steam premixtures.

Plasma-Assisted Partial Oxidation of Jet Fuel

Tests were also performed on plasma-assisted partial oxidation of JP-24-air over a range of equivalence ratios, volumetric flowrates, and applied electrical powers. A plot of the reformate concentration as a function of the equivalence ratio is shown in Figure 4. The hydrogen (H_2), carbon monoxide (CO), methane (CH_4), carbon dioxide (CO_2) and unreacted oxygen (O_2) concentrations are plotted for a case having a total flowrate of 36 SLPM with 200W of electrical power applied to generate the electrical discharge. In these tests, the JP-24-air premixture was preheated electrically to 308-324°C prior to reactor entry to prevent condensation. Also note that the water concentration is not reported, since water condensed out in the gas sampling syringe used to take the gas sample for analysis.

As shown, the H_2 concentration ranged from 9.7% to 13.5% and the CO ranged from 12.4 to 14.3%. These values are compared to the thermodynamic equilibrium H_2 and CO concentrations computed using the EQUIL subroutine in CHEMKIN-Pro with a three-component jet fuel surrogate consisting of 42.7% n-decane, 33.0% iso-octane, and 24.3% toluene [15]. This surrogate fuel blend (and similar blends) was shown to have properties similar to those of jet fuel (i.e., cetane number, molecular weight, sooting index, and hydrogen to carbon molar ratio). As shown in Figure 4, the H_2 and CO concentrations are close to the thermodynamic concentrations for equivalence ratios near 2. At higher equivalence ratios, measured values remain relatively consistent across the range of equivalence ratios, while computed thermodynamic equilibrium values are roughly 25% higher at equivalence ratios (i.e., 3.0-3.5).

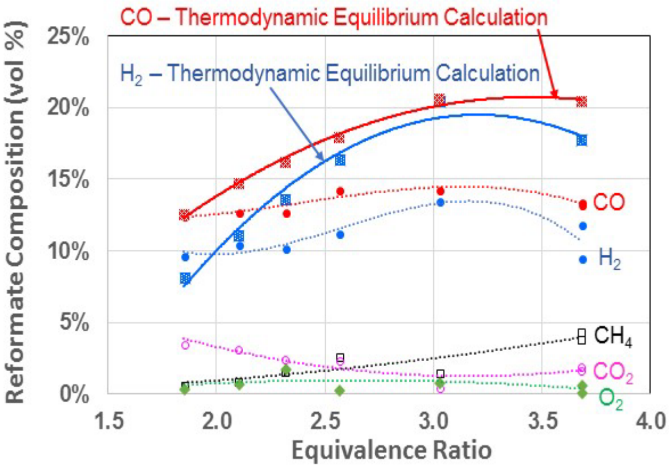


Figure 4: Species concentration measurements using a JP-24-air premixture demonstrating that plasma-assisted reforming can effectively produce a hydrogen-rich syngas with jet fuel. Total flowrate = 36 SLPM, Power = 200W, Inlet preheat = 308-324°C. Also shown are computed values of the thermodynamic equilibrium H_2 and CO concentrations.

Two key criteria for further assessing the performance of the plasma reformer include: (1) the mass of hydrogen produced per unit mass of fuel (JP-24) reformed and (2) the amount of electricity required (in kWh) per unit mass of fuel (JP-24) reformed. The intent here is to maximize the mass of hydrogen produced and minimize the electricity needed to produce hydrogen.

Figure 5 shows a representative plot of the mass of hydrogen produced per unit mass of fuel reformed vs. the amount of electricity needed per unit mass of fuel reformed for two different equivalence ratios (1.85 and 2.3). The different points correspond to the reduced data from experiments performed at different flowrates, electrical powers, and equivalence ratios. As shown, the maximum amount of hydrogen produced per unit mass of fuel reformed is about 11% on a mass basis (i.e., maximum value is 109.8 gH_2/kg JP-24). This corresponds to a conversion of 79% of all of the hydrogen contained in the JP-24 sample to hydrogen gas since the parent JP-24 fuel itself contains 13.9% hydrogen (as determined from chemical analysis of the JP-24 fuel sample at WPAFB).

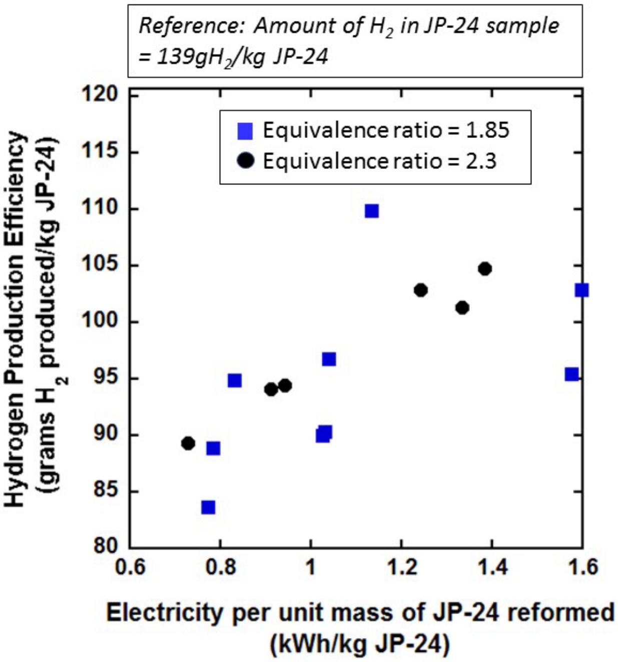


Figure 5: Representative plot showing the mass of hydrogen produced per unit mass of fuel reformed vs. the amount of electricity needed to reform the parent fuel for two different equivalence ratios.

Also, the ratio of the mass of hydrogen produced per amount of electricity needed to produce the hydrogen is of interest. For the test data reported in Figure 5, for an equivalence ratio of 1.85, this ratio ranged from 8.8 – 16.5 kWh/kg H_2 while for an equivalence ratio of 2.3, this ratio ranged from 8.2 – 13.2 kWh/kg H_2. This value essentially determines the operating cost based on the cost of electricity not including the cost of the parent fuel and transportation costs.

CONCLUSIONS

A non-thermal gliding arc plasma reformer for the production of hydrogen-rich syngas was developed and tested using methane-air, methane-air-steam and jet fuel (JP-24)-air. For methane-air, the hydrogen and carbon monoxide concentrations were shown to increase with increasing power for a fixed equivalence ratio and fixed power. Also, experimental results show reactant preheating increases hydrogen and carbon monoxide yields for a fixed flowrate, inlet composition and applied electrical power. Further experiments on partial oxidation using JP-24-air show that near equilibrium concentrations of hydrogen and carbon monoxide were achieved for equivalence ratios near 2. Thermodynamic equilibrium calculations were also performed to determine the maximum amounts of hydrogen and carbon monoxide that could be obtained for benchmarking our data reported in Figure 4. Also, the hydrogen production efficiency in grams of hydrogen produced per unit mass of JP-24 provided was computed where it was determined that up to 79% of the hydrogen contained in the parent fuel was converted to hydrogen gas. Lastly, attention was given to compute the electricity per unit mass of JP-24 reformed showing that it ranged from 8.2 – 16.5 kWh/kg H_2 for the two different equivalence ratios considered in Figure 5.

ACKNOWLEDGMENTS

For the work reported with methane-air, this material is based upon work supported by the U.S. Department of Energy, Office of Science under award number DE-SC0013821. It is further noted that Drexel supported tests with methane-air. Special thanks are also extended to Tim Edwards at Wright Patterson AFB for providing the JP-24 samples.

DISCLAIMER

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