Auto-Thermal Reforming of Jet-A Fuel over Commercial Monolith Catalysts – MicroReactor Evaluation and Screening Test Results

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Prepared for Presentation at 2004 Spring National Meeting of AIChE, New Orleans, LA

April 25-29, 2004

Fuel Processing Session III: Reactor Development and Modeling

Unpublished

Abstract

Solid oxide fuel cell systems are being studied by NASA [1] for commercial aerospace applications. These applications include on-board generation of auxiliary power and propulsive thrust. An aviation fuel cell based hybrid system will typically utilize Jet-A fuel as the feed to the fuel processing system. In this hybrid concept, a reformer must be designed to convert the liquid Jet-A hydrocarbon into a reformate rich in hydrogen (H_2) and carbon monoxide (CO). This reformate feeds directly into the solid oxide fuel cell stack where power and waste heat are produced. The reformer reactor technology necessary for deployment with on-board aircraft must have features including compactness, light-weight and high durability. Monolithic reformer catalysts can help meet these requirements because they offer high surface to volume ratios, are known to have high relative activity, are durable at extreme temperature, are resistant to vibrational affects, and produce very low pressure drop [2].

An in-house fuel processing program recently started at the NASA Glenn Research Center (GRC) has the objective to develop a reforming technology that meets the stringent requirements of commercial air transportation power systems. In addition to fuel processing studies, advanced direct fuel injection technology for reformer reactors [3] and Jet fuel/reformate desulfurization are being investigated. The vast majority of ongoing fuel processing development for SOFC systems is being carried out at atmospheric pressure, and little work has been done in the high pressure reformer area. For the NASA aircraft SOFC hybrid applications, the reformer will need to operate at high pressures. The system pressures are expected to be on the order of 3 – 5 atm in order to minimize weight and volume as well as to improve SOFC current density.

This paper describes the results of a series of catalyst screening tests conducted with Jet-A fuel under auto-thermal reforming (ATR) process conditions at the research laboratories of SOFCo-EFS Holdings LLC under Glenn Research Center Contract. The primary objective is to identify best available catalysts for future testing at the NASA GRC 10-kW_e reformer test facility. The new GRC reformer-injector test rig construction is due to complete by March 2004. Six commercially available monolithic catalyst materials were initially selected by the NASA/SOFCo team for evaluation and bench scale screening in an existing 0.05 kW_e microreactor test apparatus. The catalyst screening tests performed lasted 70 to 100 hours in duration in order to allow comparison between the different samples over a defined range of ATR process conditions. Aging tests were subsequently performed with the top two ranked catalysts as a more representative evaluation of performance in a commercial aerospace application. The two catalyst aging tests conducted lasting for approximately 600 hours and 1000 hours, respectively.

Jet-A Fuel

A commercial jet fuel was used for both catalyst screening and aging tests to allow consistent comparison of catalyst performance without fuel property interferences. The fuel used was purchased from BP Oil Company's Canton Terminal, identified from Tank 022, sampled 3/31/2003, Batch No. 4647. This fuel met all commercial Jet-A specifications [4 – 5]. Fuel compositional analysis is summarized in Tables 1 – 2 below.

Table 1 – Jet Fuel Physical Analysis [4]

Properties	Data	ASTM Method	Trace Metals	(PPM) ++
Carbon (wt %)	86.38	D-3701	Mg (PPM)	0.57
H/C (wt/wt)	0.158		Zn (PPM)	0.58
Density (g/cc)	0.814	D-71	Al (PPM)	0.23
API gravity	41.5	D-287	Cu (PPM)	0.11
LHV (Btu/lb)	18673	D-4809	Fe (PPM)	0.34
Viscosity (cs)	1.863	D-446	Ca (PPM)	1.61
Sulfur (PPMW)	1488	D-5453	++ by ASTM-E1479	

Table 2 - Preliminary Hydrocarbon Analysis Using ASTM D-2789 [5]

Species	Vol. %
Paraffins	36.5
Monocycloparaffins	35.9
Dicycloparaffins	12.8
Alkylbenzenes	10.4
Indans & Tetralins	3.3
Naphthalenes	1.3

Results — Catalyst Screening and Aging Tests

The catalyst screening studies were carried out isothermally at 750-830 °C and a constant space velocity of 12,000 hr^{-1}. Steam-to-carbon (H_2O:C) and oxygen-to-carbon (O:C) ratios were maintained at 3.51 and 0.72, respectively. The average reformer efficiencies for the catalysts tested ranged from 75 – 83 percent. The corresponding hydrocarbon conversion efficiency varied from 86 – 92% during testing. Definitions for hydrocarbon conversion (HC Conv) and reforming efficiency (Ref. Eff) are provided at the end of this paper. The mole fraction on a dry basis of H_2 and CO product in the reformate gas was about 50% for all catalysts screened. Micro-reactor monolith operating conditions were: Jet-A fuel feed of 16.2 cc/hr; water feed rate of 60cc/hr, and air feed rate of 600 sccm. The ATR monolith sample was 0.5 inch diameter by 3 inch long. Catalyst performance during the screening evaluations is summarized in Table 3.

Table 3 – ATR Catalyst Screening Summary ‡

Cat ID	Catalyst Bulk Density (kg/L)	Catalyst Cell Density (cpsi)	Total TOS (hr)	Set T (°C)	C-Bal (%)	HC Conv (%)	Ref Eff (%)	H2 Conv (%)	Dry-Basis Reformate (sccm)	H2 mol (%)	CO mol (%)	CH4 mol (%)
A-2	**0.51**	**400**	**96.6**	**760**	**101**	**93**	**80**	**32**	**1328**	**36.8**	**13.0**	**1.1**
B-6	0.38	400	100.9	789	102	86	75	25	1226	31.8	18.1	1.6
C-5	0.55	400	73.3	788	100	90	77	28	1256	34.2	16.1	1.5
D-3	0.56	300	67.3	770	99	92	78	27	1255	33.6	17.9	1.5
E-1	**0.61**	**600**	**90.1**	**750**	**101**	**95**	**83**	**35**	**1383**	**39.4**	**11.0**	**1.0**
F-4	0.49	600	102.8	777	99	92	77	30	1297	34.8	13.7	1.4

Notes: ‡ Reported values are average over the test duration for each catalyst.

Notable performance differences are observed among the six candidate catalysts. The best performing catalyst (Catalyst E-1) achieves the highest hydrocarbon conversion, and reforming efficiency with highest H_2 concentration in the reformate at the lowest reactor temperature of 750°C. In other words, catalyst E-1 is the most active and selective catalyst among the six candidate catalysts in short-term screening test. The second best performing monolith was determined to be catalyst A-2. Operation protocol was then developed to evaluate catalyst performance over time at similar operating conditions with a reduced GHSV of 6000 hr^{-1}. Table 4 below compares screening test operation to the aging test conditions.

Table 4 – Operation Comparison of Catalyst Screening & 1000-Hour Aging Test

Parameters	Catalyst Screening	1000-Hour Aging Test
Pressure (atm)	1.0	1.0
Temperature (°C)	750 – 830	750 – 840
Jet-A Feed (cc/hr)	16.2	15.8 – 16.5
Water Feed (cc/hr)	60	58 – 62
Air Feed (sccm)	600	675
Steam-to-Carbon Feed Ratio (mol/mol)	3.51	3.56
O-to-Carbon Ration (mol/mol)	0.72	0.8
GHSV (hr^{-1})	12,014	6,000
LHSV (hr^{-1})	1.73	0.83
Monolith Size	1 pc, 0.5" OD x 3" L	2 pcs, 0.5" OD x 3" L

Two candidate catalysts were evaluated in subsequent aging tests. The aging tests were set up to run at a fixed feed rate and constant operating temperature so that catalyst performance characteristics could be quantified. Operating parameters (steam:C, O:C feed ratios, reactor temperature) were only adjusted at the end of run when severe performance decline was observed to see if any regeneration effects were attainable.

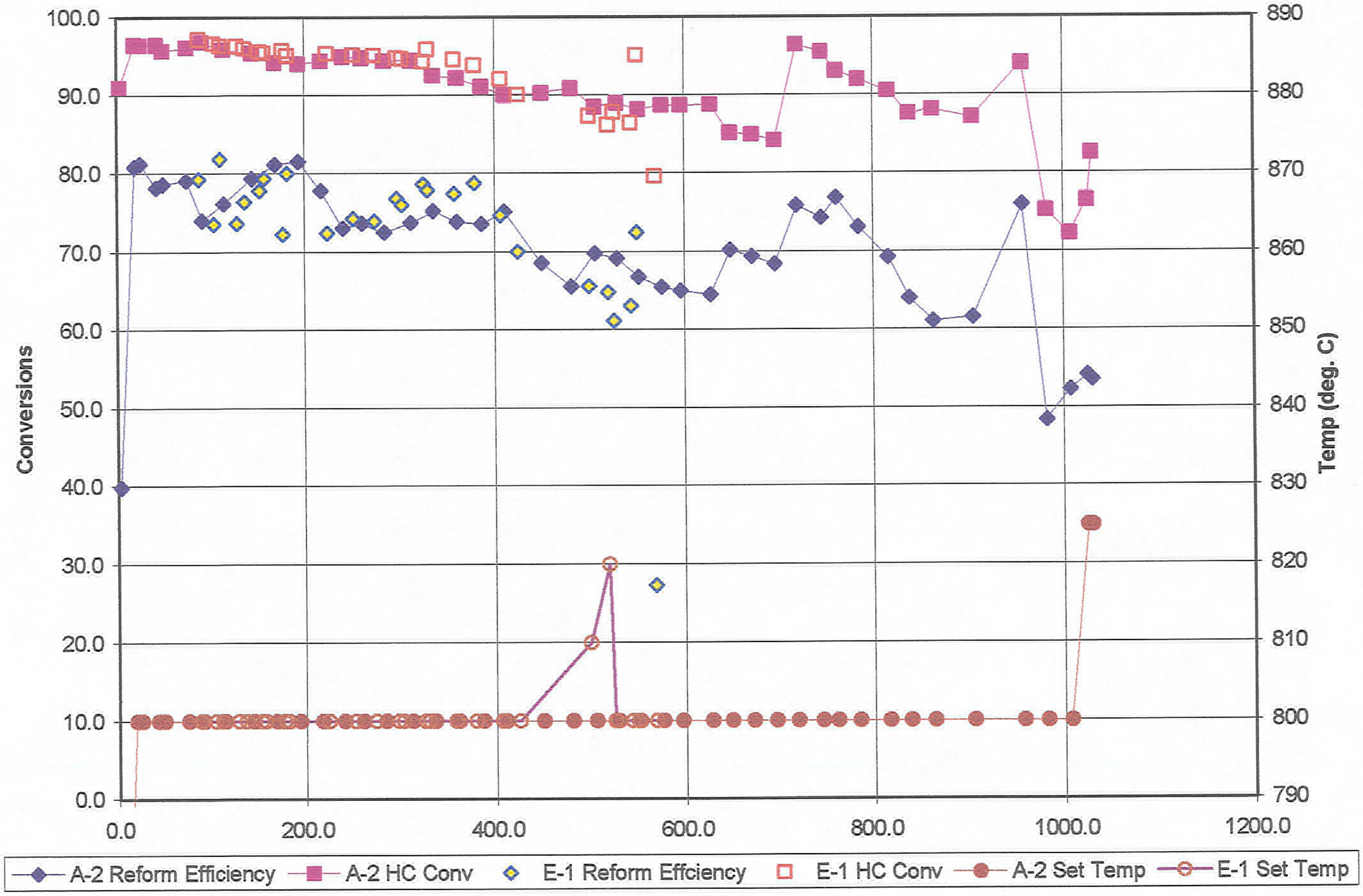
The 1000-hour aging test for the best performing catalyst (E-1) was stopped after 570 hours time on stream (TOS) due to an un-expected rapid activity decline. The second ranked catalyst (A-2) was then tested for a total of 1030 hours. Table 5 below summarizes the performance data for catalyst E-1 & A-2 during initial screening (S) tests and during aging test (A) for the initial start-of- run (SOR), steady state, and end-of-run (EOR) conditions.

Table 5 – Summary of Catalyst Performance in Screening & Aging Tests

					Dry Reformate Composition (mol %)					
Catalyst ID	Test	TOS (hr)	HC Conv (%)	Ref. Eff (%)	H_2	CH_4	C2+	CO	CO_2	N_2
E-1	S-avg.	90.1	95	83	39.4	1.0	0.16	11.0	13.0	35.4
SOR	A	87	97	79	37.8	0.6	0.02	6.6	16.0	39.1
Stable	A-avg.	88-500	95	76	34.7	1.0	0.18	12.5	11.4	40.2
EOR	A	568	80	27	18.9	1.6	2.53	6.6	11.8	58.5
A-2	S-avg.	96.6	93	80	36.8	1.1	0.37	13	11.2	37.5
SOR	A	19	96	81	37.0	0.7	0.07	9.7	13.6	39.0
Stable	A-avg.	20-957	92	72	31.9	1.0	0.54	14.7	9.1	42.8
EOR	A	1030	83	54	22.5	1.3	1.84	17.8	5.2	51.4

Figures 1 & 2 below provide a comparison of aging test data for catalyst E-1 and A-2. Note that hollow symbols correspond to Catalyst E-1, solid ones for Catalyst A-2.

Figure 1 - Compare Catalyst E-1 & A-2 Life Test



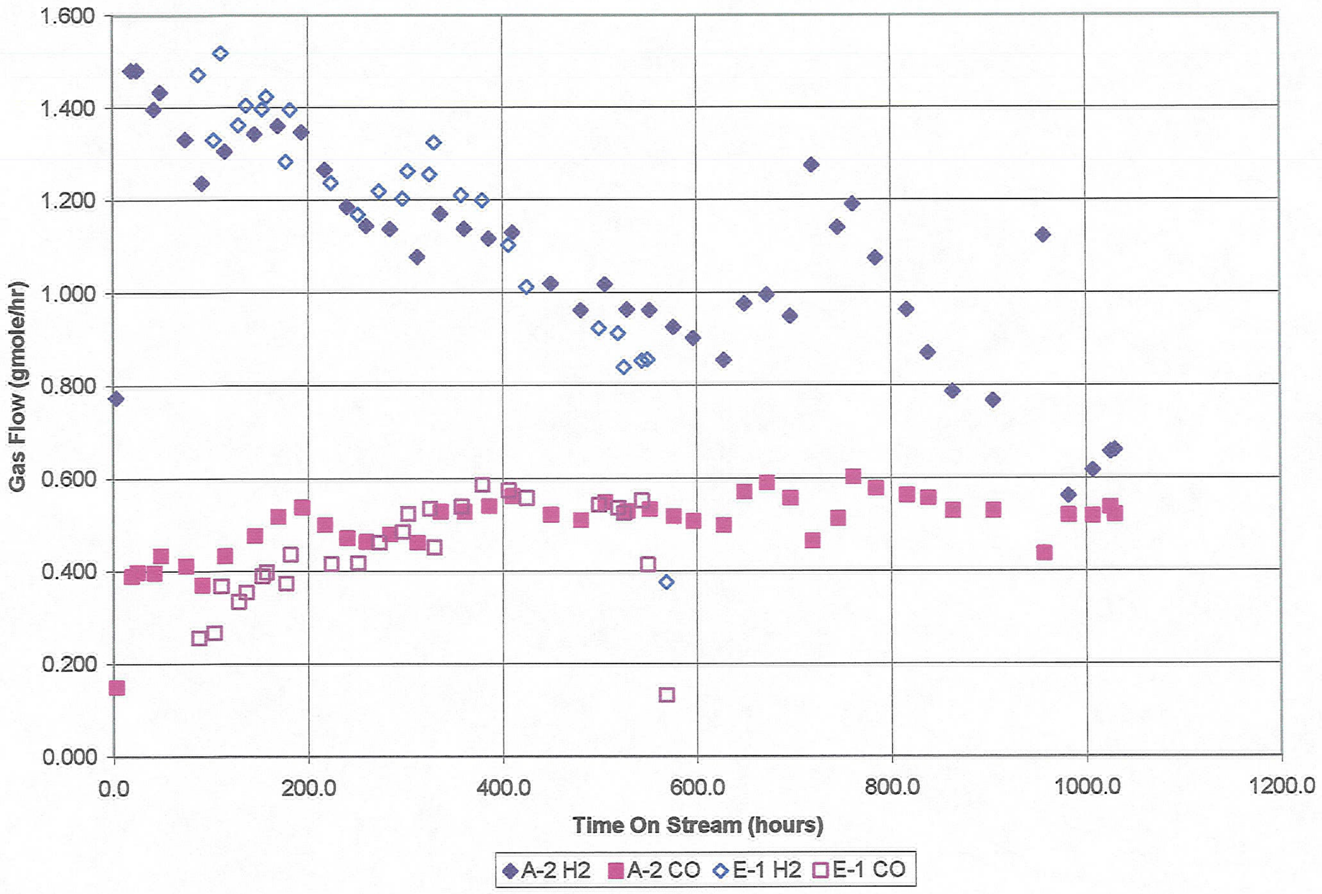


Figure 2 - Compare E-1 & A-2 Product Gas

Preliminary comparison of the data yields the following observations:

1. The catalyst E-1 activity decline rate is similar to that of catalyst A-2 based on the reformer efficiency during stable, steady operation period. The performance decline observed in catalyst E-1 is more severe and less reversible. During rate 500-570 hours TOS, several process variable changes including temperature, O/C ratio, GHSV, and temporary fuel outage, did not slow down the performance decline rate.

2. The catalyst A-2 aging test may be prolonged by further increasing the reactor operating temperature and changing other process parameters. A temporary performance improvement was observed around 718 hr and 956 hr when the fuel feed was stopped while continuing the steam and air flow.

3. Neither catalysts E-1 or A-2 aging test performance is acceptable for practical commercial aircraft application due to their activity and durability test limits.

Visual inspection of used catalysts E-1 and A-2 did not uncover any carbon deposition, channel blockage or physical damage due to thermal sintering. Both used catalysts were shipped back to the respective catalyst manufacturers for further characterization and failure analysis.

Concluding Remarks

Standardized catalyst screening tests (<100 hours TOS) provides indicative catalyst performance only. Aging tests (>1000 hours TOS) are needed to quantify the long-term catalyst performance for design. The commercial catalysts tested in our experiments did not meet long term performance expectations for aerospace application. However, catalyst A-2 has been chosen for use in the initial 10 KWe testing at NASA Glenn Research Center. Further research in catalyst formulation, activity, selectivity, and durability at high pressure operation will need to be explored before aircraft hybrid power systems implementation is possible.

Definitions of Terms

Hydrocarbon Conversion:

$\text{HC-conv} = \{1-[C_{CH4} + \sum_{i=2} (C_i * n_i)] * E_R / F_C\} *100$

Reformer Efficiency

Ref Eff = (LHV of reformate per CO, H_2)/(liquid fuel LHV)

$= (C_{CO} * LHV_{CO} + C_{H2} * LHV_{H2}) * E_R * 100/((LD_R * SG *LHV_f)$

C_{CH4} = methane concentration (mole fraction) of product in effluent gas
C_i = concentration (mole fraction) of product "i" in effluent gas
%C = weight percent carbon in hydrocarbon fuel feed
E_R = effluent gas rate in mole/hr
F_C = carbon feed rate (mole/hr) = LD_R x %C x SG/(12.01 x 100)
GHSV = gas hourly space velocity, hr^{-1}
LD_R = liquid hydrocarbon feed rate in cc/hr
LHSV = liquid hourly space velocity, hr^{-1}
LHVx = lower heating values of x; x can be CO, H2, Jet fuel (f)
SG = specific gravity of hydrocarbon fuel
TOS = time on-stream, hr

Acknowledgement

The authors would like to acknowledge the outstanding contribution by Dr. John Budge and Dr. Milind Kantak of SOFCo-EFS Holdings LLC, Alliance, OH.

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4. All analyses listed in Table 1 except total sulfur were conducted in Glenn Research Laboratory according to the ASTM methods listed. Total sulfur analyses were performed and certified by Core Laboratories at Houston, TX.

5. Jet-A Class analysis was performed by the Analytical Group at Wright Patterson Air Force Laboratory.