Hydrogen Production from Used Lube Oil

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Start Date = January 2004
Planned Completion = November 2006

Rationale

- Used lube oil is an important **local resource.**
- Each year, Floridians generate more than **45 million gallons** of used lubricating oils.
- Used lube oil is available at about **10 cents per gallon**, delivered.
- Hydrogen can be extracted from used lube oil for NASA's use.
- Lube oil contains twice as much as hydrogen as that in biomass.
- Potential to produce liquid hydrogen without generating any criteria pollutants (CO, SO_2, NO_X, etc.) & with minimal CO_2 & other GHG emission.
- Hydrogen production at costs comparable to SMR.
- Potential near term deployment.

Research Goals & Objectives

- Determine the conversion efficiencies, product yield & selectivity during steam reformation of virgin synthetic & used lube oils as a function of reaction parameters – *e.g.* pressure, temperature, residence times, etc.
- Evaluate alkali metal hydroxides as homogeneous catalysts for the steam reformation of lubricating oils – virgin & used.
- Optimize the alkali-catalyzed steam reformation of used oil process in order to maximize yield of hydrogen & minimize formation of coke and other undesirable by-products.
- Develop an Aspen-Plus™ based process simulation flowsheet for the design & costing of a 1500-8000 lbs/day LH2 production plant utilizing used lubricating oils.

Relevance to Current State-of-the-Art

- Although research related to H_2 production from vegetable oils & diesel range hydrocarbons have been ongoing, none has been reported on the production of hydrogen from used lubricating oils – FSEC's work is first of its kind in this area.

Relevance to NASA

- Allows on site hydrogen production from a locally available feedstock.
- Permits hydrogen production and delivery costs, to NASA, can potentially be lower than that generated via SMR-based processes.
- Eliminates long-distance highway transport of LH2 to NASA-KSC.

Budget, Schedule & Deliverables

FY '05 Tasks*	Q-4/ '04	Q-1/ '05	Q-2/ '05	Q-3/ '05	Q-4/ '05
Determine η, product yield & selectivity for steam reformed Mobil One™					Done
Determine η, product yield & selectivity for steam reformed used lube oil					Done
Evaluate KOH for steam reformation of n-Hexadecane as a model compound					Done
Evaluate KOH for steam reformation of lube oils – virgin/synthetic & used					Done
Optimize the alkali-catalyzed steam reformation of used oil process					
Develop an Aspen+ process flowsheet for the design & costing of a 1500-8000 lbs/day LH2 production plant					
Submit a Final Report					

*** Budget/FY'05: $325k**

Anticipated Technology End Use

- This technology is of interest to the petroleum companies interested in hydrogen production from hydrocarbon fuels especially high sulfur ones such as Diesel & jet fuels. We have already been contacted by one petroleum company - Chevron Technology Ventures, LLC Houston, Texas, to look at H2 production from high sulfur fuels.
- Both U.S. DOE & DOD are also interested in this type of R&D for the on-board reformation of logistic fuels to hydrogen gas.

Composition of Lube Oil

Used lube oil is a complex mixture of low & high molecular weight aliphatic & aromatic hydrocarbons, additives, metals and other compounds.

Compound Class	Formula	Wt% in Oil
Alkyl-Monoaromatics	$C_{10}H_{14}$-1, Butyl benzene C_7H_8, Toluene	4.2 4.2
Cycloalkanes	C_6H_{12}-1, Cyclohexane C_6H_{12}-2, Methylcyclopentane C_8H_{16}-14, n-Propylcyclopentane $C_{10}H_{20}$-1, n-Butylcyclohexane	12.0 12.0 12.0 12.0
Diaromatics (Except Naphtalenes)	$C_{12}H_{10}$, Biphenyl $C_{12}H_8O$, Dibenzofuran $C_{13}H_{10}$, Fluorene	2.1 2.1 2.2
Monoaromatics	C_8H_6S, Benzothiophene	10.8
Naphthalenes	$C_{10}H_8$, Naphthalene $C_{11}H_{10}$-1, 1-Methylnaphthalene	3.2 3.2
Polynuclear Aromatics	$C_{18}H_{12}$, Chrysene $C_{18}H_{12}$-D1, Benzanthracene $C_{14}H_{10}$-2, Phenanthrene	1.6 1.6 7.4
Straight-chain & branched	C_9H_{20}-E4, 2,4-Dimethyl-3-ethylpentane	3.4
Additives	$C_7H_6O_3$, Salicylic acid $C_4H_4O_3$, Succinic anhydride	3.0 3.0

Element	Weight %
Hydrogen	13.37
Carbon	84.35
Oxygen	2.51
Sulfur	0.22
Nitrogen	<0.5

Accomplishments & Results

- Built a bench scale supercritical water hydrocarbon cracking apparatus with hydrogen production capacity of 100 SCCM, Max. temp of 600^{o}C & Max pressure of 26MPa.
- Built a bench scale hydrocarbon cracking apparatus with hydrogen production capacity of 100 SCCM, Max. temp of 800^{o}C & Max pressure of 10MPa.
- Demonstrated continuous H_2 production using both virgin synthetic & used lube oil at sub and supercritical conditions.
- Tested the system with nickel, carbon and alkali catalysts at sub & supercritical conditions.
- Shown that the steam reforming process that employs a homogeneous catalyst generates H_2 with much higher conversion efficiency & selectivity (& with no catalyst deactivation) than those utilizing heterogeneous catalysts.

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Accomplishments & Results – FY'04

Catalyst type	Gas production rate after 1 hour, mL/min	Gas production rate after 4 hours, mL/min
Ni *(Ni 1-15% on Al_2O_3)*	65	36
Ni *(Ni 25-45% on Al_2O_3)*	71	40
Carbon *(Activated Coconut Char)*	50	30
Alkali *(KOH 0.025M)*	102	102

Temperature: 450°C
Pressure: 3200 psi
Oil/water feed ratio: 2ml/4ml

Accomplishments & Results – FY'04

Catalyst type	Performance
Ni *(Ni 1-15% on Al_2O_3)*	Low conversion, conversion drops as a result of catalyst deactivation.
Ni *(Ni 25-45% on Al_2O_3)*	Low conversion, conversion drops as a result of catalyst deactivation.
Carbon *(Activated Coconut Char)*	Low conversion & low selectivity toward hydrogen formation.
Alkali *(KOH 0.025M)*	Higher conversion & good selectivity toward hydrogen formation. No catalyst deactivation observed.

Homogeneous (Alkali) catalyst (KOH) performance was better than the earlier heterogeneous catalysts used (*i.e.* Ni & carbon) for the steam reformation of lube oil to hydrogen gas.

Accomplishments & Results – FY’05

Temperature, °C	Pressure, psi	Gas flow rate, mL/min
540	1050	407
535	1500	351
530	2000	275
525	2500	256

n-Hexadecane, $C_{16}H_{34}$

Accomplishments & Results – FY'05

Flow Rate, mL/min		Temperature, °C	Pressure, atm	Gas flow rate, mL/min
Synthetic Oil	Water			
2	6	710	1	392
2	2	715	1	698
2	1	715	1	896

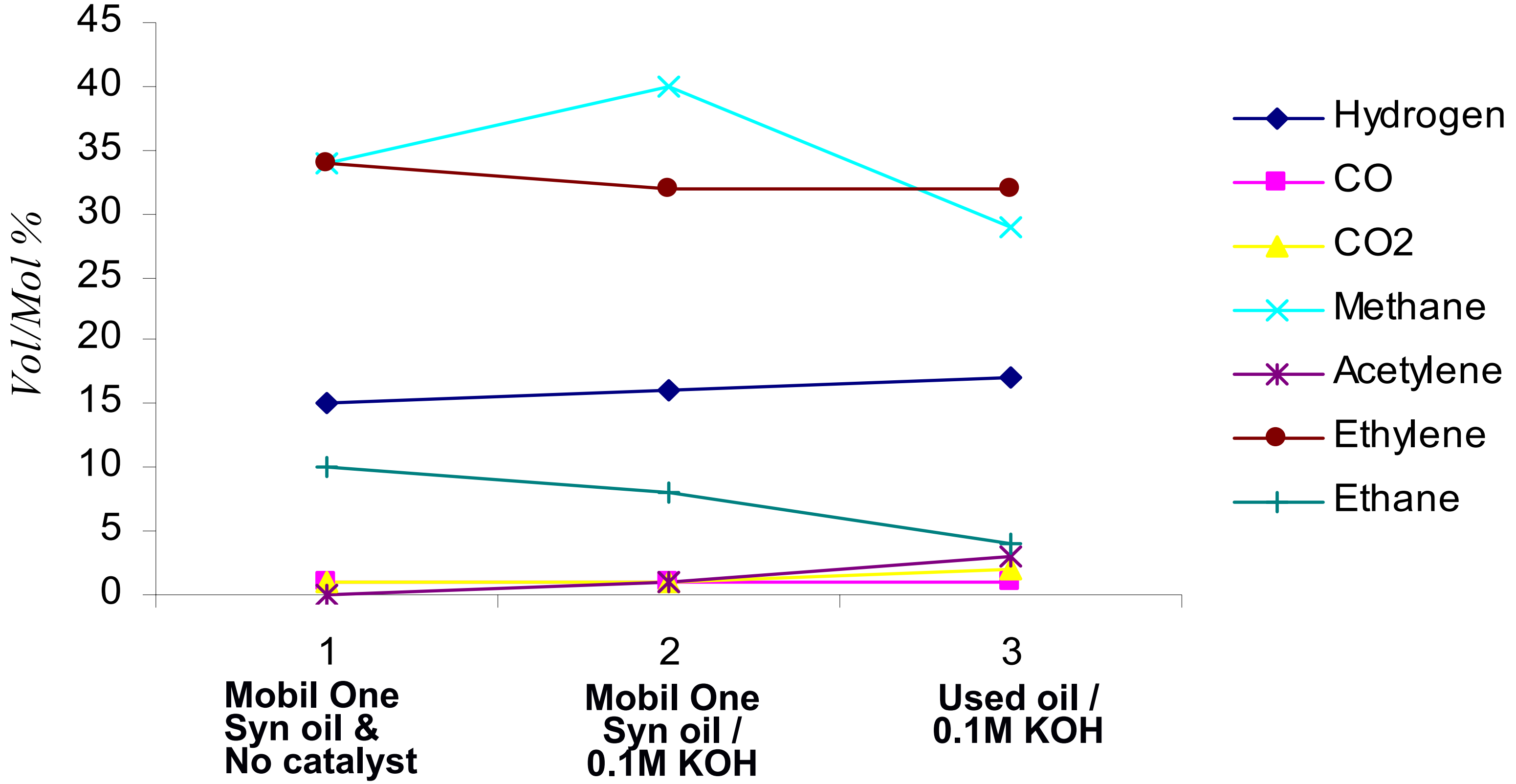
Accomplishments & Results – FY'05

Oil*	Catalyst	Temperature, °C	Pressure, atm	Gas flow rate, mL/min
Synthetic**	none	715	1	896
Synthetic	none	750	1	923
Synthetic	0.1M KOH	750	1	996
Used	0.1M KOH	755	1	728

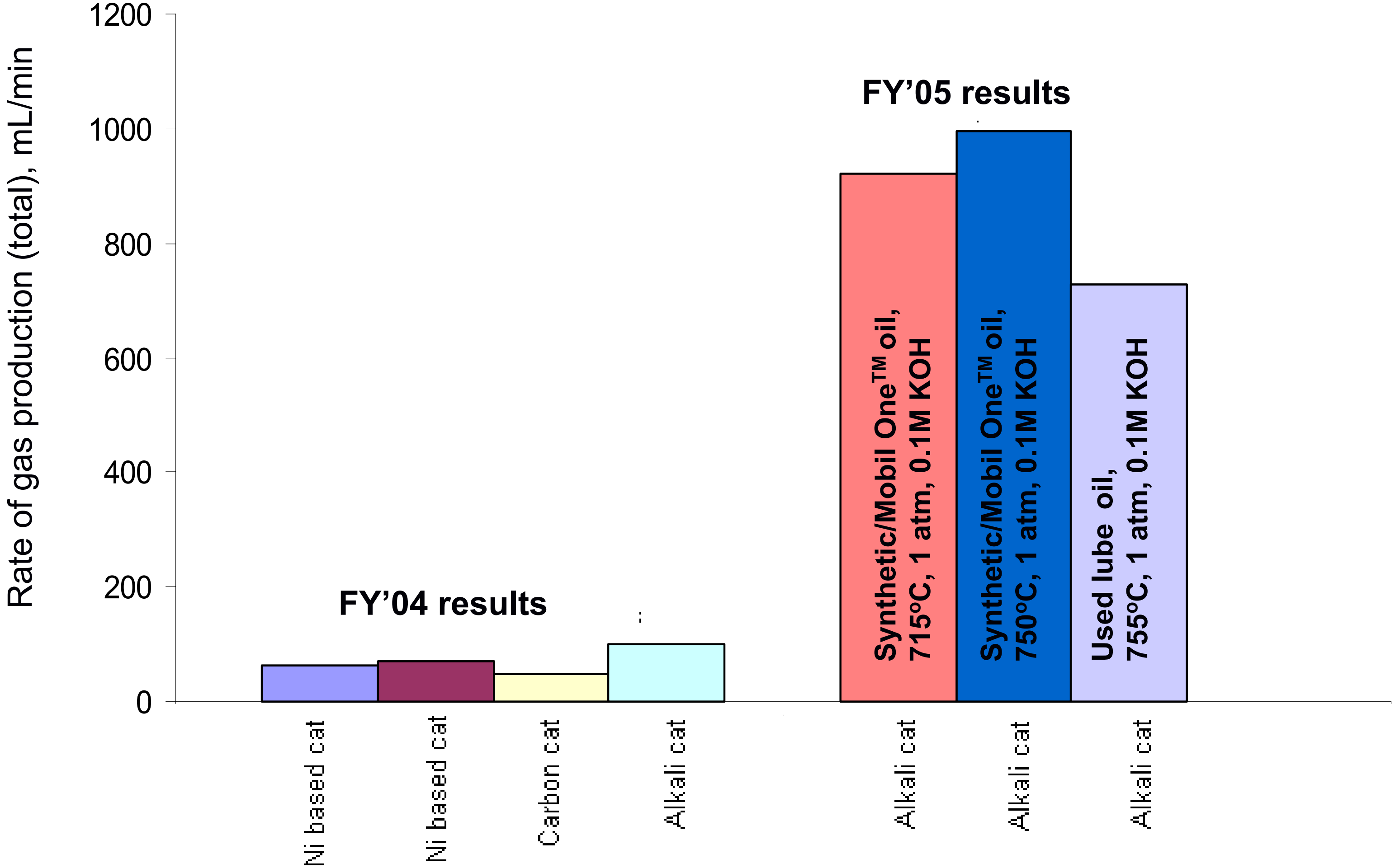
*** Oil/water feed ratio: 2ml/1ml**

**** Virgin Mobil One™ oil**

Accomplishments & Results – FY'05



Accomplishments & Results To-Date



Accomplishments & Results - Summary

- At 750^{o}C & in the presence of 0.1M KOH catalyst, steam reformation of virgin synthetic oil (Mobil One^{TM}) generated hydrogen that was 66% of that contained in the oil, in addition to lower hydrocarbons such as methane, ethane & ethylene.
- At 750^{o}C & in the presence of 0.1M KOH catalyst, steam reformation of used lube oil generated hydrogen that was 41% of that contained in the oil, in addition to lower hydrocarbons such as methane, ethane & ethylene.
- Conversions above are 8-12 times higher than those obtained during previous FY'04 activities.

Plans for FY'06 Activities

- Double the yield of hydrogen production via alkali-catalyzed steam reformation of used lube oil to 80% or higher.
- Further improve the process selectivity toward hydrogen.
- Evaluate other alkali metal hydroxides (NaOH, LiOH) & compounds such as ZrO_2, K_2CO_3, etc. as catalysts for the steam reformation of used lubricating oils.
- Evaluate kerosene range HCs for the production of hydrogen.
- Complete flowsheet analysis & costing of a 1500-8000 lbs/day LH2 production plant utilizing used lubricating oils.

Future Prospects & Proposal Activity

- Established a relationship with the Chevron Technology Ventures, LLC Houston, Texas.
- Submitted a proposal entitled "On-site Reformation of Diesel Fuel for Hydrogen Fueling Station Applications," for funding to U.S. DOE - Florida Hydrogen Initiative, jointly with the Chevron Technology Ventures, LLC Houston, Texas, in July 28th, 2005, funding requested: $500,000. This proposal is still pending before DOE/FHI.

Thank You

Questions?