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Onboard Gasoline Separation for Improved Vehicle Efficiency

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ABSTRACT

ExxonMobil, Corning and Toyota have collaborated on an Onboard Separation System (OBS) to improve gasoline engine efficiency and performance. OBS is a membrane based process that separates gasoline into higher and lower octane fractions, allowing optimal use of fuel components based on engine requirements. The novel polymer-ceramic composite monolith membrane has been demonstrated to be stable to E10 gasoline, while typically providing 20% yield of ~100 RON product when using RUL 92 RON gasoline. The OBS system makes use of wasted exhaust energy to effect the fuel separation and provides a simple and reliable means for managing the separated fuels that has been demonstrated using several generations of dual fuel test vehicles. Potential applications include downsizing to increase fuel economy by ~10% while maintaining performance, and with turbocharging to improve knock resistance.

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INTRODUCTION

Nearly all vehicles sold today specify a single fuel. For spark ignition gasoline engines the fuels are specified based on octane rating. Several fuel grades are available: In the U.S., regular or RUL typically has a pump octane rating of 87 AKI (~92 RON) and premium or PUL has a pump octane rating of 93 AKI (~97 RON), with several intermediate grades available.

Most vehicles sold today specify regular gasoline. A smaller number of high performance and luxury vehicles specify premium gasoline, and generally have higher compression ratio engines.

Increasing compression ratio has long been recognized as an effective means of improving combustion efficiency, but historically has been knock limited by the octane rating of the fuel used (1). Advances in automotive computer control of spark timing, fuel injection (both port and direct), control of air-fuel ratio, variable valve timing and cool exhaust gas recirculation, have allowed substantial increases in effective compression ratio, while allowing the use of regular ~92 RON gasoline without knock (2). In some cases the use of premium gasoline can improve peak performance, but at an added cost to the consumer, and with little effect on fuel economy, if the engine is designed to operate on regular gasoline.

Gasoline itself is a complex mixture of hydrocarbons, oxygenates and additives with a range of physical and chemical properties. The composition can vary widely. In Japan for example, there are no oxygenates and the higher octane components are typically aromatic hydrocarbons of about 105-115 RON. Aromatic levels of 25-30 vol.% are typical. In the United States, the oxygenate ethanol is presently at the 10 vol.% level, with higher levels envisioned. Ethanol has an octane rating of about 109 RON, allowing lower octane hydrocarbons blends to be used to meet the required market fuel octane rating. Non-alkylate, aliphatic hydrocarbons in gasoline average about 83 RON. The more volatile light hydrocarbons can have RONs approaching 100 (iso-pentane RON = 92), while the higher boiling aliphatics can have RONs that can be much lower (n-heptane RON =0).

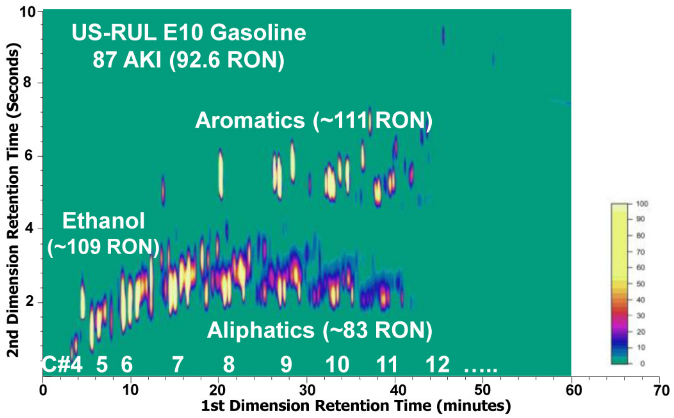


Figure 1. Gasoline composition. 2-D GC of US RUL Gasoline.

Figure 1 illustrates the compositional complexity of a U.S. RUL gasoline by 2-D GC (3). The 2D- GC technique separates components in the gasoline by boiling point (1st dimension) and polarity (2nd dimension). Gasoline is a complex mixture of C_4-C_{12} hydrocarbons and ethanol blended to obtain required octane number (to prevent engine knock) and volatility (for cold start). Additives, including antioxidants, metal inhibitors, and detergents, are used to improve fuel stability and engine cleanliness. Premium gasoline typically also includes highly branched paraffinic alkylate (isooctane), but supplies are limited by refining capacity and cost.

The effect of fuel octane number and composition on engine performance in a high compression ratio, spark ignition, direct injection (CR13, SIDI) test engine was studied in a collaborative effort by ExxonMobil and Toyota (4). Under low load, low speed stratified conditions it was found that a very low octane, 84 RON, aliphatic fuel resulted in higher efficiency and lower hydrocarbons than obtained with regular 92 RON gasoline. Spark induced compression ignition (SICI) was evident with the very low RON fuel. Furthermore, studies at wide open throttle conditions indicated that a higher octane, highly aromatic fuel (RON 103, 60% toluene) provided significant torque benefits compared to pure isooctane (RON=100) greater than expected based on RON alone.

Octane Requirement Map

Subsequent engine tests, using the same 2 liter 13CR SIDI described (4), under both stratified, lean burn conditions, and homogeneous stoichiometric conditions, using a variety of fuel compositions with RON from 84 to 103, at several load points were made confirming these results. From these data an "Octane Requirement Map" was developed. Lower RON fuels gave higher brake efficiency at low loads in stratified operation. At intermediate loads and stoichiometric operation, maximum efficiency was obtained with the intermediate RON fuels. At higher loads and stoichiometric operation the higher RON fuels gave the best efficiency and were required to avoid knock. Spark advance for each fuel was set by trace knock limit (TKL).

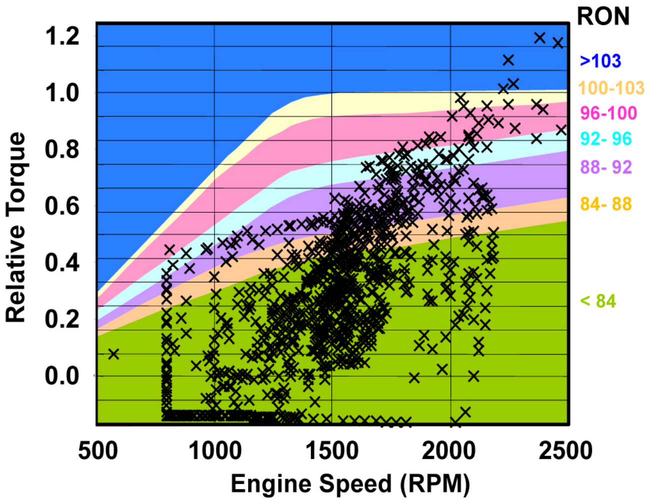


Figure 2. Octane Requirement Map for LA-4 Drive Cycle

The optimal conditions and fuel required for each operating point in the LA-4 drive cycle was determined using the assumption of switching point on mode map, as shown in Figure 2. LA-4 is the EPA Urban Dynamometer Driving Schedule, or UDSS, which represents city driving conditions (22). The total quantity of each RON fuel was then determined by integrating fuel use over the cycle. The relative percentage of each shown in the "pie chart" as Figure 3 shows that optimal engine efficiency requires only modest amounts of >96 high RON fuel, even with 13:1 CR. Most of the drive cycle required <92 RON fuel for optimal efficiency. The results suggest that <84 RON fuel may be acceptable under some low load conditions, but 84 RON was lowest RON tested.

The "Optimal RON Map" fuel requirements for the LA-4 cycle using the SIDI 13:1 high compression engine data just described were used to estimate potential fuel economy credits.

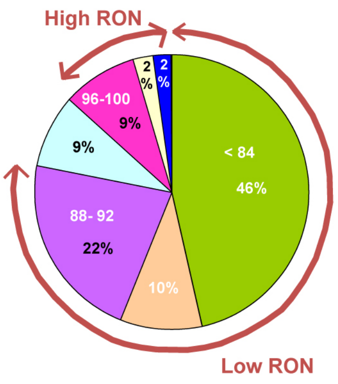


Figure 3. RON Distribution required for LA-4 Drive Cycle.

Fuel economy credits were estimated to be 8.5% by using the optimal fuel octane throughout the LA-4 drive cycle. The 13% increase in torque available with 13:1 CR engine operated on the highest octane fuel allows for a reduction in displacement resulting and in another 7% potential improvement in fuel economy while maintaining constant performance. All totaled, potentially a 15.5% increase in fuel economy. About half the fuel economy benefit came from the higher compression ratio of 13:1, compared to the base compression ratio of 9.8:1; and half from the torque increase, thereby allowing a smaller displacement engine or higher gearing.

These results were intriguing. This "Octane Requirement Map" indicated that nearly 80% of the fuel requirement using a very high compression engine might be met with conventional regular gasoline having RON 92 or less. When under load, about 20% premium gasoline of RON 97 or greater would be required for optimal performance. Notably, even with premium fuel it would not be possible to reach MBT under all conditions at 13 compression ratio. However, concentrating the higher octane components in gasoline, such as aromatics and/or ethanol (in some markets), might provide the higher RON and ignition characteristics required.

This suggested potential for a dual (or multi) fuel strategy to realize significant efficiency and emissions benefits. Recognizing the difficulties of providing multiple fuels to a vehicle, and the desirability of providing a higher RON fuel than commonly available, the thought of separating gasoline onboard was raised.

CONCEPT OF HIGH COMPRESSION ENGINE WITH ONBOARD SEPARATION SYSTEM

The Onboard separation concept arose from the fundamental combustion research jointly conducted by ExxonMobil and Toyota (4). From these studies we learned that aromatics have higher knock resistance than other molecules at the same octane. The high octane fuels used in the studies described above to establish the Octane Requirement Map had high percentages of aromatics' e.g. 60% vol.% at 103.

Recognizing that aromatics are among the highest octane components present in all gasoline, we developed the concept of separating the gasoline into high and low octane fuels onboard a vehicle by means of a pervaporation membrane process (5). Using engineering models for ExxonMobil's proprietary aromatic selective membranes (6, 7), we found that conceptually an onboard system could be developed to provide about 20% yield of 100 RON (research octane number) from typical 92 RON regular gasoline.

Onboard Separation

Onboard separation, or OBS, is a membrane based process that separates gasoline into higher and lower octane fractions, allowing optimal use of fuel components based on engine requirements. The conceptual scheme is shown in Figure 4.

When regular grade gasoline of about 92 RON is separated, two fuels are produced. The higher octane fraction can reach about 100 RON, while the corresponding lower octane fraction is typically 90 RON, or less, depending on yield. About 20% yield of the higher octane fuel can be obtained with most regular gasolines. Both yield and octane can vary with gasoline composition and fuel demand.

The availability of about 100 RON fuel enables the efficient use of a higher engine compression ratio thereby improving engine efficiency and torque. Each fuel is provided to the engine as required to obtain optimal performance.

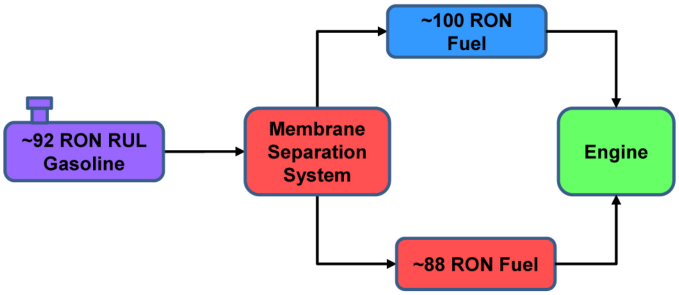


Figure 4. Onboard Separation Concept

Fuel Compositions

Typical regular unleaded gasolines were used for most vehicle, membrane and OBS system evaluations. Japan RUL gasolines having about 90 RON were sourced from a Japanese refinery. Typical aromatic contents were 25-30 vol.%, depending on season sampled. U.S. RUL E10 gasoline having 87 AKI (92 RON) was obtained from a U.S. East Coast terminal. Additional properties and compositions of these fuels are provided in tables that follow.

Ethanol was also splash blended at 10 vol.% with the Japan RUL for membrane lifetime and performance testing. This increased the octane number from 90 to about 93 RON.

Several fuel blends were prepared to simulate the separated fuels. The blend compositions were based on both laboratory membrane separations of gasoline and engineering models of the membrane system. Fuels were blended from refinery products to simulate separated fuel compositions and properties. Fuel properties are shown in Table 1. These fuels were used for initial dual fuel engine bench tests and tuning of the test vehicles.

Table 1. Fuel Properties for Bench Tests

Fuel	W-RUL	Lo RON	Mid RON	Hi RON	Max RON
RON	91.7	89.4	96.6	99.3	101.8
MON	82.7	81.3	85.6	87.7	91.3
AKI	87.2	85.4	91.1	93.5	96.6
Aromatics, wt%	32.2	24.9	59.3	68.6	78.0
LHV kJ/g	43.2	43.4	42.2	42.0	41.6
RVP kPa	92	87.8	36.1	30.2	23.0
T10 %vol, C	51	41	77	84	99
T50 %vol, C	101	88	120	126	129
T90 %vol, C	157	139	159	162	153

The base winter grade fuel W-RUL had RON 91.7 and RVP 92 kPa with aromatic content of 32 wt.%. The LoRON fuel blend RON was 89.4 with RVP 88kPa and aromatic content of 24.9%. Several HiRON blends were made with octane numbers of about 97 to 102, with increased aromatic contents from 59 to 78 wt.%. All HiRON blends had lower vapor pressures consistent with the actually separated fuels. The HiRON blend at 99 RON was similar to actually separated fuel.

Dual Fuel Engine with DI and PFI

Toyota D-4(S) 1AZ-FSE 2L engines were modified, increasing compression ratio from 9.8 to 13:1, while maintaining Direct Fuel Injection (DFI) for the lower octane fuels, and adding Port Fuel Injection (PFI) for the high octane fuel to evaluate dual fuel operation on both the test bench and in the OBS test vehicles, as shown in Figure 5.

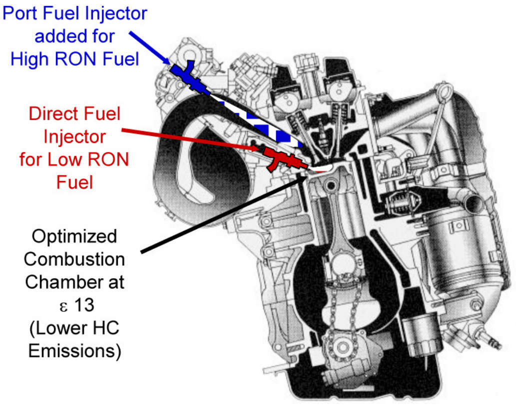


Figure 5. Dual Fuel DI+PFI SI Engine, based on 1AZ-FSE.

This injector configuration was used to minimize fouling of the direct injectors, while providing adequate performance with HiRON fuel when under load and stoichiometric to rich conditions. The system is similar to that described for the dual injector 2GR-FSE engine (14).

The original deep cavity pistons designed for stratified charge applications were replaced with shallow cavity pistons as used in the stoichiometric D-4S (13), with an aim for lower HC emissions. Variable valve timing was not used. Specifications are provided in Table 2.

Table 2. Specifications for a modified engine, with both direct and port fuel injection.

Displacement	1998 cc
Compression Ratio	13.0:1
Bore * Stroke	86 * 86 mm
Valve Mechanism (fixed timing)	16-valve DOHC, Chain Drive
Direct Injection	D4 Fan Spray Injector at 12 MPa
Port Injection	PFI- Multi at 400-500 kPa

Wide open throttle (WOT) testing of this dual fuel engine on the dynomometer confirmed the expected improvements in torque and fuel consumption on increasing compression ratio from 9.8 to 13:1 when using the higher octane fuels and port fuel injection, as shown in Figure 6. Torque was up 12% and achieved MBT at all engine speeds with the nominal 103 RON fuel (actually MaxRON =102 RON). Fuel consumption (BSFC) decreased by about 10% at 4000 rpm.

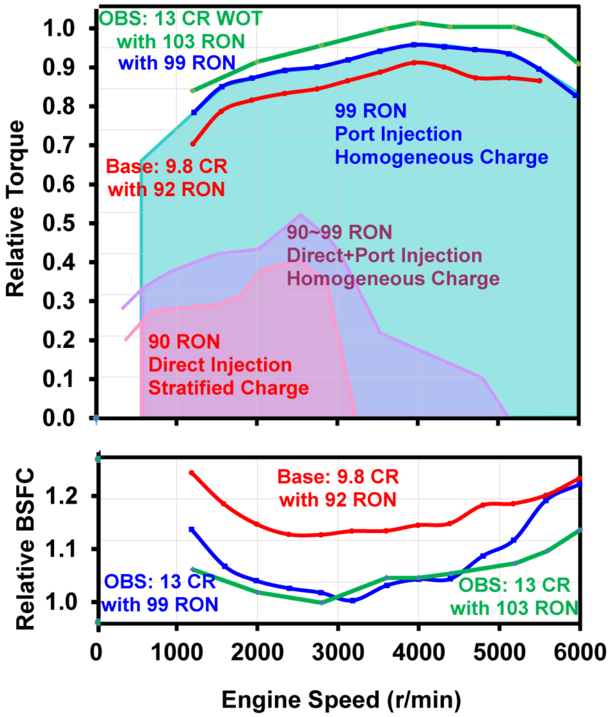


Figure 6. Dual Fuel 13CR Engine Test at WOT

At 99 RON, torque was up about 5% at the TKL and did not achieve MBT spark timing. Although not at MBT spark timing, fuel consumption improvement was comparable to that achieved with the higher octane fuel, except at the highest engine speeds.

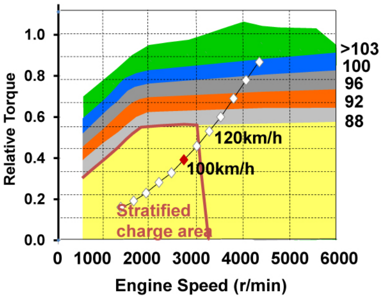
Figure 6 also indicates the regions of the engine map corresponding to use of direct injection with stratified fuel charge at low load using lower octane fuels, the transition region where both direct and port injection are used to meet intermediate octane requirements, and the homogeneous port injection region using high octane fuel at higher loads.

SICI combustion was not apparent with the 88-90 RON low octane fuels actually separated, thereby limiting the effectiveness of the stratified charge approach originally envisioned (4). The engines were therefore operated stoichiometrically, after the initial trials.

Drive Cycle Octane Requirements

A simplified Octane Requirement Map, shown in Figure 7 and similar to that shown in Figure 2, was used to estimate drive cycle octane requirements based on load and engine speed required at 13 CR. In emission evaluation mode, HiRON requirement is less than 20%. In high speed, high load cycles, the optimal HiRON requirement can be more than 40%.

For example, in the Japan 10-15 mode, only 2% HiRON fuel would be required, leading to a calculated fuel economy improvement of up to 5.8%. Other representative drive cycles include LA#4 (EPA Urban), EPA Highway, and EC (European City) mode.



Mode	HiRON %	LoRON %
Japan 10-15	1.4	98.8
LA #4	7.8	92.2
Highway	4.9	95.1
EC	13.8	86.2
US06	43.9	56.1

99 RON / 88 RON % Required

Figure 7. Drive Cycle HiRON / LoRON Octane Requirements

In a sustained US06 high speed, high load mode about 40% fuel of >96 RON would be required. The fuel economy improvement was estimated to be 8.8% with a 50/50 split of 99 RON HiRON and 88 LoRON. Estimates with performance maintained showed the following, with an expected 20/80 HiRON/LoRON split the fuel economy gain decreased to 2.9%. If no HiRON was available, fuel economy would be −0.3% relative to the base engine.

This same map was also applied to the dual fuel engine management system to control fuel delivered. The dual fuel DI+PFI engine was tested both on the engine stand and in a RAV4 test vehicle. Separate fuel tanks were used for the regular 92 RON gasoline, 89 RON LoRON fuel and 102 RON HiRON fuel blends. Each fuel was delivered to meet the Octane Requirement Map as required. The results are shown in Figures 8.

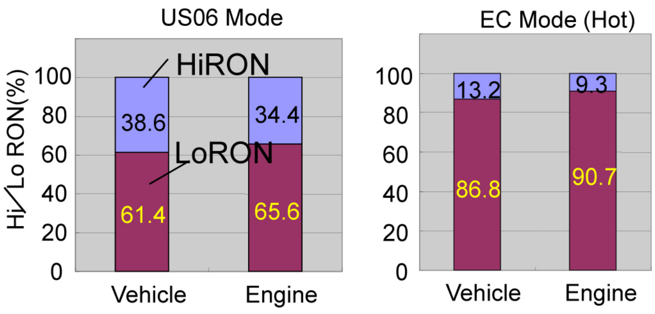


Figure 8. Drive Cycle HiRON / LoRON Octane Requirements

Actual fuel use on the bench and with the vehicle was very consistent with the initial estimates and each other. In the US06 high load mode the test vehicle used about 39% HiRON fuel. In the less severe EC mode (hot), the vehicle used 13% HiRON fuel.

Additional testing was done to determine vehicle performance. As expected, the increased torque available with the 13:1 CR engine operated on the 102 RON HiRON fuel provided a substantial improvement in acceleration when compared to results obtained using the 92 RON regular gasoline. Acceleration times from 40-80 km/h were improved by 7%. The improvement was essentially the same when the optimal RON fuel mixtures were delivered as shown in Figure 9.

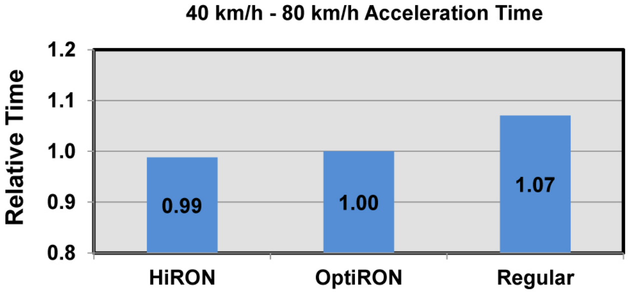


Figure 9. RAV-4 Dual Fuel DFI+PFI Vehicle Performance

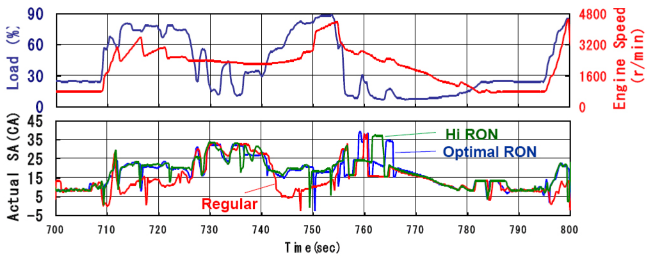


Figure 10. Spark Timing with Optimal RON Fuel: US06

Full power was delivered with minimal HiRON fuel consumption when following the optimal RON blend map developed from the bench data. Spark timings were essentially the same, and not retarded with the optimal RON when compared to use of the 102 RON high octane fuel. The results for a portion (700-800 seconds) of the US06 high load condition, accelerating from 0 to 110 km/h and then decelerating back to 0 km/h, are shown in Figure 10. There appears to be some fluctuation in spark advance response time, most likely because of operator variance, primarily on deceleration. The curves track well when under load.

In this test the Optimal RON fuel required was obtained by injecting the 90 RON Regular fuel by DI and 102 RON fuel by PFI proportionally, as needed.

The rapid spark timing changes to limit engine knock and fuel enrichment to control of exhaust gas temperature, while maintaining adequate performance are important considerations for an OBS vehicle.

DEVELOPMENT OF AN ONBOARD SEPARATION SYSTEM

OBS Vehicle System

The OBS System consists of the Membrane Module, Heat Pipe (exhaust to fuel heat exchanger), Integrated Heat Exchanger (fuel coolers), a Modified Fuel Tank and a Dual Fuel Engine, along with fuel management software. The OBS vehicle system is illustrated in Figure 11.

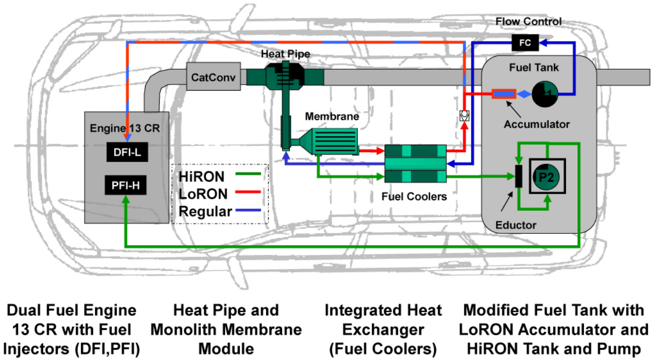


Figure 11. OBS Vehicle System.

On-board membrane separation requires heating and partially vaporizing about 0.5-3 g/s gasoline to about 140-160°C at 400 kPag. This is nominally the same pressure required for fuel rail. The fuel rate to the membrane is similar to the average fuel use rate, or about 1 g/s. Variable fuel rate is also needed to control fuel temperature in response to exhaust energy.

Hot engine exhaust provides the 0.5 to 1 kW heat required by means of a heat pipe. Several heat pipe designs were tested. The heat pipe is basically a sealed tube containing a small amount of water under vacuum. The water is vaporized by heating at one end and condensed by cooling at the other, thereby transferring energy. The condensed water returns by gravity and/or capillary forces to be re-vaporized creating an internal circulation of "steam" and hot water. Heat pipes can have exceptional thermal conductivities, up to 10x greater than pure copper (15).

Because of the wide range of exhaust gas temperatures (300-800°C) and rates (5-100 g/s) experienced in real driving, water charged to the heat pipe is limited. Using only 3-4 g of water safely limits the internal steam temperature and pressure at high exhaust energies. Heat transfer effectively stops when all of the water is vaporized at the exhaust heat exchanger end.

The vapor-liquid fuel mixture is separated into a high octane "HiRON" permeate and lower octane "LoRON" retentate by the Membrane Module. The hot products are cooled by preheating the gasoline feed and/or by air fin cooling in the Integrated Heat Exchanger.

LoRON product is provided to the Direct Fuel Injector. Excess LoRON returns to the tank through a LoRON Accumulator volume. At high demand, gasoline flows to the DFI through the Accumulator buffer volume. This design limits dilution of the main tank fuel.

HiRON product is obtained under vacuum provided by an Eductor using pressurized HiRON fuel circulating to the Port Fuel Injector by means of a second Fuel Pump. HiRON product is stored in a small ~2-4 liter HiRON Tank, located within the main Fuel Tank. The vapor space is shared, so no additional fuel vapor management is needed. The volume of HiRON fuel varies considerably when in use, but is replenished continuously on separation of the main tank fuel.

Figure 12. First OBS RAV-4 Dual Fuel Test Vehicle

A Toyota RAV-4 served as the primary OBS test vehicle. Several versions of dual fuel engines were used, transitioning from the stratified charge DFI to stoichiometric PFI for the LoRON fuel, while using a second PFI for HiRON fuel. The initial test vehicle mounted an OBS system in the cargo bay, along with tanks for both the HiRON and LoRON products. This vehicle is shown in Figure 12, with glycol heated, early spiral wound PEI-2 membranes (2), pre-flash and vacuum pump, and separate Hi/Lo RON tanks (in addition to main fuel tank).

This system was greatly simplified and miniaturized as the program proceeded. In subsequent vehicles the heat pipe, membrane module and heat exchangers were mounted under the floor of the vehicle. Initial tests of the system were conducted with laptop based controls and data-logging for both engine management and OBS flow control.

A Camry test vehicle was also used in the most recent tests, with under-floor OBS System, EMRE-Corning Polymer-Ceramic Composite Membrane, Heat Pipe and Integrated Fuel Coolers, and with integration of the controls into the vehicle ECU. A dual fuel, stoichiometric 2.4 liter engine was used. Significant simplifications and improved packaging of the OBS components under-floor of the vehicle are shown in Figure 13.

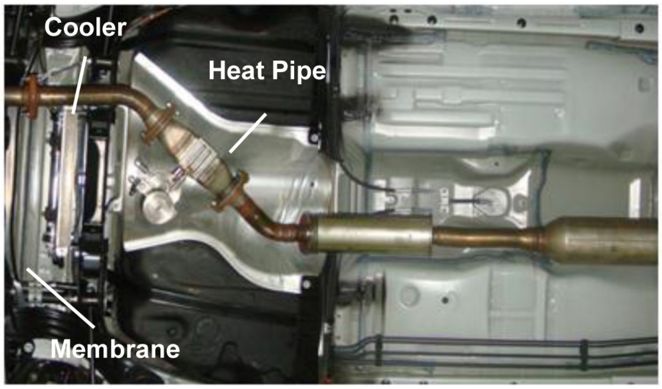


Figure 13. 2011 OBS Camry Dual Fuel Toyota Test Vehicle

Membranes for Gasoline Separation

A polymer coated ceramic monolith membrane element is used to separate gasoline into high and low octane fractions.

Several polymer formulations have been evaluated. Our initial membranes used the diepoxide cross-linked/esterified polyimide polyester copolymers (PEI-2) developed for separating aromatics from refinery streams (6,7). Both spiral wound and ceramic monolith configurations were used. Unfortunately, these formulations were not stable to ethanol.

New cross-linked polyether-amine/epoxy polymer formulations were developed that are stable to ethanol in gasoline while separating ethanol and aromatics from the lower octane aliphatic components in gasoline (8). A preferred polymer (9) was prepared from 400 mw polypropylene oxide diamine (Jeffamine® D400) and diepoxy-n-octane (DENO).

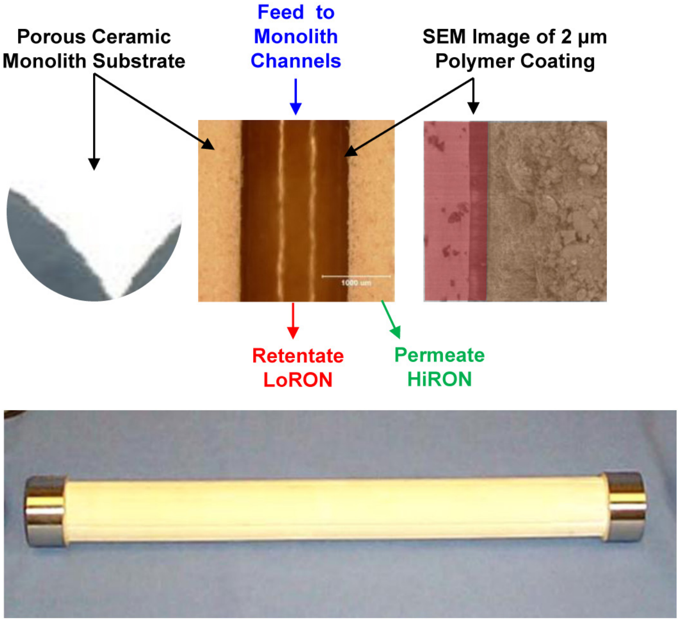


Figure 14. Composite Polymer-Ceramic Monolith Membrane Test Unit.

The composite polymer-ceramic monolith membrane is shown in Figure 14.

The monolith structure is very much like automotive mobile emissions substrate and is made from an asymmetrically porous ceramic, preferably based on Cordierite (8). Channel sizes from 1 to 2 mm are typical, with test element surface areas ranging from 0.1 to 0.4 m^2 and volumes of 0.15 to 0.6 liters. Most test monoliths used on the vehicle were 25 mm OD × 304 mm long, with 2 mm channels having 0.1 m^2 surface area.

The membrane itself is a very thin, typically 2 microns thick, polymer coating on the inside of the channels, supported by a thin layer of micro-porous metal oxide having a porosity of 0.01 to 0.5 microns. The underlying monolith porosity is about 10 microns or greater to minimize pressure drop. We have found this composite coating to be very stable and the monolith very robust mechanically.

Gasoline is separated by the polymer membrane into high and low octane fractions by a process known as pervaporation. Preheated gasoline feed at ~150°C flows through the monolith channels at an average rate of about 1 g/s.

Separation of a model fuel illustrates membrane performance as shown in Table 3. Conditions used were DENO-D400 polymer membrane 0.01 μm porosity, 0.1 m2 ceramic monolith; 1 g/s feed rate, 155°C, 520 kPag, and 15.9 kPa permeate pressure (vacuum). Data were taken after being lined-out at 525 Hours on Stream. Pervaporation concentrates ethanol and aromatics in the permeate that passes through the membrane. Transport is by solution-diffusion mechanism, coupled with component vapor partial pressure driving force (chemical potential gradient).

Table 3. Membrane Separation of a Model Fuel

Membrane Separation	Feed	Retentate	Permeate
Rate, g/s	1.03	0.74	0.29
Yield, wt.%	100.0	72.4	27.6
n-Heptane	45.6	55.2	20.4
Toluene	45.3	42.5	52.6
Ethanol	9.1	2.3	27.0

High octane aromatics, and ethanol, in the gasoline feed are preferentially absorbed by the membrane polymer. Vacuum is applied to the opposite side of the membrane pulling the concentrated aromatics and ethanol as vapor through the porous membrane support. Permeation rates of 0.1 to 0.4 g/s are typical. The vapors are condensed by cooling, and the high octane fuel is stored in a small tank until needed.

The present OBS Membrane Module consists of the Polymer Coated Ceramic Monolith Element sealed, typically with Viton O-rings, into a coaxial tubular stainless steel housing, typically with removable ends, but some have been welded. The inlet end is typically fitted with a nozzle, or equivalent, which effectively distributes the mixed phase vapor/liquid membrane feed uniformly to the monolith channels. A thermocouple located in the nozzle spray provides the temperature of the feed to the membrane.

Early OBS Membrane Performance

Separation of gasoline in both the laboratory and on an early test vehicle (Figure 12) using spiral wound membranes made with PEI-2 polymer provided the higher and lower octane fuels anticipated based on an ExxonMobil refinery model. The results are shown in Table 4, for the RAV4 with two PEI-2 Spiral Wound Membrane Modules of 2.2 m^2. Conditions used were1 g/s feed rate, 5 g/s retentate recycle, 250 kPa Backpressure, 15 kPa permeate pressure (vacuum), ~ 102°C. In this early test the feed to the membrane system was provided by a separate fuel pump at 250 kPag and heated to ~110°C using an independent hot glycol heat exchanger. Retentate was reheated to ~110°C and recycled by means of a separate pump was used to maintain temperature across the membrane element. Vacuum on the permeate side of the membrane was obtained by means of a 2 stage diaphragm vacuum pump.

Table 4. Early OBS Separated Fuel Yields and Properties.

Products from OBS RAV-4 using PEI-2 Spiral Wound Membranes with Pre-flash		Japan RUL Gasoline	Low RON	High RON
Rate (out)	g/s	1.02	0.81	0.21
Yield	wt. %	100.0	79.4	20.6
Density (OBS)	g/cc	0.73	0.71	0.81
RON		90	88	98.5
Distillation D86	T10	45.5	40.5	96.5
Distillation D86	T50	88	78.5	116.5
Distillation D86	T90	138	140.5	142.5
FIA Aromatics	vol.%	25.5	16.4	61.8
Aromatics	wt.%	35.1	26.1	70.9
RVP	kPa	86.5	93.7	15.3
Sulfur	ppm	102	78	170

The separated products were clear and bright. HiRON fuel was obtained having 98.5 RON at 21% yield on 90 RON regular gasoline feed. Aromatics increased from 35% in the feed to 71% in the HiRON product. The corresponding LoRON fuel had a RON of 88, with aromatics reduced to 26% and higher RVP. Additives and dyes remained in the LoRON product.

Sulfur was concentrated in the HiRON product. This could improve 3-way catalyst performance, by processing more sulfur at higher exhaust temperatures.

Several issues were noted in these early tests: the fuel required a pre-flash to limit light hydrocarbons in the high octane product, and the large spiral wound membranes used required about 30 minutes or more to warm up to operating temperature using an externally heated glycol heat exchanger and retentate recycle. Temperature was limited to less than120°C. Also, the LoRON product required chilling to prevent loss of light hydrocarbon vapors, when collected at ambient conditions.

Initial experiments, with the PEI-2 polymer coated on porous ceramic monoliths, led to substantially improved initial membrane performance. Membrane area requirements decreased from 2.2 m^2 at 120°C to about 0.2 m2 at 150°C, partially as a result of higher operating temperature and also much thinner polymer coatings. The higher operating temperatures allowed the fuel system to operate at normal 4 barg pressure, thereby allowing OBS LoRON product to be used directly at the fuel rail. Higher temperatures also allowed partial vaporization of the gasoline feed, eliminating the pre-vaporization step, while improving selectivity to aromatics.

Unfortunately, it also became apparent that the polyimide-polyester PEI-2 polymer was unstable in ethanol containing fuels at these conditions, as a result of trans-esterification of the ester linkage.

Ethanol Stable Membrane Performance

Polymer -ceramic composite membranes prepared from the ethanol stable cross-linked polyether-amine/epoxy were evaluated for gasoline separation both in the laboratory and on the test vehicles. Membranes were prepared by slip coating the Corning pre-coat monolith with pre-polymer emulsions and solutions to obtain dense coatings (21). The 0.13 m^2 elements contain 0.6 to 0.8 g polymer after curing, corresponding to an average thickness of about 5 microns.

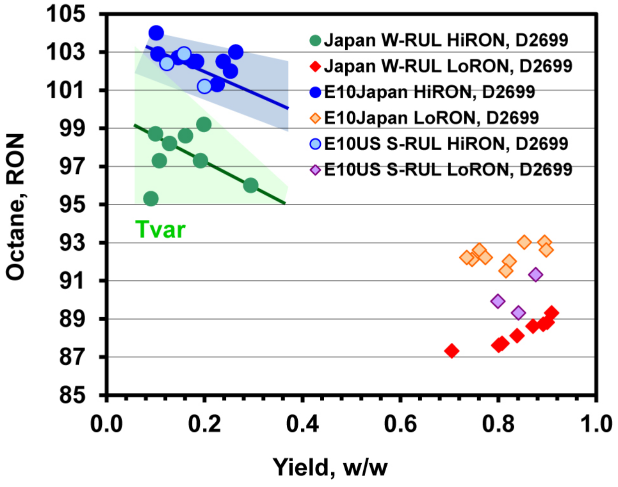


Figure 15. Separation of Gasoline Yield-Octane Relationship Process Variable Study

Laboratory process variable studies were conducted on both conventional Japan RUL gasoline and E10 gasoline (E10Japan blend and E10US S-RUL). The results are shown in Figure 15. Feed pressure was maintained at 400 kPag. Feed rate was varied from 0.5 g/s to 1.5 g/s while maintaining 145°C. Temperature was varied from 105° to 165°C while maintaining 400 kPag and 0.5 g/s feed rate. Permeate pressure varied with product vapor pressure from about 20 to 45 kPa, averaging about 30 kPa.

The results demonstrate separation of market RUL gasoline into high (97-103 RON) and low (88-92 RON) octane fractions. Higher yield-octane was obtained when processing the E10 ethanol-gasoline blends.

With E10 gasoline, HiRON octane was 101 RON at 20% yield. The LoRON product had about 90-92 RON, corresponding to differences in the feed RON. At constant temperature, HiRON octane increased as yield decreased with increasing feed rate. The absolute permeate rate increased slightly as feed rate increased. The HiRON octane changed only 1-2 RON as temperature was varied. Compositions at 20% HiRON yield are shown in Table 5. Both ethanol and aromatics were concentrated in the HiRON E10 product. Ethanol content increased to 25%.

Table 5. OBS Membrane Separated Fuel Yields: Composition and Properties with E10 Gasoline.

OBS Products from E10 US-RUL Gasoline at 152 C, 23 kPa		US S-RUL Feed	Low RON Product	High RON Product
Yield	wt. %	100.0	79.9	20.1
Density (OBS)	g/cc	0.7496	0.7427	0.7809
RON		92.0	89.9	101.2
C1-C5	wt.%	11.5	12.3	8.6
C6+ Non-aromatics	wt.%	47.3	52.2	27.8
Aromatics	wt.%	30.4	28.3	38.8
Ethanol	wt.%	10.7	7.2	24.8

The ethanol free Japan RUL gasoline HiRON product provided 97 RON at 20% yield. The corresponding LoRON product had about 88 RON. At constant temperature, HiRON octane increased as yield decreased with increasing feed rate. Again, the absolute permeate rate increased slightly as feed rate increased.

The HiRON octane changed significantly as temperature was varied. Increasing the temperature from 145° to 160°C, increased RON from 97 to 99. However, lowering temperature to about 135°C resulted in a HiRON product having only 95 RON. Clearly, the separation is more sensitive to conditions when processing Japan RUL gasoline. Compositions at 20% HiRON yield are shown in Table 6. Aromatics were concentrated in the HiRON product. The vapor pressure of the LoRON product increased, based on the increase in light hydrocarbons.

Table 6. OBS Membrane Separated Fuel Yields: Composition and Properties with Japan RUL (no ethanol).

OBS Products from Japan W-RUL at 158 C, 34 kPa		Japan W-RUL Feed	Low RON Product	High RON Product
Yield	wt. %	100.0	79.9	20.1
Density (OBS)	g/cc	0.7386	0.7283	0.7827
RON		90.1	87.8	97.4
C1-C5	wt.%	20.5	22.5	12.7
C6+ Non-aromatics	wt.%	42.1	45.3	29.3
Aromatics	wt.%	37.3	32.1	58.0
Ethanol	wt.%	0	0	0

Experiments were conducted in the laboratory to look into the long term stability of the composite polymer-ceramic membranes. Tests with E10 model feed showed essentially no aging and no apparent degradation of the polymer in continuous tests conducted for up to 2000 hours. The model feed results shown in Table 3 were obtained at 525 hours on stream, and were essentially identical to data taken 141 hours on stream, after an initial lineout period where flux increased from 1.45 to 2.64 g/s-m^2 on initial swelling of the polymer.

Initial results with actual E10 gasoline were not so encouraging. Processing the E10Chiba blend at 150°C 400 kPag, after lining out on E10 model feed, resulted in a yield loss from 27% to 15%, after only 500 hours. Some of this loss was attributed to a re-equilibration of membrane swelling to the differences in feed composition, but fouling was clearly evident. The membranes became very dark in color on contact with the fully additized gasoline. Several attempts to maintain yields of 20% for more than 500 hours were made without success.

Analysis of the used membranes implicated the trace high boiling aromatics and additives in the gasoline. 13C-NMR analysis of the used polymer-ceramic composite after processing E10 gasoline showed the presence of high mw multi-ring aromatics. The data also indicated the polymer was intact. The results are shown in Figure 16.

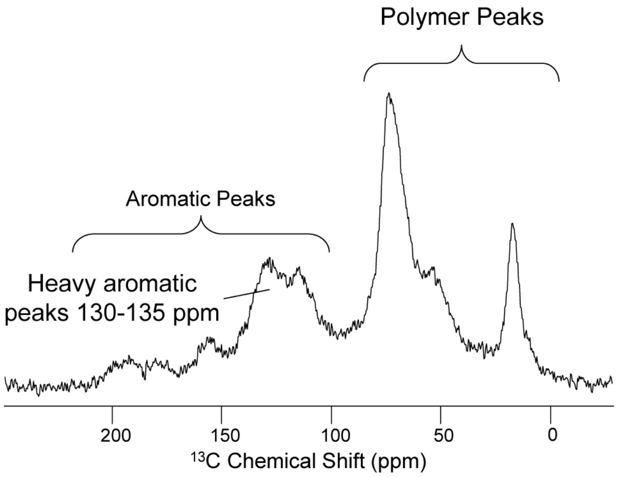


Figure 16. NMR of Used Membrane after 2000 hours on E10 feed

Based on these observations, a special cyclone separation inlet was constructed to bypass the highest boiling liquid fraction of the partially vaporized gasoline feed. The saturated vapor portion, about 70-80% of the feed, was processed over the membrane. The cyclone bottoms were combined with the retentate product and taken as LoRON

The results were dramatic. In initial tests processing the colorless cyclone overhead as feed, there was virtually no aging of the membrane over a period of 200 hours. Processing the cyclone bottoms resulted in a loss of more than half the initial flux over the same time period.

Using this inlet, membrane lifetimes were extended to well beyond 2000 hours when processing fully additized E10 gasoline feed. The life test experiment shown in Figure 17 was conducted using one section of the Corning Partitioned Monolith shown in Figure 18. This 2.3″ dia. × 8″ long monolith has a total area of 0.34 m^2 with a volume of 0.6 liters. Each partitioned section has an area 0.085 m^2, and operates independently of the adjacent sections. Feed rate throughout the test was 0.5 g/s to one section only, with the cyclone inlet at 160°C and the membrane inlet at 145°C and 400 kPag. Permeate pressure was 25 kPa by means of the eductor operating on condensed HiRON product.

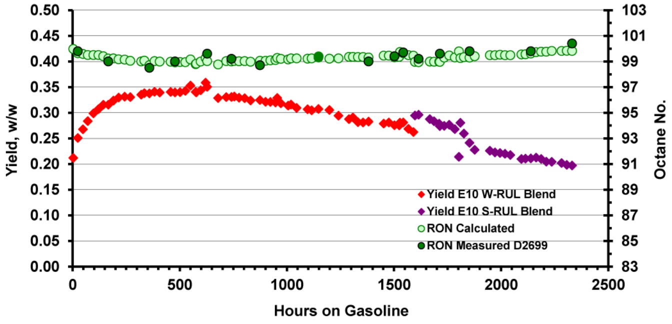
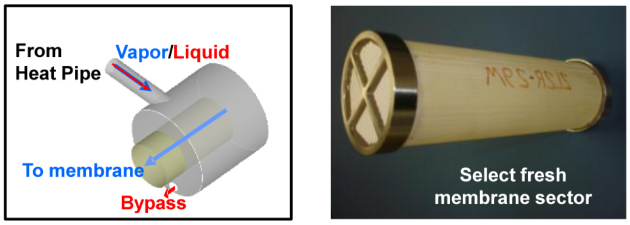


Figure 17. Life Test with E10Chiba Gasoline Blend: Section #2

HiRON yield was greater than 20% throughout the 2300 hour run. Some swelling of the membrane occurred over the first 500 hours, with yield increasing from 20% to 35% on total E10 gasoline feed. HiRON octane decreased slightly from 100 RON to 99 RON, and then increased slowly back to 100 RON as the membrane slowly aged back to 20% yield at about 2300 hours on stream. Analysis of the final HiRON product gave 100 RON/87 MON for 93.5 AKI, with an ethanol content of 18 vol.%. The LoRON product had 91.9 RON/82.3 MON for 87.1 AKI, with ethanol at 5.3 vol.%. Both products passed all oxidative stability tests.

Two adjacent sections of this membrane were used in a similar manner, accumulating more than 4000 hours on stream on this membrane module. One section remained unused. To provide some perspective, more than 2500 gallons (45 drums) of fuel was processed using a membrane module of about 0.5 liters. The partitioned membrane element used in the life test offers flexibility. In the experiment, single partitioned sections were used in turn at 0.5 g/s. Higher flow rates could be processed by using multiple sections. For example two sections could be used at 1 g/s or all four sections at 2 g/s, while maintaining the same membrane lifetime. Alternatively, lifetime could be at least doubled by using two sections at 1 g/s and then the two fresh sections are used to double the lifetime of the module.



Cyclone to Bypass Foulants

Partitioned Membrane Element
(2.3" dia. x 8"; 0.6 liters, 0.34 m^2)

Figure 18. Cyclone Inlet and Corning Partitioned Monolith Membrane.

Results of OBS Vehicle Testing

The OBS system shown in Figure 13 was tested on the vehicle. Both dynamometer and road tests were conducted to confirm OBS system performance and dual fuel engine drivability.

Temperature Control

One of the more challenging aspects of OBS system is control fuel temperature when heated by the exhaust. Exhaust temperatures transition quickly from less than 400° C to more than 700° C, with energy levels of less than 5 to greater than 50 kW. Duties for heating the fuel to 160°C are substantially less, from about 0.5 to 1.5 kW, not including heat losses, which can be significant when vehicle is in motion. OBS loads decrease exhaust temperature by about 100°C.

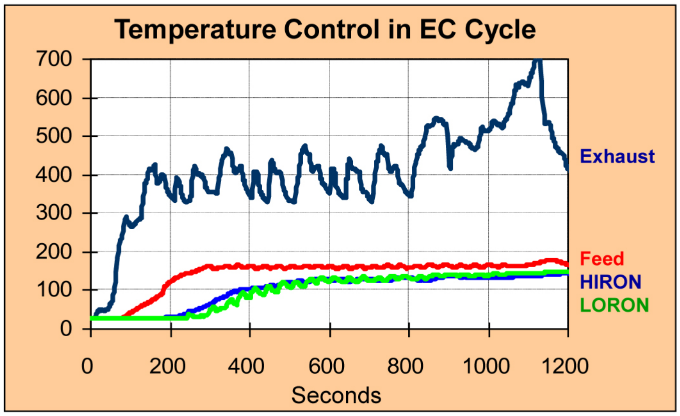


Figure 19. OBS RAV-4 Dynamometer Test of Heat Pipe

Figure 19 shows an example of the temperature control profiles for the feed and OBS membrane products in response to exhaust energy in the EC Cycle on the dynamometer. Feed rate was varied from 0.5 to 2.0 g/s as needed by the control system to hold the membrane feed temperature at 160°C. In this test, pressure drop across the flow controller limited feed flow to the heat pipe to 2 g/s resulting in about 20°C over-temperature at peak load with the exhaust temperature exceeding 700°C.

This was corrected by changing the flow controller and modifying the heat pipe design in subsequent tests. In this relatively mild startup, feed to the membrane reached operating temperature in 300 seconds, with full HiRON rate available at about 560 seconds or less. Faster startups are achieved with reductions in thermal mass and increased exhaust duty. Lower ambient temperatures had minimal impact on startup times.

HiRON Vacuum

An eductor in the HiRON pump loop provides the vacuum necessary to recover HiRON permeate. The maximum vacuum at the suction inlet of the eductor is set by the vapor pressure of the circulating HiRON fuel. This in turn reflects the operating conditions at the membrane and the fuel composition being processed. Tests were conducted in the laboratory and the environmental dynamometer shed to determine the impact of ambient temperatures on the vacuum. Permeate pressures varied directly with temperature, from about 20 kPa at 10°C to 42 kPa at 40°C. The octane number decreased about 1-2 RON over the temperature range. Figure 20 shows the OBS RAV-4 during the climate controlled Dynamometer test.

Figure 20. OBS RAV-4 Climate Controlled Dynamometer Testing

The temperature of the circulating HiRON fuel also was affected by the energy input from the HiRON pump of 58 watts and dissipation of the heat from the small HiRON tank.

Confirmation of Fuel Production on OBS Vehicle

Several experiments were run to confirm OBS functionality on the test vehicles. Both Japan RUL and US E10-RUL gasolines were run. Typically, the OBS system was brought to operating temperature of 150 C and HiRON products collected by condensing with a cold trap. These test confirmed that 100 RON permeate products were obtained at ~20% yield.

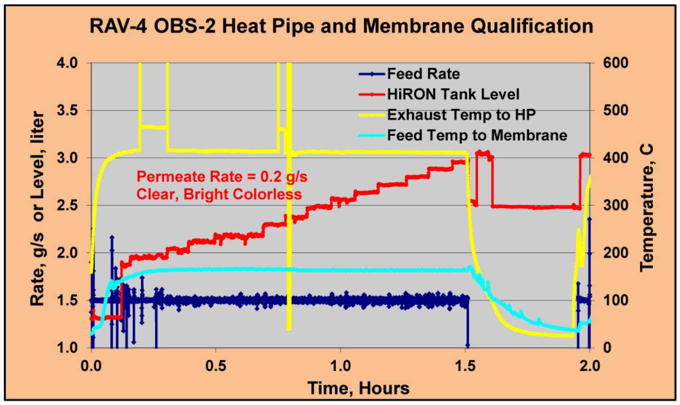


Figure 21. OBS RAV-4 Climate Controlled Dynamometer Testing

Figure 21 shows the accumulation of HiRON fuel during an extended system test. Monitoring the HiRON tank level during the driving and dynamometer tests indicated fuel accumulation in the HiRON tank at expected rates, but the HiRON tank level varied significantly when in use.

Fuel Economy

Fuel economy measurements made on the engine dynamometer for the Japan 10-15 Mode are shown in Figure 22 for the DI+PFI OBS RAV-4 vehicle dual-fuel engine configuration. Base fuel was 90 RON Japan RUL. The optimal RON fuels were obtained from the 89 RON and 102 RON test fuel blends. Fuel economy was improved by 5.2% over the Base. Extending the DI+PFI test to the vehicle resulted in a 5.1% improvement in fuel economy.

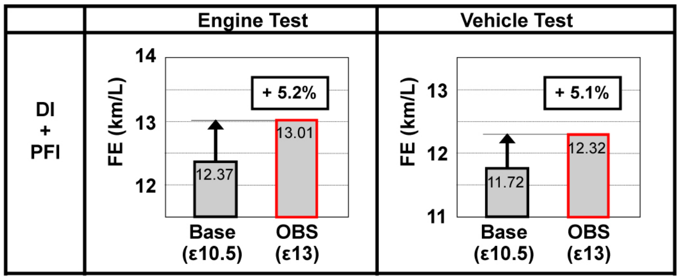


Figure 22. OBS RAV-4 Fuel Economy Japan 10.15 Mode with 2L Dual Fuel Engines

When torque gains and peak power available are considered for potential downsizing or gearing changes a further increase in fuel economy is expected. The WOT bench tests indicate that the dual fuel engines increase torque by 8-10% depending on the HiRON octane rating. With 102 RON aromatic fuel, the 13 CR engine could obtain MBT at almost all engine speeds.

OBS fuel economy credits for Japan 10-15, including downsizing to equivalent performance and debit for OBS parasitic power requirement are shown in Figure 23.

Parasitic power losses from the additional HiRON fuel pump (58 W) and HiRON injectors (14 W) were measured for EC mode at 1.36% of the fuel energy (1.975 kWh) and calculated assuming 70% alternator efficiency. The relative power consumption would drop with higher fuel consumption.

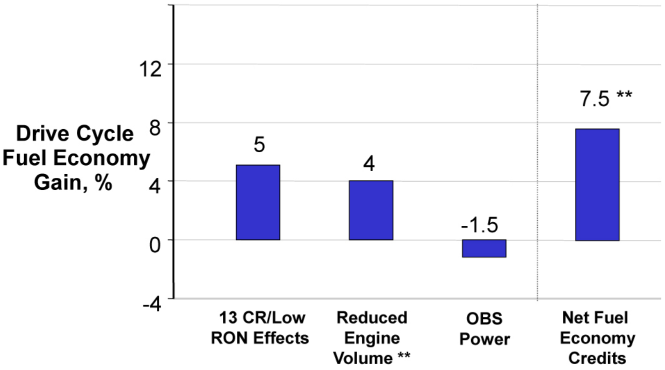


Figure 23. OBS Fuel Economy Credits Japan 10.15 Mode

OBS dual fuel vehicles could achieve 7.5% net fuel economy gain with downsizing, as shown in Figure 23. Estimates assume constant tail pipe emissions. Engine volume was reduced by taking advantage of higher peak torque, +8% with about 100 RON fuel, at equivalent peak power of 9.8 CR base case.

Issues and Opportunities for OBS

Onboard separation enables the use of very high compression ratio engines with regular gasoline. Performance gains are a direct function of the octane number and fraction of the HiRON fuel produced. Both depend on the composition of the gasoline used, which can vary widely in different markets. The impact of fuel composition needs further study.

In high load driving, such as on the highway, the consumption of high RON fuel for optimal fuel economy exceeds the present ability of OBS. Yield and octane are tradeoffs. Improvements in both the production and effective use of the high octane components present in regular gasoline can be improved. Premium gasoline is often specified for high performance vehicles. OBS could be applied to premium fuels as well.

The use of premium fuel only with direct injection and high compression could result in similar fuel economy and performance gains, but at substantial increase in fuel cost over time. The added cost of the OBS system must therefore be competitive with this option.

The use of ethanol at 10% volume throughout the U.S. market in both regular and premium fuels may open up additional opportunities for OBS. The ethanol stable membranes created as part of this project could be used to recover ethanol more effectively when present in the fuel consistently. Fuels with over 35% ethanol content and 102 RON have been separated from E10 gasoline by optimizing conditions. These fuels offer potential in direct injection turbocharged engines where the cooling effects of ethanol enable higher boost pressures without knock and hence greater efficiency (11). Alternative separation schemes have been reported (12)

OBS application to flex fuel vehicles could be considered. These vehicles are designed to operate on regular gasoline and ethanol blends up to E85. Present compression ratios are relatively low to accommodate the regular gasoline at AKI 87 that most flex fuel owner's use. OBS could enable higher compression ratio and improved performance, fuel economy and cold start for all fuels from E10 to E85.

Lower startup emissions are also possible with the higher volatility LoRON fuels produced by OBS. In the present configuration these are available at startup because the LoRON fuel is effectively stored in the line to the fuel rail, and isolated from the main tank by the accumulator volume. Preliminary tests have shown a 35% decrease in NMHC on startup, but more work is needed. Compliance emissions have not been determined at this time.

SUMMARY/CONCLUSIONS

Working together, we have conducted research to confirm and demonstrate the potential of onboard separation technology. A new novel ethanol stable aromatic selective pervaporation membrane has been developed to separate gasoline (8). Laboratory tests have shown that about 20% yield of 100 RON fuel can be obtained from typical regular 92 RON gasoline, including E10 gasoline. Bench and vehicle engine testing has confirmed the potential of using separated fuels to increase engine fuel economy by about 5% with torque up by 8-10%, or potentially 8% in fuel economy at constant performance. Dual fuel engines were tested using separated fuels both on the bench and in test vehicles equipped with the dual fuel engine and several generations of onboard membrane separation systems.

The onboard separation system offers the potential to obtain most of the benefits of operating on premium high octane fuel while using less expensive regular grade gasoline more effectively. Potential applications include improving performance while realizing modest fuel economy gains and downsizing for maximum fuel economy with equivalent performance. The high octane product is stored in a small ~2-4 liter tank, located within the main fuel tank, is expected to provide adequate reserve for most driving conditions. If no high octane fuel is available due to extended driving at high load conditions, adequate performance can be maintained with a temporary loss in fuel economy by using the main tank fuel.

In the face of more stringent fuel economy standards in the future, concepts that build on existing fuel and vehicle platforms, such as the OBS system, will likely garner increased interest from auto manufacturers. The OBS system will, of course, require further development to be ready for commercial consideration.

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DEFINITIONS/ABBREVIATIONS

2D-GC - 2-Dimensional Gas Chromatography
AKI - Anti Knock Index (RON+MON)/2
CR - Compression Ratio
DI (DFI) - Direct Fuel Injection
E10 - Gasoline with 10 vol.% Ethanol
ECU - Electronic Control Unit
HC - Hydrocarbon
MON - Motor Octane Number
MBT - Maximum Break Torque
mw - Molecular weight
NMR - Nuclear Magnetic Resonance
OBS - Onboard Separation
PFI - Port Fuel Injection
PUL - Premium Unleaded Gasoline
RON - Research Octane Number
rpm - Revolution Per Minute
RUL - Regular Unleaded Gasoline
RVP - Reid Vapor Pressure
SA - Spark Advance
SICI - Spark Ignition Compression Ignition
SIDI - Spark Ignition Direct Injection
S-RUL - Summer Grade RUL
TKL - Trace Knock Limit
W-RUL - Winter Grade RUL
WOT - Wide Open Throttle