

SESSION IV.

Fuels and Lubrication Technologies

Session Chair: Robert Beyerlein
U.S. Department of Energy

Dr. Jerry Wiens
California Energy Commission

EFFECTS OF ENGINE SHUTDOWN TIME ON DIESEL AUTOMOBILE EMISSIONS

**Edward King
Ford Motor Company**

ABSTRACT

To develop new fuel efficient hybrid vehicle concepts with internal combustion engines, the influence of engine shutdown time on exhaust emissions and fuel consumption is of major interest. In order to determine this influence, the operational behavior of three passenger cars with different engine concepts was evaluated on a chassis dynamometer. Exhaust emissions and fuel consumption was measured over the Federal Test Procedure (FTP) and the Highway Fuel Economy Test (HWFET). Furthermore, a specially configured test procedure was used in which the engine shutdown time was varied.

EFFECTS OF ENGINE SHUTDOWN TIME ON DIESEL AUTOMOBILE EMISSIONS

Edward King
Transmission & Engine
Systems Department



Hybrid Program

ACKNOWLEDGEMENT

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INTRODUCTION

To develop new fuel efficient hybrid vehicle concepts with internal combustion engines, the influence of engine shutdown time on exhaust emissions and fuel consumption is of major interest. In order to determine this influence, the operational behavior of three passenger cars with different engine concepts was evaluated on a chassis dynamometer. Exhaust emissions and fuel consumption were measured over the Federal Test Procedure (FTP) and the Highway Fuel Economy Test (HWFET). Furthermore a specially configured test procedure was used in which the engine shutdown time was varied.



Hybrid Program

DIESEL VEHICLE SELECTION

- Audi A4 1.9L Turbocharged Direct Injection (TDI)
- VW Golf Ecomatic 1.9L Turbocharged Diesel (IDI)
- Ford Mondeo 1.8L Turbocharged Diesel (IDI)



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FTP and HWFET TESTING

- Fuel: Low sulfur (<500 ppm) cetane >50 diesel
- VW Ecomatic run in "Ecomatic Mode" on and off
- Emissions(gm/mi): HotFID HC, CO, NOx, CO2, PM
- Fuel Economy (mpg): bag 1, 2, 3, City, Hwy & M/H
- Continuous (sec-by-sec) undiluted volumetric emissions (HC, CO, NOx, CO2) in PPM upstream & downstream of catalyst



Hybrid Program

FEDERAL PASSENGER CAR EMISSIONS STANDARDS

TAILPIPE EMISSION STANDARDS (g/mile)

	<u>GASOLINE/NG/METHANOL/DIESEL/LPG</u>					<u>DIESEL</u>
	<u>THC</u>	<u>NMHC</u>	<u>CO</u>	<u>NOx *</u>	<u>PM</u>	<u>NOx</u>
Tier 0	0.41	.34 (%)	3.4	1	0.2	1
Tier I	0.41	.25 (.31)	3.4(4.2)	.4(6)	.08(.10)	1.0(1.25)
Tier II	0.41	(.125)	(1.7)	(.2)	(.08)	(.2)

THC = Total Hydrocarbon - NO REQUIREMENT FOR NGV

PM = Particulate Matter

NMHC = Nonmethane Hydrocarbon

* Gas/NG/Methanol/LPG only

% NG Only

TESTING WAIVER AVAILABLE

Stds: 5 yrs/50,000miles (13 yrs/100,000 miles)

NB: Tier II = Clean Air Act (CAA) Default



Hybrid Program

CALIFORNIA PASSENGER CAR EMISSIONS STANDARDS

TAILPIPE EMISSION STANDARDS (g/mile) TO 2003

	GASOLINE/METHANOL				DIESEL				
	NMHC	NMOG	CO	NOx	NMHC	CO	NOx	PM	HCHO
Tier 0	.89		7.0	.4	.46	8.3	1.0	.08	
Tier 1	.25(.31)		3.4(4.2)	.4(.6)*	.31	(4.2)	(1.0)	(.08)	.015^
TLEV		.125(.158)	3.4(4.2)	.4(.6)	Same as gas			(.08)	.015(.018)
LEV		.073(.090)	3.4(4.2)	.2(.3)	Same as gas			(.08)	.015(.018)
ULEV		.040(.055)	1.7(2.2)	.2(.3)	Same as gas			(.04)	.008(.011)

NMHC = Nonmethane Hydrocarbon

NMOG = Nonmethane Organic Gas

PM = Particulate Matter

HCHO = Formaldehyde

* 100K Req; 1996+

Sds: 5 yrs/50,000 miles (10 yrs/100,000 miles)

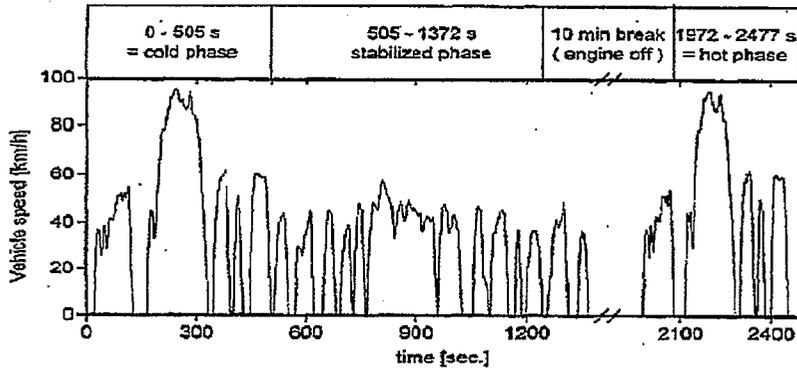
^ = Methanol car standard only



Hybrid Program

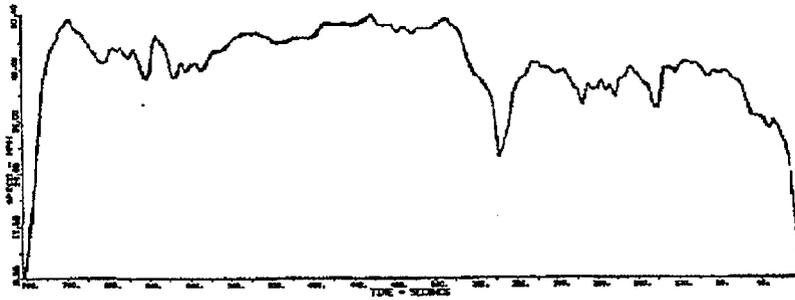
FTP DRIVING CYCLE

Cycle distance: 11.116 miles Average speed: 34.1 km/h
 Cycle duration: 1877 + 600 s break Maximum speed: 91.2 km/h



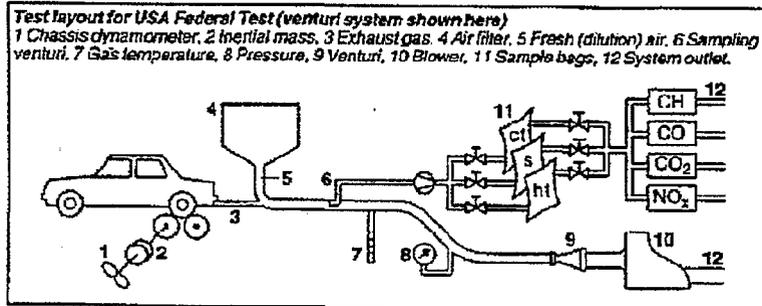
Hybrid Program

HWFET Test



Hybrid Program

TEST LAYOUT & SAMPLING



Source: Automotive Handbook (2nd Ed.)
 Robert Bosch GmbH



Hybrid Program

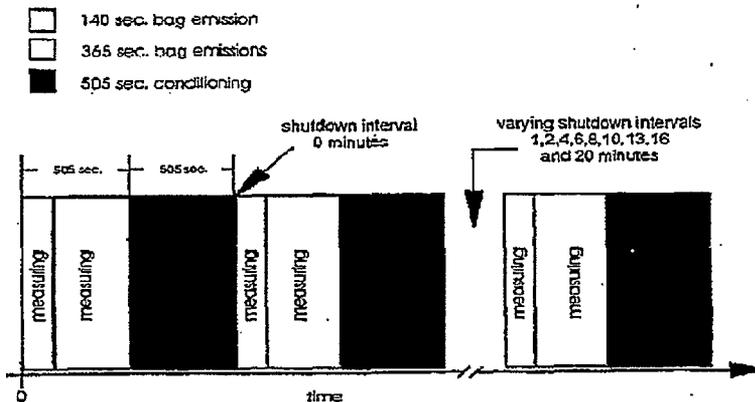
SHUTDOWN/RESTART TEST

- VEHICLES: VW Golf (Ecomatic Off), Audi A4, Mondeo
- PROCEDURE: Drive 2 consecutive 505's with shutdowntime between 505 pairs varied from 0, 1, 2, 4, 6, 8, 10, 13, 16, 20 minutes. Emissions taken on first 505. The sample 505 split into 2 periods; 0-140 seconds and 140-505 seconds.
- Bag emissions: HotFID HC, CO, NOx, CO2
- Continuous undiluted volumetric emissions: HC, CO, NOx, CO2 in PPM before & after catalyst



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SHUTDOWN/RESTART FIGURE



Hybrid Program

DATA CAVEATS

- All vehicles have EGR to varying degrees
- All have diesel oxidation catalysts(DOX) that work on HC CO PM to varying degrees
- All vehicles are European calibrations...Unique start, loading characteristics, catalyst lightoff
- Dynamometer loading slightly different on each car
- 21 MB of data
- Test-to-test repeatability



Hybrid Program

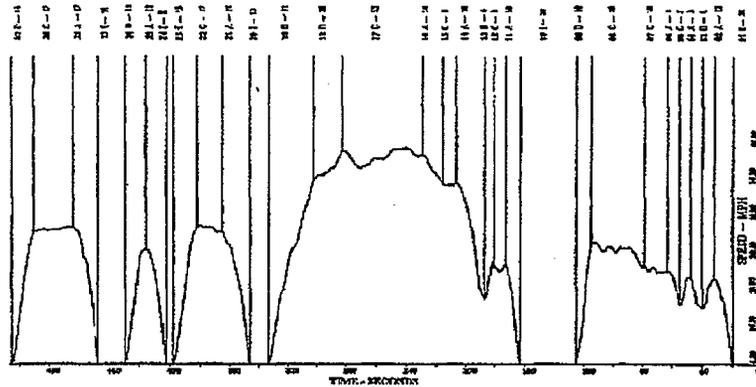
FTP EMISSION DATA

VEHICLE	HC	CO	NOx	PM	MPG	
VW ECOMATIC (DI)						
Economic OFF	0124	0.485	1.015	0.079	54.46	
3000W/TW	0046	0.510	0.858	0.071	53.97	
190N @ 80KPH	0160	0.523	0.907	0.075	53.29	
5.84 HP @ 50mph	0169	0.506	0.927	0.073	54.36	Ave
VW ECOMATIC (DI)						
Economic ON	0164	0.392	0.821	0.067	57.85	
	0054	0.569	0.802	0.082	56.65	
	0047	0.383	0.782	0.065	57.75	
	0063	0.359	0.802	0.071	57.42	AVE
	38%	25%	13%	6%	8%	Improvement
AUDI A4 1.9TD						
3250MW	0048	0.117	0.509	0.127	53.85	
237N @ 80KPH	0071	0.085	0.792	0.130	54.58	
7.05 hp @ 50mph	0074	0.100	0.777	0.163	54.97	
	0064	0.101	0.826	0.140	54.47	Ave
	BETTER	BETTER	BETTER	WORSE	EVEN	Compared to Eco OFF
	EVEN	BETTER	EVEN	WORSE	WORSE	Compared to Eco ON
Ford Merco 1.8 TD (DI)						
1500N/TW	0041	0.148	0.891	0.068	50.94	
212N @ 80KPH	0103	0.153	0.911	0.091	51.00	
6.3 hp @ 50mph	0048	0.187	0.948	0.068	50.90	
	0064	0.161	0.915	0.089	50.95	Ave
	BETTER	BETTER	EVEN	WORSE	WORSE	Compared to Eco OFF
	EVEN	BETTER	WORSE	WORSE	WORSE	Compared to Eco ON



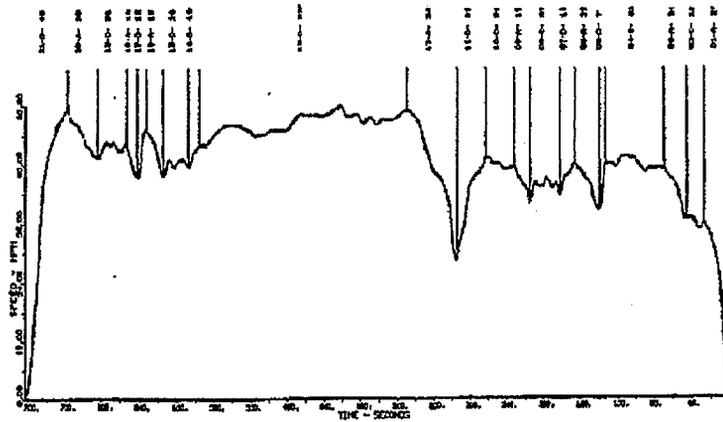
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FTP 80 MODES (First 30 Modes Shown)



Hybrid Program

HWFET 21 MODES



Hybrid Program

FTP & HWFET IDLE & DECEL

- BAG 1 & 3 18.6% Idle, 24.8% decel
- BAG 2 16.9% Idle, 23.3% decel
- HWFET 0% Idle, 16% decel



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BAG-BY-BAG EMISSIONS

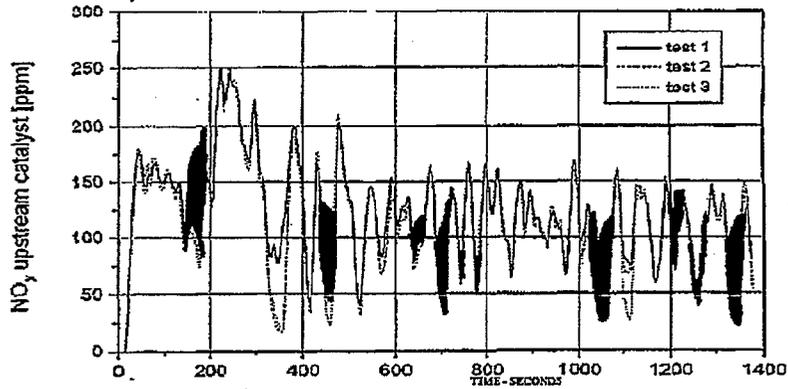
ECONOMY/ON/OFF DATA (3 Test Ave)

ECONOMY	ON Bag 1	ON Bag 2	ON Bag 3	ON HWFET	OFF Bag 1	OFF Bag 2	OFF Bag 3	OFF HWFET
MPG	34.16	37.79	39.49	52.06	33.07	33.64	37.72	51.25
Improvement	3.30%	12.30%	4.70%	1.60%				
HC	0.159	0.084	0.0465	0.075	0.0676	0.066	0.184	0.069
Improvement	14.58%	2.33%	74.73%	-8.70%				
NOx	0.817	0.8244	0.748	0.595	0.917	0.977	0.838	0.6773
Improvement	10.90%	15.60%	10.70%	12.15%				
PM	0.0744	0.0718	0.0633	0.0423	0.0784	0.0763	0.0666	0.0439
Improvement	1.30%	3.30%	4.90%	3.64%				



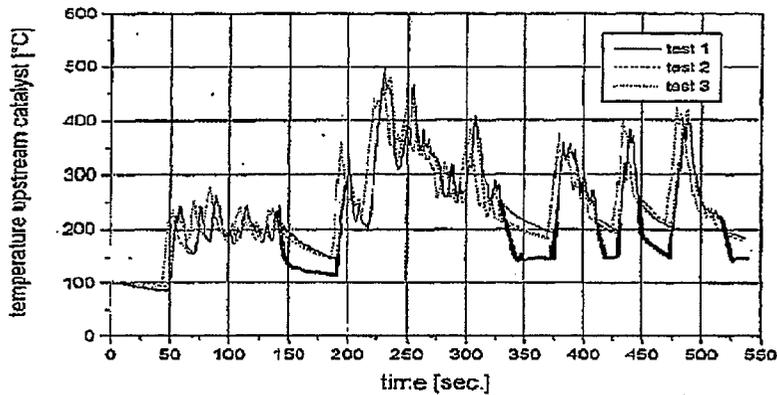
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NO_x EMISSIONS with/without SHUTDOWN (Black areas = No_x not generated)



Hybrid Program

STOP/START CAT TEMPS (Dark line shows cat cool-down during engine idle)



Hybrid Program

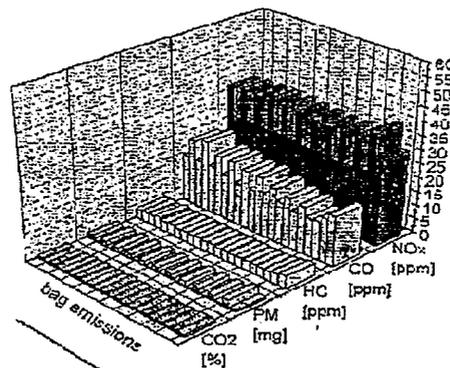
STOP/START CONCLUSIONS

- Decel and Idle shutdowns measurably reduce emissions and improve FTP FE
- IMPROVEMENTS (in a cycle with >40% idle & decel): 8% FE, 6% PM, 13% NOx, 25% CO,% HC
- IMPROVEMENTS apply & probably increase in real-world "commuter/gridlock" scenarios
- In heavier load HWFET with minimal decel & idle, NOx improvement significant, possible HC cost
- Suggest further studies in heavier load non-FTP/HWFET scenarios to understand potential NOx benefits
- Consider capitalizing on secondary effect of catalyst heat retention in stop/start



Hybrid Program

SHUTDOWN/RESTART DATA



Hybrid Program

SHUTDOWN/RESTART CONCLUSIONS

- Emissions of a fully warmed up diesel engine after 1 minute or 20 minute shutdown are essentially equal



Hybrid Program

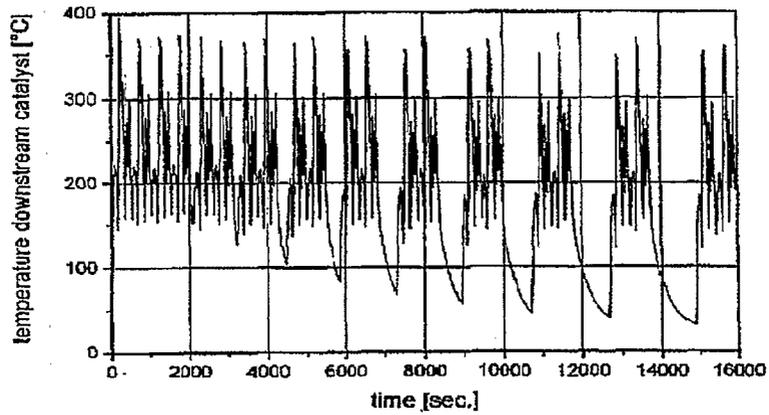
OTHER OBSERVATIONS

THERMAL MANAGEMENT



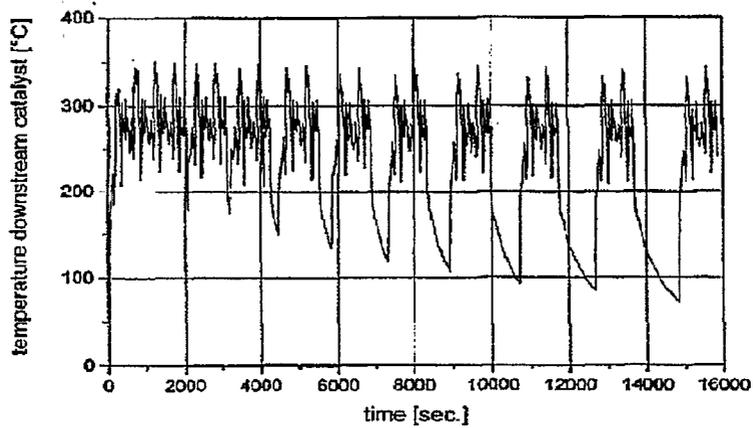
Hybrid Program

UNDERBODY MOUNT CAT TEMPERATURE WITH VARYING SHUTDOWN TIMES



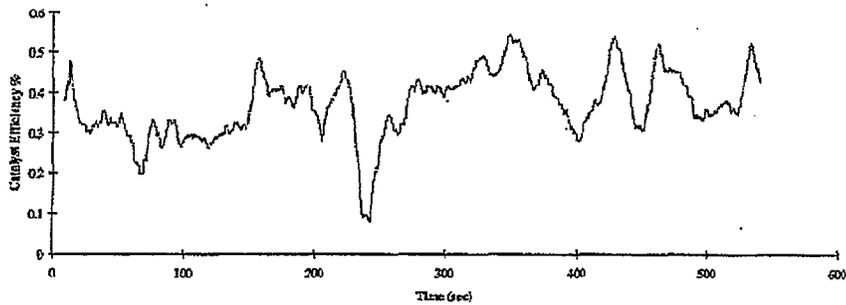
Hybrid Program

CLOSE COUPLED CAT TEMPERATURE WITH VARYING SHUTDOWN TIME



Hybrid Program

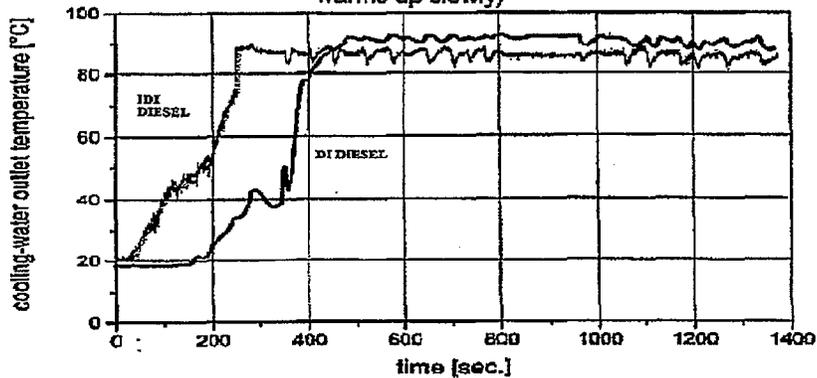
DOX CATALYST EFFICIENCY (With Ecomatic OFF)



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WARMUP CHARACTERISTIC DI vs IDI DIESEL

(NOTE: DI has 1.2kW electric heating element in coolant and still
warms up slowly)



Hybrid Program

CONCLUSIONS & OBSERVATIONS

- Diesel/Hybrid vehicle designers need to understand DI diesel exhaust energy & its management
- DOX catalysts are "different"
- Thermodynamics of high efficiency TDI engines can affect cooling systems, heating & A/C, FEAD, alternator, and electrical systems and NVH



Hybrid Program

ADVANCES IN TURBOCHARGER TECHNOLOGY FOR FUEL ECONOMY AND EMISSIONS CONTROL

S. M. Shahed
AlliedSignal Turbocharging Systems

Heavy duty diesel engine development has resulted in 80% reduction in NOx and 90% reduction in PM. Simultaneously, Europe has been increasingly turning to diesel engines for passenger cars for fuel economy improvement. Turbocharging and aftercooling has contributed greatly to the improvement of heavy duty truck diesel engine and passenger car fuel economy while at the same time meeting stringent emissions regulations.

It is shown that advances in turbocharging technology continue to be made to meet upcoming challenges of emissions reduction and fuel economy improvement. Improvements in turbocharger technology include Variable Nozzle Turbine (VNT)TM Turbocharging and electrical turbocompounding.

Several VNT Turbocharger mechanisms for light duty passenger car diesel engines and for heavy duty truck diesel engines are described. Mechanisms by which VNT turbochargers improve engine response and fuel economy are discussed.

Further improvements in the future are possible with the use of electrically assisted turbocharging. Electrical turbocompounding can improve fuel economy by 6-10% at the same time providing a means to improve turbocharger response. Alternatively, a turbocharger mounted generator can readily provide high voltage power for non thermal plasma NOx reduction devices.

This paper additionally shows that turbocharging can also be applied to gasoline engines to improve their fuel economy by as much as 8%.

INTRODUCTION

Heavy duty diesel engine development has resulted in 80% reduction in NOx emissions and 90% reduction in particulate matter (PM) emissions since the early 70s. At the same time, significant power density and fuel economy improvements have been achieved. Literature on diesel emissions control technology shows that this is in substantial part due to the effect of air fuel ratio and intake manifold temperature. Thus

turbocharging and aftercooling has greatly contributed to the reduction of diesel engine emissions. As a result, nearly 100% of heavy duty and 80% of light duty passenger car diesel engines in the United States and Europe are turbocharged and aftercooled.

In spite of the substantial reductions in emissions already achieved, there continues to be a need to further reduce emissions and improve fuel economy. The purpose of this paper is to show that turbocharging technology continues to make substantial progress and will help further reduce emissions as well as improve fuel economy. Only two advanced technologies - the development of variable geometry and electrically assisted turbochargers are dealt with in this paper. It is a further purpose of this paper to show that turbocharging can be (and is) also applied to gasoline engines to improve fuel economy.

TURBOCHARGING GASOLINE ENGINES

Historically, gasoline engine turbocharging had been used to generate high power (top speed) and high performance (acceleration). As a result, turbocharging gasoline engines has acquired the false reputation of being exclusively relevant for this "Power and Performance" niche market. When used in this way, turbocharging gasoline engines may indeed result in poor fuel economy. However, it is also possible to improve fuel economy and still get quick acceleration and top speed with a turbocharged gasoline engine.

To prove this, a database of 376 gasoline powered vehicles, both naturally aspirated and turbocharged, was constructed. The database contains manufacturer certified, published information on speed, power, torque, acceleration, fuel consumption and vehicle weight. All vehicles were tested over the same load speed cycle as prescribed by European test procedures. Fuel economy numbers are directly comparable and test data are "certified" - part of European test procedures. The database was analyzed to examine the effects of turbocharging on various engine power and vehicle weight brackets. Figure 1 shows that 3-8% improvement in fuel economy is achieved with turbocharging.

VNT TURBOCHARGERS FOR LIGHT DUTY PASSENGER CAR DIESEL ENGINES

It has already been stated that turbocharging greatly improves emissions and fuel economy of diesel engines. However, there is a fundamental mismatch between the flow characteristics of a reciprocating engine and a turbocharger. If the turbocharger is matched for proper flow at low to medium engine speeds, then it results in too much flow at high engine speed. On the other hand, if the turbocharger is designed to handle this high flow rate, then the flow area is so large that the turbocharger response becomes too slow. To counter this, wastegate valves were developed. At high speed a wastegate valve opens so that some of the exhaust bypasses the turbine. By definition, a wastegate valve "wastes" exhaust energy. A more elegant design using variable geometry turbines has been developed.

Figure 2 shows a variable geometry turbocharger with multiple vanes in the turbine housing. A unison ring swings the vanes "in unison" and provides control of flow area and flow direction. Under low speed and light load conditions, vanes are closed to reduce the flow area. This results in desired high turbocharger speeds (at low engine speeds), favorable air fuel ratio and fast turbocharger response. At high loads and high speeds, the vanes are opened up to permit low back pressure on the engine, improving fuel economy as well as preventing overboosting. Figure 3 shows how one engine/car manufacturer used this technology to improve the power density and driveability of the engine/car. Simultaneously, improvement in fuel economy and smoke was obtained.

Figure 4 shows a variable geometry turbocharger with a sliding vane mechanism. In this case, vanes are cast as one piece with a slider which moves in the direction of the turbocharger axis. Vane geometry does not change in the radial flow direction, but the flow width in the axial direction is controlled. Vanes move through corresponding slots in the back plate/heat shield of the turbine. The effect on engine performance is similar to the multiple vane variable geometry turbocharger.

VNT TURBOCHARGERS FOR HEAVY DUTY DIESEL ENGINES

Turbochargers in heavy duty diesel engines are subjected to greater thermal and mechanical stresses than in light duty diesel engines. In addition, high power absorption during engine decompression braking is a significant requirement. Many heavy duty diesel engines are

equipped with decompression brakes. When these brakes are in operation, high pressure, compressed air is discharged into the exhaust manifold. Under these conditions, if the vanes of a VNT turbocharger are closed, then turbocharger speed is increased, which correspondingly increases the intake manifold pressure causing the engine to do more pumping/compression work. This increases the power absorbed and aids in vehicle braking.

The proven design of light duty diesel engine VNT turbochargers was improved to meet the more exacting demands of heavy duty diesel engines. In this design, the movable vanes are hinged on a "double axle", one on each side of the vane. In addition, the pressure at the ends of the double axle are balanced to allow easy rotation and controllability of the vane position.

ELECTRICALLY ASSISTED TURBOCHARGERS

The fundamental mismatch between reciprocating engine and turbocharger flow characteristics has already been mentioned. Another way of stating this mismatch is that the turbocharger develops too much power at high engine speed and too little power at low engine speed. A motor generator set can be designed into the turbocharger such that it delivers excess power (in the form of electrical power) at high engine speeds and (momentarily) accepts electrical power for better acceleration at low engine speeds. There are several issues that this arrangement can present which can best be discussed by considering the following three system levels.

Level 1 System

This system, shown in Figure 5, uses a 12 or 24 V battery to drive a motor on the turbocharger shaft. It has serious limitations (a) power electronics costs at these voltages are very high (b) current requirements can be as high as 150 A (c) energy storage limitations prevent sustained use (d) there is no way of using excess turbocharger energy at high speeds. The only advantage such a system can provide is fast acceleration. VNT turbochargers can adequately address this issue in a far more economical way.

Level 2 System

This system, shown in Figure 6, uses energy directly from the alternator at between 50 and 100V. Current levels are still high and there is no way to use excess turbocharger energy.

Level 3 System

This system, shown in Figure 7, has a motor/generator set on the turbocharger and an additional motor/generator in the engine drivetrain. The voltages of the two can be compatible and high (say 300 V). When the turbocharger needs energy for acceleration the motor/generator on the engine driveshaft can supply it. At high engine speeds, when there is excess turbocharger energy, it can supply it to the motor in the drivetrain. This is electrical turbocompounding and addresses all the issues identified above. This system has two additional advantages. It can be used to (a) drive exhaust gas recirculation (EGR) because it operates at high engine back pressure and (b) the energy generated by the turbocharger mounted generator can be used in a non-thermal plasma NOx reduction device.

Figure 8 shows the calculated fuel economy benefits of going to a Level 3 electrical turbocompounding system in a high speed, 2.5 liter DI diesel engine. It is seen that 6-10% improvement in fuel economy is possible. However, it should be pointed out that fuel economy benefits are system dependent. In a high speed engine a large fraction of the flow at high engine speed is "wastegated". Therefore, the potential fuel economy benefits can be high. On the other hand such engines do not operate at a very high load factor. Hence the benefits over a typical duty cycle may not be that high. Benefits would have to be estimated for specific systems under given duty cycles.

Figure 9 shows how turbocharger response time can be improved by using various degrees of electrical assist. It should be noted that such assist is used only temporarily. The calculations of Figures 8 and 9 were done using baseline data of a typical high speed DI diesel engine together with basic turbocharger energy balance. Sophisticated transient cycle simulation calculations were not conducted at this stage of the investigation. Also, it is possible the use of variable geometry turbocharging along with electrical turbocompounding will minimize the need for electrical assist while at the same time further improving fuel economy benefits at high speeds.

CONCLUSIONS

It has been shown that turbocharging has contributed greatly to the significant reductions in emissions and improvement in fuel economy already made by both heavy duty and light duty diesel engines. Turbocharging technology

continues to improve with variable geometry turbochargers now available for the full range of engine sizes. In the longer term, electrically assisted turbochargers in the electrical turbocompound configuration offer the potential of further fuel economy improvements and emissions reductions. Turbocharging is effective not only in diesel engines but also in gasoline engine powered vehicles. It is shown that turbocharged gasoline engine cars give 3-8% improvement in fuel economy.

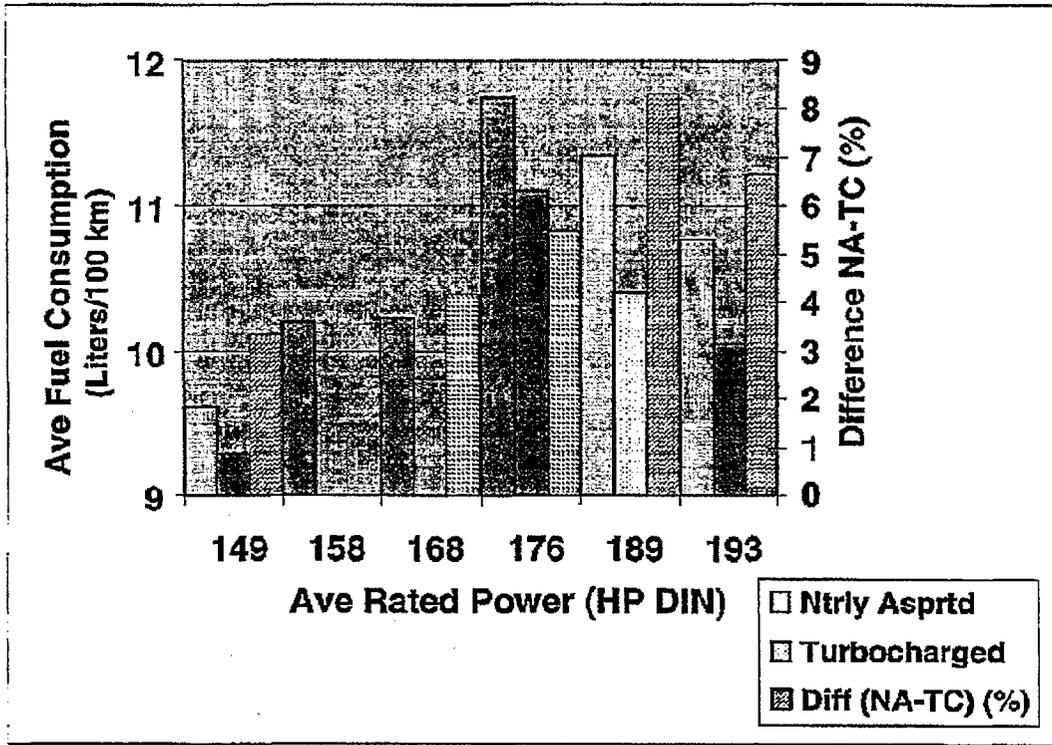


Figure 1. Fuel Consumption by Rated Power Brackets Gasoline Engine Powered Pass Cars

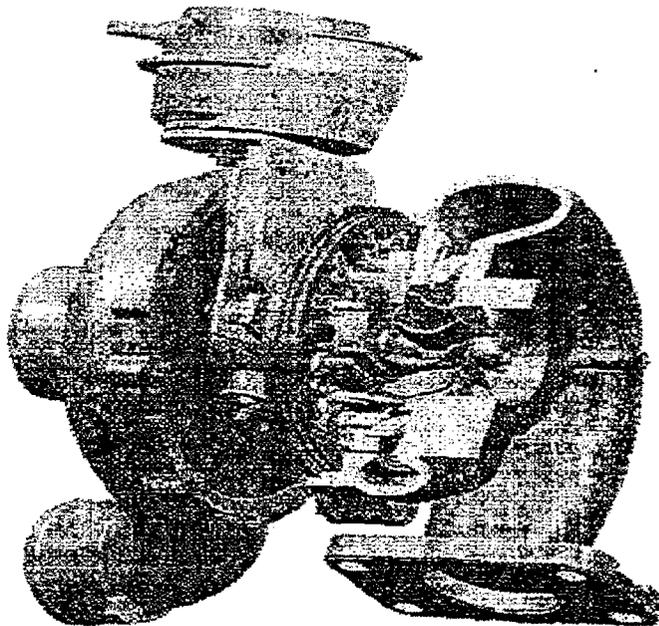


Figure 2. Multivane™ VNT™ Turbocharger

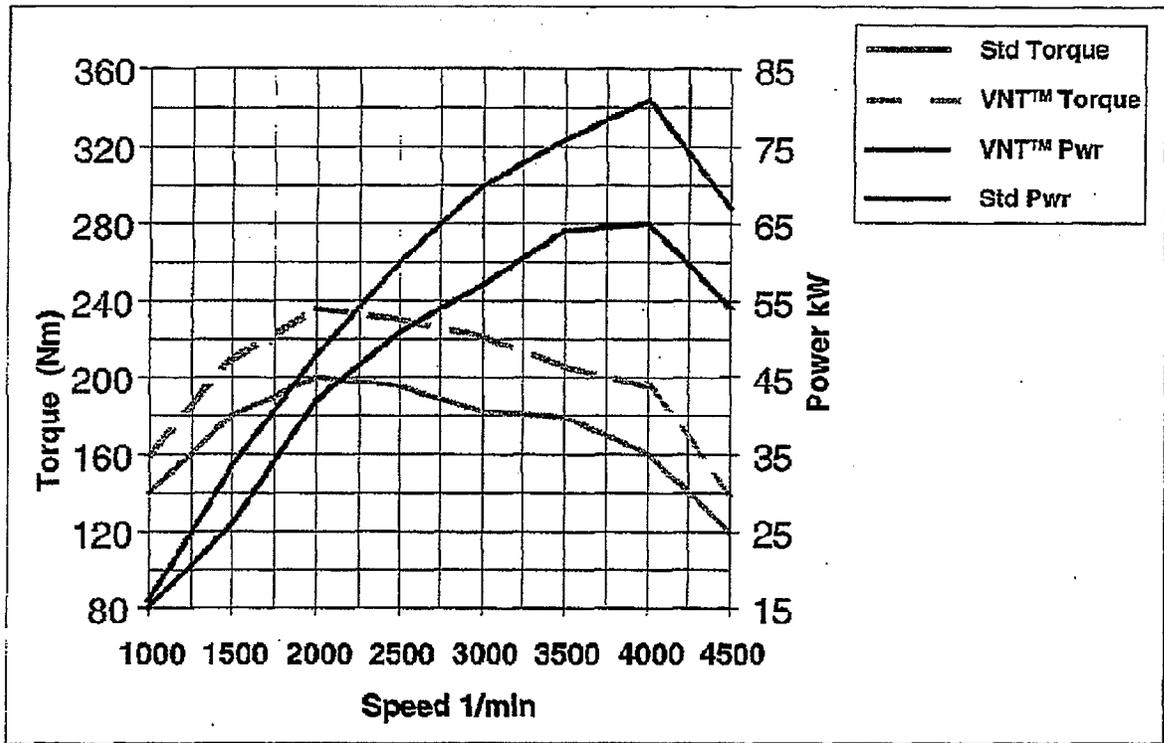


Figure 3. VW Engine for Golf, Passat and Audi Same Engine with VNT™ vs Std Turbocharger

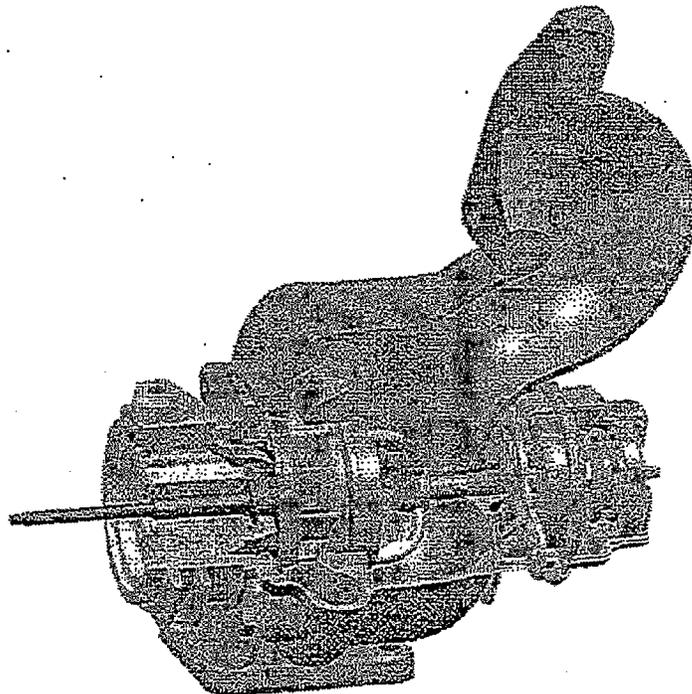


Figure 4. Slidevane™ VNT™ Turbocharger

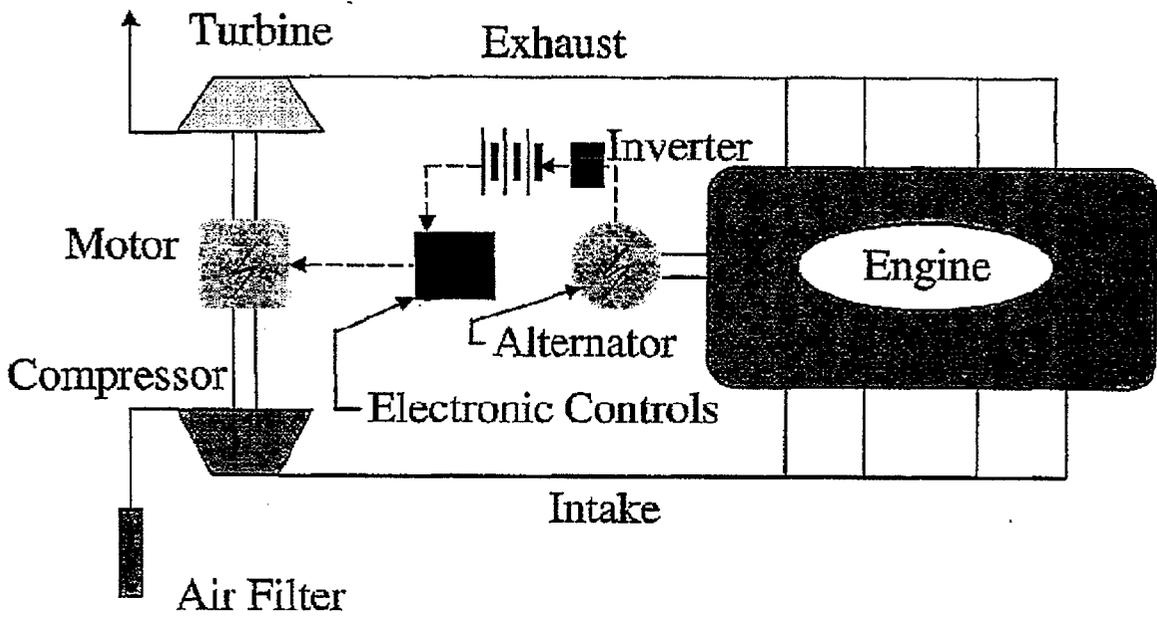


Figure 5. Level I Electrically Assisted Turbocharger System Schematic

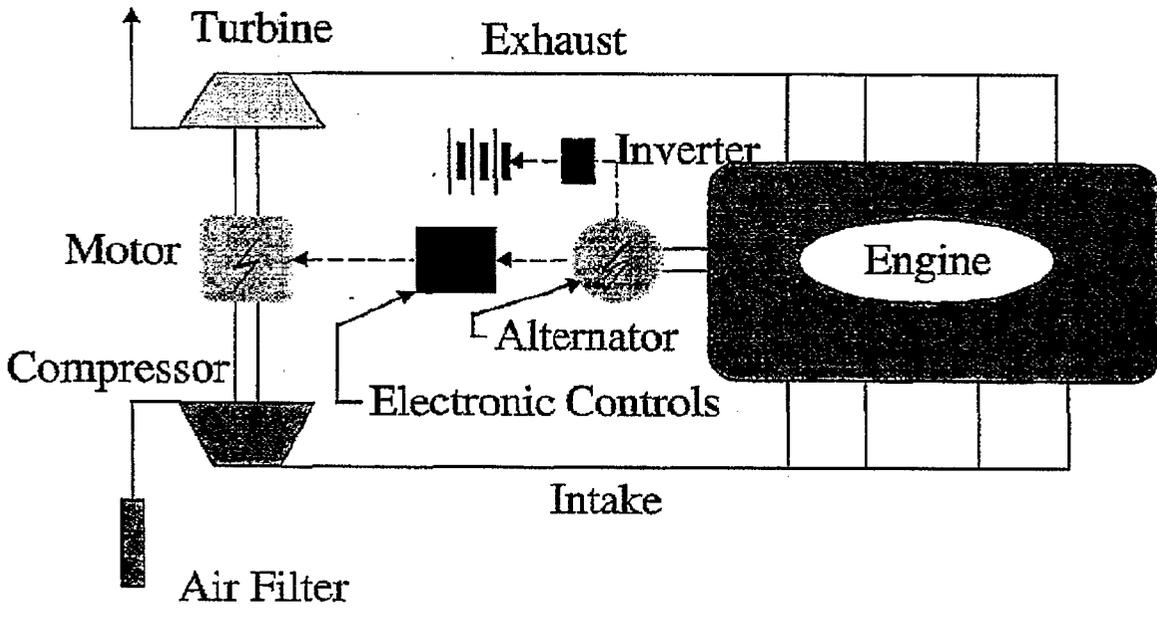


Figure 6. Level II Electrically Assisted Turbocharger System Schematic

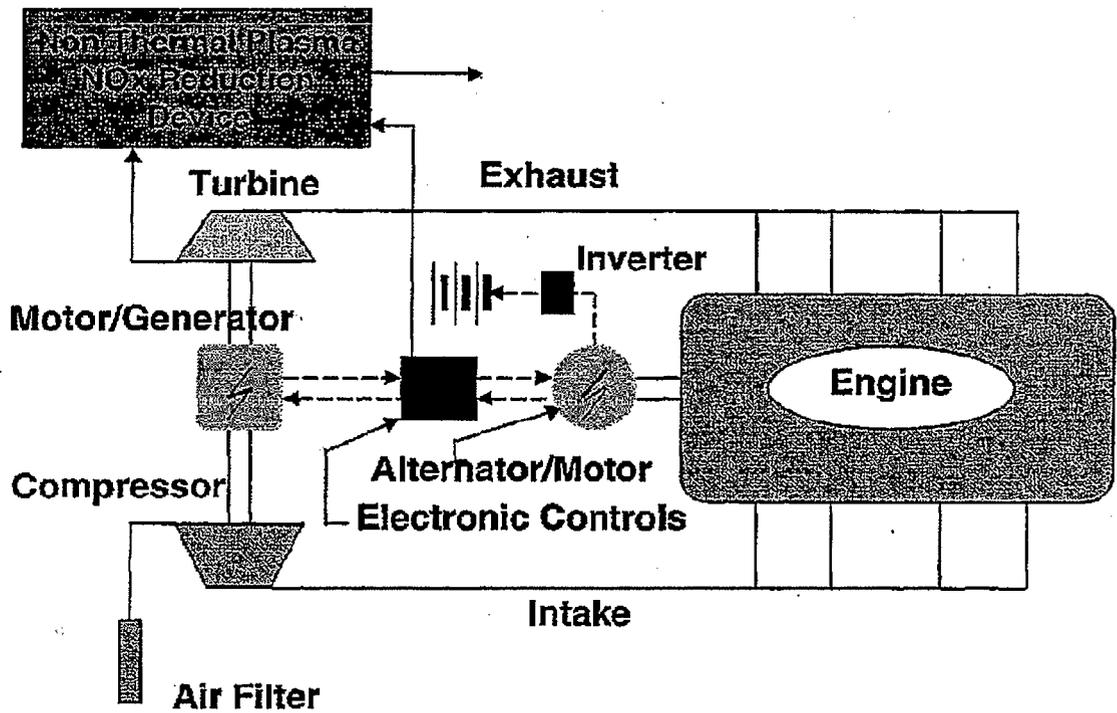
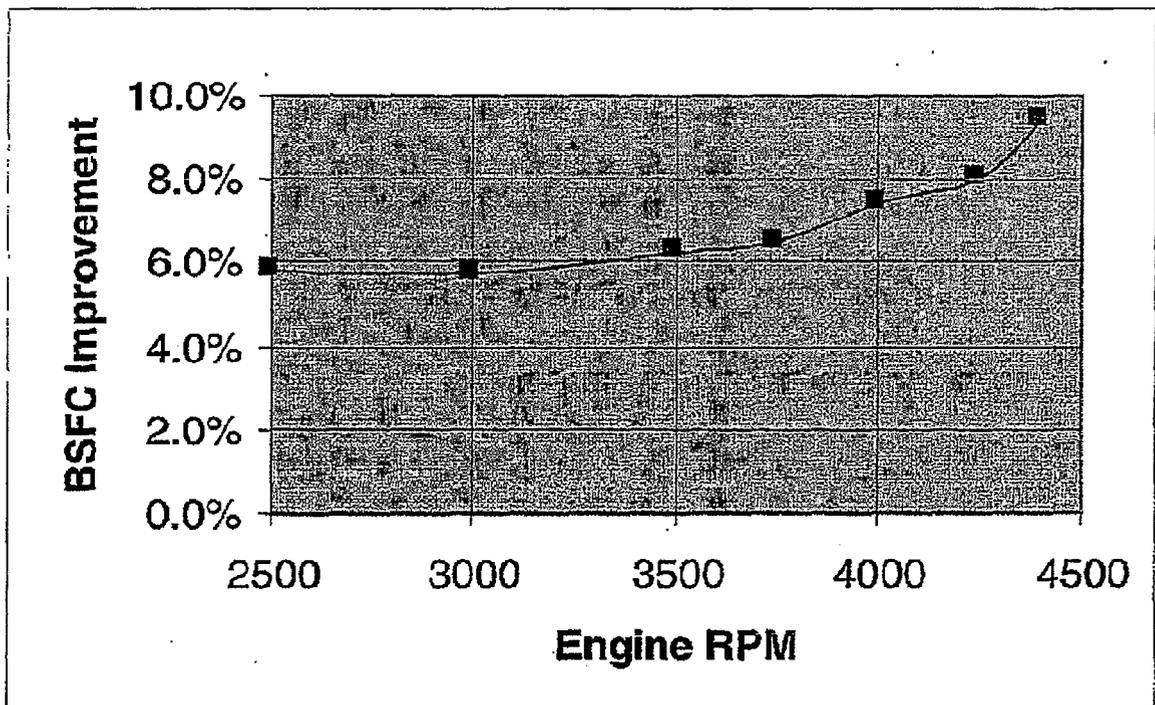


Figure 7. Level III Electrically Assisted Turbocharger System Schematic



Note: Vehicle Improvement Dependent on Duty Cycle

Figure 8. BSFC Improvement with Electrical Assist - 2.5 Liter Engine Full Load Conditions

**Transient Response with Electrical Assist
Delta Boost vs. Time**

1000 ERPM

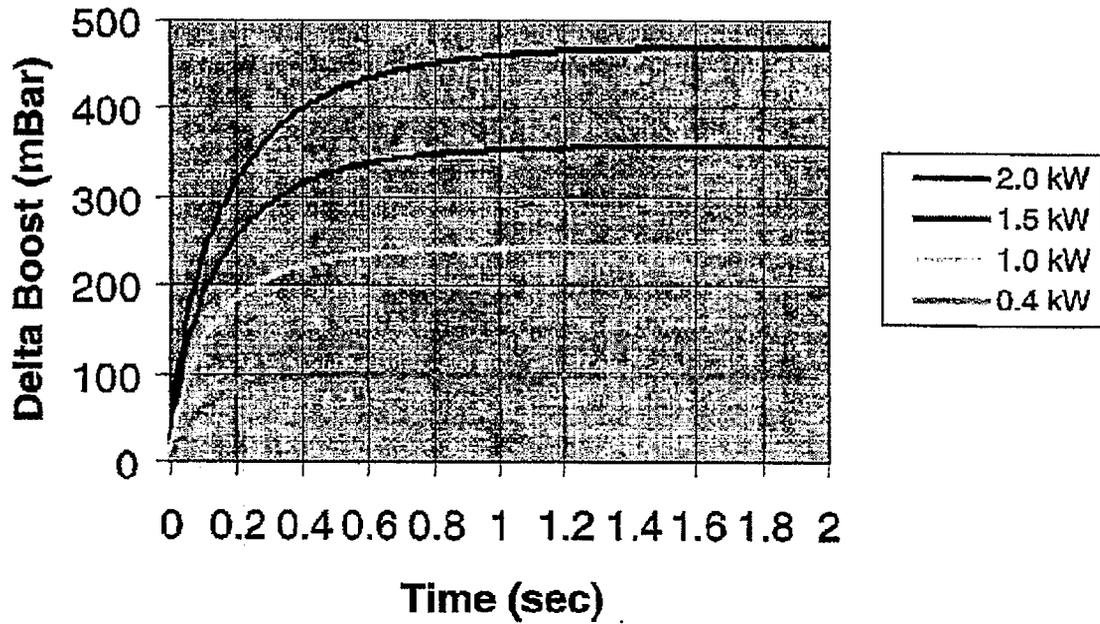


Figure 9. Fuel Consumption by Rated Power Brackets Gasoline Engine Powered Pass Cars

REFORMULATED DIESEL FUEL - THE CHALLENGE FOR U.S. REFINERIES

Barry McNutt
U.S. Department of Energy

Jerry Hadder
Oak Ridge National Laboratory

BACKGROUND

Diesel engines have potential for use in a large number of future vehicles in the United States. However, to achieve this potential, proponents of diesel engine technologies must solve diesel's pollution problems, including objectionable levels of emissions of particulates and oxides of nitrogen. To meet emissions reduction goals, diesel fuel quality improvements could enable diesel engines with advanced aftertreatment systems to achieve the necessary emissions performance, and it is likely that diesel fuel would have to be reformulated to be as clean as future gasolines.

If adequate volumes of reformulated diesel (RFD) fuel can be produced at reasonable cost, then the full market potential for advanced diesel engine vehicles could be realized. With evidence that RFD will be available in adequate volumes at reasonable costs, policy makers could better defend current activities like the promotion of diesel engine technologies in vehicles developed through the Partnership for a New Generation of Vehicles.

However, if it is shown that RFD cannot be supplied in adequate volumes at reasonable costs, then policy makers can make informed and appropriate responses, for example, by defining new research programs for diesel engine combustion or aftertreatment catalysts.

While the actual changes needed in future diesel fuels are not known, we have assumed that petroleum refineries would produce RFD by reducing sulfur and aromatics in the fuel. These property changes would be accomplished by changing blendstock qualities and/or blendstock percentages. In addition to reformulation of diesel fuel, we have assumed that vehicle fleet changes will result in a significantly greater fraction of RFD and a lesser fraction of gasoline. Because of the increased processing difficulty and costs for fuel property improvements, a large

demand for RFD will present technical and economic challenges for the U.S. refining industry. It is important to the national economy and security that these challenges to the U.S. refining industry do not adversely affect the efficiency and reliability of the transportation fuel production and distribution system. RFD could have significant impacts on:

1. Shifts in diesel fuel blendstocks, possibly including refinery purchases of ultra-clean blendstocks from gas-to-liquids (GTL) plants.
2. Refinery investment.
3. Refining costs, fuel product costs, and refinery energy use.
4. Refinery viability.
5. Refinery technology.
6. Global shifts in production and imports/exports of distillates and gasoline.

This paper presents an evaluation of the first two items in the list of significant impact areas, highlighting the types and costs of refinery changes required to make RFD. Results are based on a qualitative analysis drawn from limited published information. No new quantitative analysis or modeling has been done. Therefore, projected impacts should be viewed as preliminary and directional in nature, with the understanding that required changes will differ among individual refineries.

CURRENT DIESEL FUEL PRODUCTION

Tables 1 and 2 show current diesel fuel production and quality data (DOE 1998; API/NPRA 1996). For the combined regions listed in the tables, the average sulfur content of diesel fuel sulfur is well above 340 ppm and the average aromatics content is above 31 volume percent. Because Petroleum Administration for Defense District III (PADD III, U.S. Gulf Coast) produces the greatest amount of diesel fuel, the analysis of RFD production will focus on that region.

Typical blendstocks for low sulfur diesel fuel produced in PADD III are summarized in Table 3, which shows only two blendstocks (hydrotreated and hydrocracked light distillate) with sulfur contents less than 100 ppm. These blendstocks comprise only 7 volume percent of the low sulfur diesel fuel product (API/NPRA 1996).

ASSUMPTIONS

We assume that RFD will be required in year 2005 for all diesel vehicles, and low sulfur gasoline will be required for gasoline-powered vehicles. Greater volumes and proportions of diesel fuel will be required. Current (1997) diesel fuel production in PADD III is 960 MBD, or 12 percent of total production of refined products in that region (DOE 1998). Production of RFD in year 2005 is assumed to be 1450 MBD, which is based on an assumed 25 percent increase in on-road diesel fuel to satisfy new Light Duty Vehicle demand and expected growth in current Heavy Duty Vehicle markets, plus constant production of off-road diesel fuel. Table 4 shows that the premised RFD will have very low sulfur and aromatics contents. T90 will be lower and cetane number will be higher. We also assume that additive technologies will be developed so that acceptable diesel fuel qualities such as lubricity and pour point can be maintained.

RFD PRODUCTION

To achieve RFD quality and production requirements, refiners will have to improve the quality of blendstocks through operational changes and investment in desulfurization and dearomatization technologies. Additionally, we should expect changes in volume percentages of blendstocks through operational changes in the hydrocracker, and introduction of ultra-clean stocks from GTL technologies.

A spreadsheet technique has been used to derive a blendstock mix which could satisfy RFD requirements. The technique accounts for blendstock quality improvements through operational changes, limits on refinery stream availability, and the plausibility of alternate disposition of streams within the refinery. RFD blendstocks are shown in Table 5, with volume percentages, sulfur and aromatics contents, and key processes for blendstock production. Production of blendstocks for RFD will require rebalancing of refinery operations, with a 15 percent reduction in gasoline production. The fluid catalytic cracker and hydrocracker will shift from gasoline to distillate production modes. There will be adjustments in the utilization of gasoline production processes (e.g., reformers,

alkylation, etc), Fischer-Tropsch (F-T) blendstocks will be purchased from GTL plants, and there will be substantial refinery investment. We use SynSat (licensed by ABB Lummus Crest Inc./Criterion Catalyst Co.) to represent deep desulfurization and dearomatization technologies, although competitive technologies will be available from other licensors (Gulf Publishing Co. 1994). Refinery investment in SynSat and supporting hydrogen capacity is shown in Table 6. If typically-sized units were installed, then sixty percent of the refineries in PADD III would invest in SynSat capacity. Total refinery investment would be \$3.8 billion for the region.

The RFD sulfur specification can be achieved, albeit with virtually no margin for blending error, with SynSat technology. However, the aromatics specification cannot be met unless cleaner-than-SynSat blendstocks are used. To satisfy the RFD aromatics specification, aromatics-free F-T blendstocks could be purchased. Fifteen percent of RFD would be F-T blendstocks, and there would be no margin for aromatics blending error. Production of F-T for RFD would require an investment of \$8 billion in GTL processes, as shown in Table 7 (Pennwell Publishing Co. 1998).

Capital costs are very sensitive to costs reported for SynSat and GTL investments. Operating costs are not estimated in this analysis.

CONCLUSIONS

Depending on the volume and specification requirements, RFD could be a "big deal" for refiners and others in the fuels industry. Refinery investment in desulfurization, dearomatization, and hydrogen production would be about a third of current refinery market value. The refinery capital cost component alone would be 3 cents per gallon of RFD.

Outside of refineries, the GTL capital cost component would be 3-6 cents per gallon of RFD. With total projected investments of \$11.8 billion (6 to 9 cents per gallon of RFD), financing would be a major issue/uncertainty for both refinery and GTL investments.

Processing adjustments needed for RFD could have significant interactions with crude oil and gasoline quality issues. Purchase of ultra low sulfur/low aromatics blendstocks (like F-T) may be an important part of compliance strategies. The low aromatics specification is binding and has a big influence on RFD production. If the aromatics target had been 12 vol percent, instead of 10 vol percent, then F-T blendstocks would not have been used in the RFD production example.

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Table 1. Diesel Fuel Production in 1997 for U.S. Excluding PADD V (West Coast)
(Source: DOE 1998; API/NPRA 1996)

Fuel	1000 barrels per day (MBD)	Sulfur, ppm	Aromatics vol percent
Low sulfur diesel	1810	340	32
Off- road diesel	>480	3000	31

Table 2. U.S. Regional Production of Low Sulfur Diesel Fuel in 1997
(Source: DOE 1998)

Region	Percent of total national production
PADD I (East Coast)	8
PADD II (Midwest)	33
PADD III (Gulf Coast)	53
PADD IV (Rocky Mountain)	6

Table 3. Typical Blendstocks for Low Sulfur Diesel Fuel in PADD III
(Source: API/NPRA 1996)

Blendstock	Vol percent	Sulfur ppm	Aromatics vol percent	Key processes*
Straight-run	10	570	27	CRU
Cracked unhydrotreated	1	4400	40	FDS, FCC
Hydrotreated (Non-cracked and cracked):				
Naphtha (200-370 °F)	1	430(?)	11	HDS, H2
Light distillate (350-500 °F)	6	70	21	HDS, H2
Heavy distillate (500-650 °F)	71	540	39	HDS, H2
Light gas oil (650-700 °F)	6	1000	50	FDS, FCC, HDS, H2
Hydrocracked:				
Light distillate	1	10	31	HCR, H2
Heavy distillate	3	270	24	HCR, H2

*CRU - crude distillation; FDS - desulfurization of feed for fluid catalytic cracker (FCC); HDS - hydrotreating; H₂ - hydrogen production; HCR - hydrocracking.

Table 4. Reformulated Diesel Fuel Assumed Requirements

Production in PADDs I - IV	2740 MBD*
Production in PADD III	1450 MBD*
Sulfur ppm	30
Aromatics vol percent	10
Cetane number	Higher
T90	Lower
Lubricity**	Maintain quality
Pour***	Current specifications
Flash point, etc.	Current specifications

*On-road diesel fuel with an assumed 25 percent increase to meet increased Light Duty Vehicle demand + plus off-road diesel fuel.

**Lubricity can be degraded with hydrocracked blendstocks.

***Fischer-Tropsch (F-T) blendstocks can have high pour points.

Table 5. Blendstocks for Reformulated Diesel Fuel in PADD III

Blendstock	Vol. percent	Sulfur ppm	Aromatics vol percent	Key processes
Straight-run	0	570	27	
Cracked unhydrotreated	0	4400	40	
Deep Hydrotreating:				
Naphtha	nil	10	10	SynSat, H2
Light distillate	7	10	10	SynSat, H2
Heavy distillate	46	10	10	SynSat, H2
Light gas oil	11	10	10	SynSat, H2
Hydrocracked:				
Light distillate	8	7	12	HCR, H2
Heavy distillate	12	10	21	HCR, H2
Other:				
F-T diesel (purchased)	15	0	0	GTL
Total reformulated diesel	100	8	10**	

*SynSat is hydrosulfurization/dearomatization process licensed by ABB Lummus Crest Inc./Criterion Catalyst Co (Gulf Publishing Co. 1994).

**Binding specification.

Table 6. Refinery Process Investment Including Offsites
(Based On: Gulf Publishing Co. 1994; Oak Ridge National Laboratory Refinery Yield Model)

Process	Typical Unit		Total new capacity in PADD III	Total investment in PADD III, millions\$
	Size	Cost millions\$		
SynSat	25 MBD	68	940 MBD	2600
Hydrogen production	60 million cubic feet per day (MMcfd)	83	850 MMcfd	1200
Total				3800

**Table 7. GTL Investment Including Offsites
(Based on: Pennwell Publishing Co. 1998)**

Process	Typical Unit		Total new capacity for PADD III	Total investment for PADD III, million\$
	Size	Cost million\$		
GTL	65 MBD	1650	320 MBD	8000

FISCHER-TROPSCH LIQUIDS AND HOMOGENEOUS CHARGE COMPRESSION IGNITION

Thomas W. Ryan III and A. William Gray
Southwest Research Institute

INTRODUCTION

The future emissions standards for both light duty and heavy-duty vehicles are very stringent and may not be achievable using conventional diesel combustion technology. In our presentation at this meeting last year [Dickey and Ryan, 1997] it was shown that the application of conventional diesel emissions control technologies, such as Exhaust Gas Recirculation (EGR), water fuel emulsions, charge temperature control, and timing retard will not be sufficient to achieve the future heavy duty diesel emissions standards (1.0 gm/hp-hr NO_x). It was also demonstrated that Homogeneous Charge Compression Ignition (HCCI) is a very low emissions combustion system that might offer an opportunity to achieve low emissions and high efficiency.

HCCI is an engine fuel reaction system in which the fuel and air are premixed, either in the intake system, or in-cylinder using early injection, and reaction is initiated by compression. Experimental work performed over the past three years at Southwest Research Institute (SwRI) [Ryan and Callahan, (1996), Gray and Ryan (1997)] has indicated that the timing of the start of reaction and the reaction rates are fundamentally related to the temperature history during the intake and compression processes. This temperature history in turn is controlled by the intake charge temperature and EGR rate. The resulting reaction is characterized by a two-stage process in which the main reaction is preceded by a smaller pre-reaction. The timing of the pre-reaction is dependent on the time in the cycle when the mixture reaches the auto-ignition temperature of the fuel. The phasing of the main reaction after the pre-reaction appears to be a kinetic process that depends on the thermodynamic conditions in-cylinder and the fuel composition. Thus, fuel composition is an important factor in HCCI operation, but there are currently no fuel specifications that address the ignition and combustion requirements of an HCCI engine.

*Brackets denote entries in Reference Section

The goal of this paper is to summarize the SwRI HCCI work and to present preliminary fuel effects results.

APPARATUS AND PROCEDURES

The HCCI engine development at SwRI has been performed in a single cylinder research engine that incorporates several features that simplified the development process. The most useful of these features included a variable compression ratio, a two-piece piston, an EGR system, and a simulated turbocharger system. These features allowed for examination of the effects of compression ratio, intake manifold pressure, and EGR on the start of reaction (SOR). The two piece piston made it possible to examine the effects of combustion chamber shape and surface coating on HCCI operation.

Figure 1 is a schematic of the test engine. The schematic shows the EGR system and the location of the fuel injection nozzle in the intake system well upstream of the intake port. The initial effort focused on creation of a homogeneous mixture of fuel vapor and air in the intake runner. This required very high air and surface temperatures because diesel fuel was selected as the fuel of choice for heavy-duty engine applications. The initial experiments demonstrated, however, that the fuel did not have to be totally vaporized. It is sufficient to create a homogeneous mixture of small fuel droplets and air. This finding led to the development of a port-fuel injection scheme in which an air assist fuel injector is located in the intake port, targeted at the intake valve. This configuration is shown schematically in Figure 2.

The intake air to the engine was supplied using an external compressor and air-conditioning system that made it possible to control the intake manifold pressure and temperature. The EGR rate was controlled by adjusting the engine back pressure to create the appropriate pressure differential for the desired EGR flow. EGR rate was monitored using simultaneous CO₂ measurements in both the intake manifold and the exhaust manifolds.

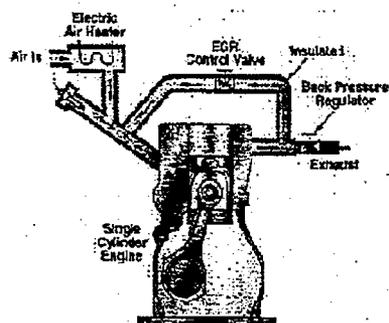


Figure 1. Schematic of Single-Cylinder Test Engine Installation

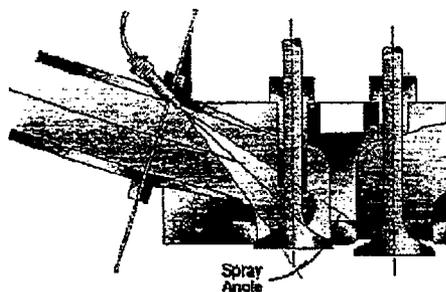


Figure 2. Schematic of Port Injection Configuration

The engine was equipped with a SwRI develop engine control system that allowed for control of the injection timing and quantity. A wide range oxygen sensor in the exhaust was used to set and control the equivalence ratio. The equivalence ratio was also computed based on the gaseous emissions measurements. Exhaust particulate (PM) measurements were made during the initial experiments, but it was observed that the PM soot levels are always near zero when operating in HCCI mode. It was also observed that the Bosch Smoke (BSN) provided a similar indication of the successful achievement of HCCI operation. BSN was used as the indicator of the PM levels as well as an indicator of HCCI operation.

The fuel injector was an air assist injector developed at SwRI to produce a very finely atomized spray. The injector was characterized by measurements of the drop size distribution using a laser diffraction instrument. The results of these measurements are presented in Figure 3. The results indicate that the SMD is generally less than 10 microns. Droplets in this size range will follow the airflow and generally behave aerodynamically as gaseous fuel. All subsequent

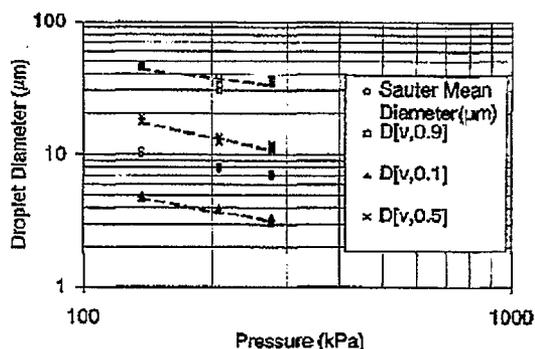


Figure 3. Sauter Mean Diameter Versus Air Supply Pressure

tests were performed using the air assist injector installed in the port injection configuration.

EXPERIMENTAL RESULTS

The experiments using diesel fuel have indicated that there are a number of conflicting issues related to the relationship between intake air temperature, the timing of the SOR, and the onset of soot formation. It was observed that an increase in soot formation, as indicated by an increase in BSN from zero, signals the on-set of non-HCCI operation. The onset of soot formation for diesel fuel occurs at intake air temperatures below 150°C. The initial fuels experiments were performed with blends of gasoline in diesel fuel. It was felt that the increased volatility and lower cetane number of gasoline would improve the mixture preparation and ignition characteristics for HCCI operation. The onset of soot formation occurs in the range of intake air temperatures from 130 to 150°C, for the blends of gasoline and diesel fuel. These trends are demonstrated in Figure 4, where the BSN is plotted versus intake air temperature. In general, the presence of gasoline tends to reduce the temperature, but the limit is still above 130°C. This temperature is of concern because of the potential impact on the

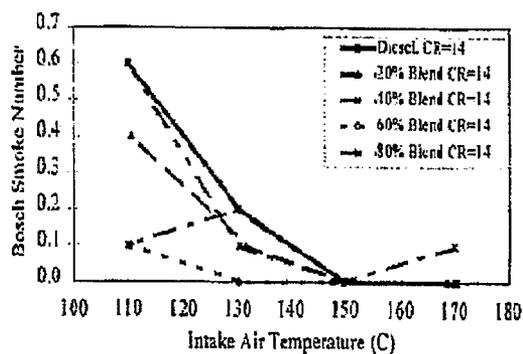


Figure 4. BSN Versus Intake Air Temperature

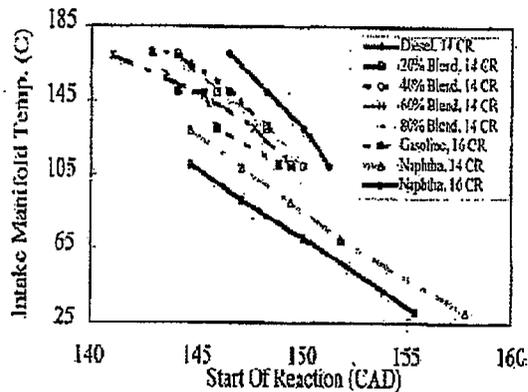


Figure 5. Intake Manifold Temperature Versus Start of Reaction

volumetric efficiency. In addition, it was observed that this intake temperature leads to early SOR for diesel fuel and all of the blends with gasoline.

The high intake temperature requirements for maintenance of HCCI operation appears to be related to issues associated with mixture preparation, possibly connected to fuel vaporization during the compression process. The SOR for diesel fuel occurs during the compression stroke, even with lower than typical diesel engine compression ratios. Early SOR with diesel fuel is related to the fact that diesel fuel has

an autoignition temperature that is too low. This problem is exacerbated by the fact that the mixture preparation requirements for diesel fuel HCCI are for high intake air temperatures, which further advances the SOR. The SOR is dominated by the autoignition temperature of the fuel and the temperature history of the fuel air mixture. Based on the results with the gasoline-diesel fuel blends it appears that the autoignition temperature does not blend linearly because the SOR timing was not retarded significantly with the addition of the gasoline. This is demonstrated in Figure 5, where the intake manifold temperature is plotted versus the SOR. Also shown in the plot are the corresponding data for naphtha produced from Fischer Tropsch processing of natural gas. In an effort to address the temperature requirements, different fuels were considered, and a naphtha fraction from Fischer Tropsch processing of natural gas was selected for testing. The naphtha fraction was chosen because the boiling point distribution is lower than diesel fuel, possibly reducing the mixture preparation temperature requirements. Also, the naphtha fraction typically has a lower cetane number, and therefore a higher autoignition temperature than diesel fuel, possibly retarding the SOR at diesel engine compression ratios.

The results shown in Figure 5 for the blended fuels indicate that the higher percentages of gasoline actually produces a decrease in the required intake temperature, as indicated by a decrease in the intake manifold temperature at any selected SOR. The DF-2 fuel exhibits the latest SOR at each test condition for temperatures greater than 110°C. For these conditions the gasoline blended into the diesel fuel is acting to decrease the ignition delay, or temperature of reaction, of the fuel. Rather than delaying SOR and peak HR, the blends advance them significantly. In general the greater the blend percentage of gasoline the shorter the ignition delay. The gasoline fueled HCCI runs also exhibit earlier SOR than those of the diesel only runs. This may be caused by greater vaporization of the gasoline.

The results for the naphtha fuel used in testing are encouraging with respect to intake temperature and combustion characteristics. Naphtha has reaction timing similar to that of DF-2 fuels at similar temperatures, however it also provides the HCCI reaction at ambient intake air temperatures. There is no comparison of the smoke levels of the two fuels because naphtha fueled HCCI produced zero smoke at all test conditions. Figures 6-9 below show a comparison of results for DF-2 and naphtha runs taken during the fuels evaluation testing. The runs were chosen based on similar power levels. Figure 6 shows the operating conditions for the two runs. Figures 7-9 show comparisons of combustion analysis data.

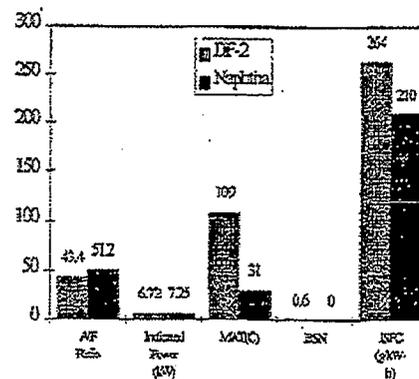


Figure 6. Operating Conditions for Comparison Runs

Review of the combustion data reveals that the peak cylinder pressure is greater for naphtha fueled HCCI (Figure 7), the peak value of the main heat release rate is less (Figure 8), and the

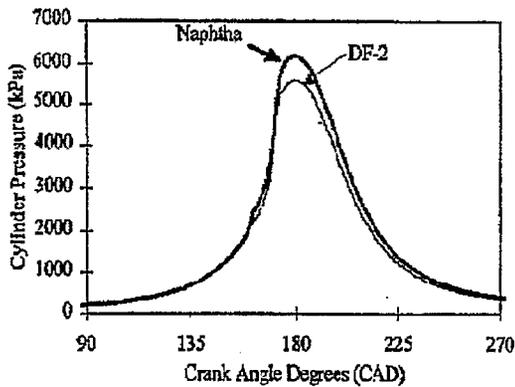


Figure 7. Cylinder Pressure Comparison

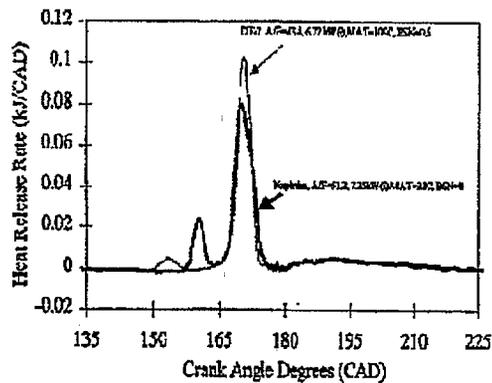


Figure 8. Heat Release Rate Comparison

cumulative heat release is greater (Figure 9). The most noticeable difference in the shape of the heat release shown in Figure 8 is that the initial heat release of the naphtha runs is greater than that of the diesel fueled runs. The SOR occurs later in the engine cycle and a greater fraction of the fuel is consumed during the initial heat release. This has the effect of moving the peak cylinder pressure closer to TDC.

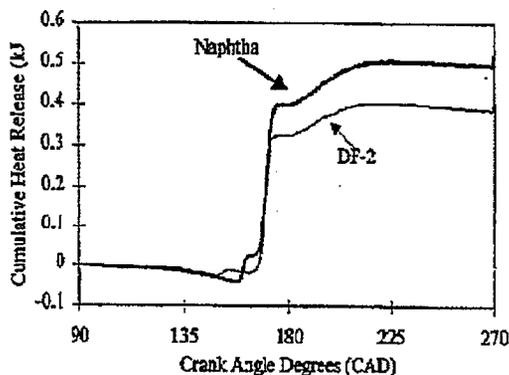


Figure 9. Cumulative Heat Release Comparison

The stability of the HCCI reaction is also enhanced through the use of naphtha. It is possible to start the engine from room temperature (30°C) with the naphtha fuel and not produce soot (BSN=0). The naphtha was also tested at higher compression ratios. The results of the combustion analysis are presented in Figure 10. The heat release rate diagrams for the naphtha are plotted in Figure 11 for different intake manifold temperatures. As can be seen, both the timing of the initial heat release and the phasing between the initial and the main reaction events are affected by the intake temperature, with the initial reaction delayed and the phasing reduced as the intake temperature was reduced.

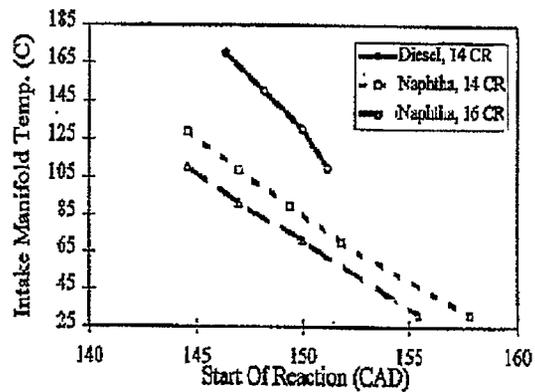


Figure 10. Intake Manifold Temperature Versus Start of Reaction

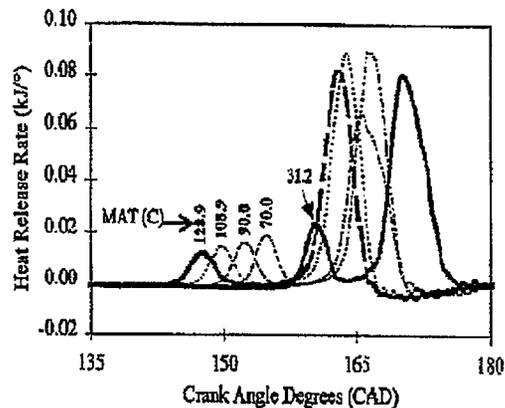


Figure 11. Heat Release Rate Diagrams for Different Intake Temperature

SUMMARY

The results of the HCCI engine development at SwRI have indicated that HCCI can be successfully achieved using a state-of-the-art air-assist port fuel injector, located in the typical port

fuel injector location. These results indicate that it is not necessary to create a homogeneous mixture of fuel vapor and air, but rather a homogeneous mixture of small drops in air in order to achieve HCCI operation.

The results of the gasoline-diesel fuel blend tests indicated that the SOR is dominated by the ignition characteristics of the lowest ignition temperature component, suggesting that the SOR characteristics of fuels do not blend linearly. These results also suggest that significant effort should be devoted to development a new fuel specification for HCCI engines. It is clear from the results of these tests that both the gasoline and diesel fuel specifications are inadequate for HCCI engines.

Development of the fuel specification should include consideration of the properties that affect the mixture preparation and ignition temperature. Mixture preparation in an HCCI engine is probably dominated by the boiling point distribution. The SOR characteristics of the fuel are reflected in the autoignition temperature and possibly in the volatility of the fuel.

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INCORPORATING OXYGEN IN DIESEL FUEL AS A MEANS OF REDUCING ENGINE EMISSIONS

A. L. Boehman

The Pennsylvania State University, University Park, PA 16802

P. J. A. Tijm

Air Products and Chemicals, Inc., Allentown, PA 18195

ABSTRACT

Dimethyl ether (DME) and a liquid fuel additive made from dimethyl ether offer the promise of reduced Diesel engine emissions without a sacrifice in performance. The liquid fuel additive, CETANER™, offers the additional benefit of a seamless transition to cleaner burning, reformulated Diesel fuel. Inclusion of oxygen in Diesel fuel is known to reduce particulate emissions. But, DME and CETANER™ offer the additional benefit of a high cetane number. DME has a cetane number of 55 and CETANER™ can be formulated to have a cetane number as high as 125, making CETANER™ both an oxygenating and a cetane boosting fuel additive. Both fuels can lead to cleaner burning Diesel engines and potentially, to greater market acceptance of Diesel powered vehicles.

INTRODUCTION

Due to the nature of the compression-ignition process and Diesel fuel composition, particulate and nitrogen oxides (NO_x) emissions are the chief concerns for Diesel engines. Without a viable "Lean NO_x" catalyst, effective control of particulate emissions is needed to allow the flexibility to use exhaust gas recirculation (EGR) to control NO_x. Effective control of particulate emissions can be achieved with fuel reformulation using current engine hardware.

In this paper, we describe two on-going research studies in which oxygen is being incorporated into Diesel fuel to reduce emissions. The oxygenates of interest are CETANER™ and Dimethyl Ether (DME). Both fuels can be most economically produced from syngas using Air Products and Chemicals, Inc. liquid phase process technology. Figure 1 shows a diagram of how these fuels can be incorporated into the transportation sector.

DME, used predominantly as an aerosol propellant, has shown promise as an alternative Diesel fuel, yielding emission levels at or below

those proscribed by the California ULEV standard [1-7]. If commercialization of a new, lower cost production method is successful, DME may also find use as an alternative utility fuel [8]. The primary commercial process for production of DME today involves the dehydration of methanol. Dehydration is satisfactory for DME production geared toward current demand, but it is not cost effective for the mass production of DME required for widespread fuel use [7]. The recent and intense interest in DME as a transportation fuel has arisen from development of new methods to produce DME on a larger scale from natural gas [7] and from syngas in a one step slurry phase process [9]. The latter approach is a promising new method of producing DME directly from syngas in a single, slurry-phase reactor using a physical mixture of a commercial methanol synthesis catalyst and a proprietary dehydration catalyst, slurried in mineral oil [9]. This Liquid Phase Dimethyl Ether (LPDME™) process can be incorporated into an integrated gasification combined cycle (IGCC) plant to fully utilize the capacity of the gasifier(s). It can also be a stand-alone process to produce DME for use as a replacement Diesel fuel, a domestic fuel, or a chemical building block [9].

CETANER™ is produced through an oligimerization of dimethyl ether, which could be added as a process step during the LPDME™ process to produce CETANER™ from syngas. CETANER is expected to be produced at roughly the price of Diesel fuel, and it is miscible in Diesel fuel at high concentrations [9]. So CETANER™ represents a tremendous potential for reducing the emissions and from stationary Diesel powered systems, as well.

What follows is a summary of progress to date on two projects: one involving a detailed experimental study of various oxygenates, including CETANER™ in a laboratory engine; and one involving a demonstration vehicle that will be operated on blends of DME and Diesel fuel. The

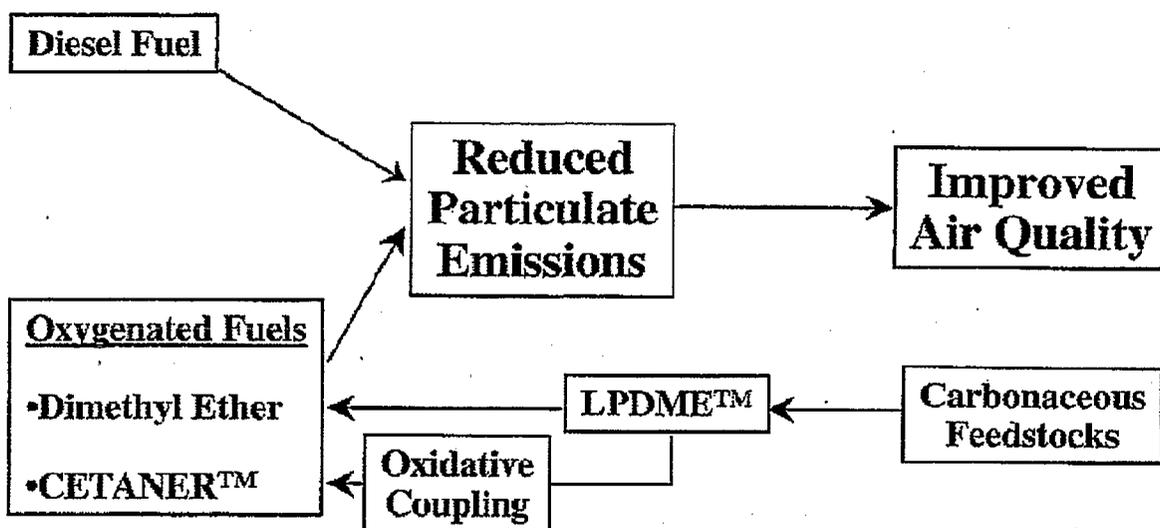


Figure 1. Approaches to Incorporate Oxygen in Diesel Fuel Using Air Products' Liquid Phase Dimethyl Ether (LPDME™) Process Technology.

objective of both projects are to reduce Diesel particulate emissions through incorporation of oxygen in Diesel fuel.

EFFECT OF OXYGENATED CETANE IMPROVER ON DIESEL ENGINE COMBUSTION AND EMISSIONS

Introduction

Oxygenated fuel blends produce a significant reduction in emissions of particulate matter from Diesel engines. The reformulated fuel can effectively deliver oxygen to the pyrolysis zone of the burning fuel, resulting in reduced particulate matter generation [10,11]. Although several oxygenate types are available for blending with Diesel fuel, the most effective oxygenates for particulate matter reduction are vegetable oil-derived esters and ethers. Blending of vegetable oils with Diesel fuel has been evaluated; however, a blend with 30% vegetable oils has been shown to result in a significant power reduction [12]. Much research has instead focused on utilizing methyl esters derived from the transesterification of vegetable oils [13,14]. In addition, several glycol ethers have also been shown to successfully inhibit particulate formation [15-17]. Also, CETANER™ has demonstrated a high cetane response when blended in Diesel fuel [9].

In this study, the objective is to understand how different oxygenates function in Diesel fuel and their potential for particulate emissions reduction. The work completed thus far has been through a graduate-level problem-based learning course. A group of five graduate students obtained the data

reported here through their course of study. The work presented here focuses on measurement of the physical properties of blends of Diesel fuel and various oxygenates, and the particulate emissions reductions that these blends can provide. The students' target was to reduce particulate emissions from a laboratory engine by 30% through fuel reformulation.

Experimental Approach and Results

For this experimental work, glyme, diglyme, triglyme, CETANER™, DGME and methyl soyate were selected. Data reported by Liotta and Montalvo indicated that particulate matter reductions of 4-10% could be achieved for each 1% of oxygen blended into Diesel fuel [15]. Based on this assumption, 4 wt% oxygen in the blends was chosen in order to reach the target 30% reduction. Blend ratios are listed in Table 1.

Each of the oxygenate blends was tested for viscosity, density, cloud point and flash point, for comparison with the baseline fuel. In addition, the results were compared to the ASTM D 975 specifications for No. 2 Diesel fuel [18]. Data for the baseline and the blended fuels is shown in Table 2.

Several oxygenate blends did not meet all ASTM specifications. The methyl soyate blend did not pass the cloud point specification, an indication of potential low-temperature concerns. The glyme

Table 1. Oxygenate Blends Selected for Evaluation.

Oxygenate Blended	Structure	Notation	Wt% Oxygen	Blend Ratio
diethylene glycol methyl ether	$\text{CH}_3\text{OC}_2\text{H}_4\text{OC}_2\text{H}_4\text{OH}$	DGME	40.0	10/90
CETANER™* 96% 1,2-dimethoxyethane 4% dimethoxymethane	$\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3$ $\text{CH}_3\text{OCH}_2\text{OCH}_3$	CETANER™	36.5 (35.6) (59.3)	11/89
triethylene glycol dimethyl ether	$\text{CH}_3\text{O}(\text{C}_2\text{H}_4\text{O})_3\text{CH}_3$	Triglyme	36.0	11/89
Diethylene glycol dimethyl ether	$\text{CH}_3\text{O}(\text{C}_2\text{H}_4\text{O})_2\text{CH}_3$	Diglyme	35.8	11/89
1,2-dimethoxyethane	$\text{CH}_3\text{O}(\text{C}_2\text{H}_4\text{O})\text{CH}_3$	Glyme	35.6	11/89
Methyl Soyate	Mixed esters	Me Soyate	11.0	35/65

*Simplified mixture chosen to represent a potential CETANER™ formulation.

Table 2. Results from Testing of Several Fuel Properties.

Oxygenate Blend Tested	Saybolt Viscosity (SUS), 100°F	API Gravity and Density (g/cm³)	Cloud Point (°F)	Flash Point (°F)
ASTM Method	D 445	D 287 / D 1298	D 2500	D 93
ASTM Specification	32.6-40.1	API 30	0	125
No.2 Diesel	32.67	0.8050	< 0	173
Diglyme	30.33	0.8124	< 0	156
Triglyme	29.86	0.7935	< 0	185
Glyme	30.14	0.8025	< 0	78
DGME	28.83	0.8150	< 0	189
CETANER™	27.70	0.8233	< 0	71
Methyl Soyate	30.23	0.8257	8	207

and CETANER™ blends were each found to have a low flash point, which could lead to storage concerns. Further, while the baseline Diesel fuel was at the lower specification for Saybolt viscosity, all the blends were below spec.

Engine testing was completed using a single-cylinder indirect injection (IDI) Yanmar TS-180 Diesel utility engine with a continuous rating of 15 HP (11.2 kW) at 2400 rpm, coupled with a Clayton CAM-50 water brake dynamometer. No adjustments were made to the engine operating parameters (e.g., fuel injection timing was not modified). A DAS-8/PGA data acquisition and control board from Keithley Metrabyte was used to log real-time engine speed, torque and power, as well as exhaust, lube oil and coolant temperatures. Testing was completed as per International Standards Organization (ISO) 8178 Standard type E3 protocol [19]. Table 3 lists the conditions of this test matrix.

with a constant dilution air / sample flow ratio of 5. Particulate collection occurred on Pallflex TX40H20WW filters, conditioned in an environmental chamber at 25°C and 45% relative humidity before and after sampling. Evaluations during each mode were begun once the RPM and loads were within 5% of the target test conditions. An extended warm-up period was used to prepare the engine for testing. Dwell time for each mode was ten minutes, with a minimum ten-minute stabilization period between the modes.

From each test, fuel consumption data was collected. Based on the power output for each mode, specific fuel consumption was calculated and is shown in Figure 2. The Specific Fuel Consumption (SFC) results show some variation, especially in mode 4, which is completed at the lowest RPM and load settings. Increases in SFC for the triglyme and CETANER™ blends are seen in mode 4; however, the scale accuracy is

A portion of the exhaust gas was passed through a Sierra Instruments BG-1 mini-dilution tunnel

Table 3. Engine Test Matrix Based on ISO 8178 Type E3 Test Protocol

	Mode 1	Mode 2	Mode 3	Mode 4
Speed (RPM)	2200	2002	1760	1386
% Rated Speed	100	91	80	63
Power (hp)	12.26	8.77	5.32	2.03
% Rated Power	81.7	58.5	35.5	13.5
Weighting Factor	0.2	0.5	0.15	0.15

approximately $\pm 10\%$ for this mode, and further experimentation with a scale with higher sensitivity is recommended before drawing conclusions on the SFC data presented. In addition, there were difficulties in maintaining speed and power settings for mode 4 of several tests due to engine knock, which contributed to the variability. Finally, it is important to also note that although the use of these oxygenated fuel blends may negatively impact SFC on a g/kWh basis (as seen in Figure 2), the improvements in the combustion process that are provided by these blends lead to improvements in specific energy consumption (SEC, MJ/kWh).

Conclusions

The results presented indicate that significant particulate matter emission reductions can be achieved without any modifications to the engine operation parameters (e.g., fuel injection timing). In particular, the CETANER™ blend showed the highest reduction in particulate matter, with a 32.8% reduction from the baseline when blended with No. 2 Diesel fuel. However, this specific CETANER™ blend has a flashpoint of 71°F, which presents potential safety and handling concerns. It is important to also note that CETANER™ consists primarily of glyme; however, particulate matter emission results from

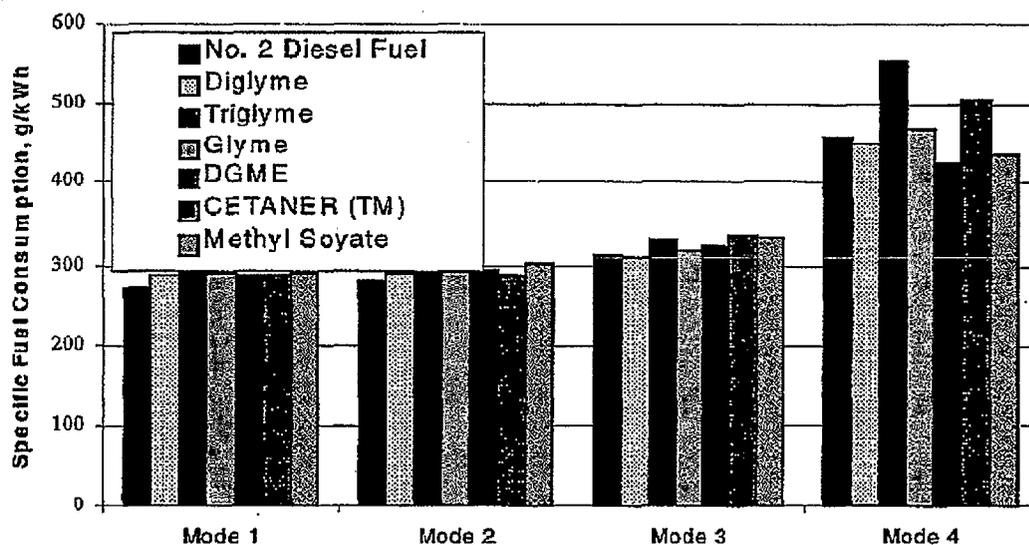


Figure 2. Specific Fuel Consumption Results, g/kWh.

The raw particulate emission data were converted to brake-specific particulate emissions which is shown in Figure 3. Overall particulate emissions were calculated based on the weighting factors for each mode of the ISO 8178 test protocol. The aggregated brake-specific particulate matter emissions are shown in Table 4.

the fuel blends of these two additives were significantly different. It is believed that the differences were due to less than ideal operating conditions during testing of the glyme blend; further testing of the glyme blend is recommended, taking into account the composition of CETANER™ and perhaps

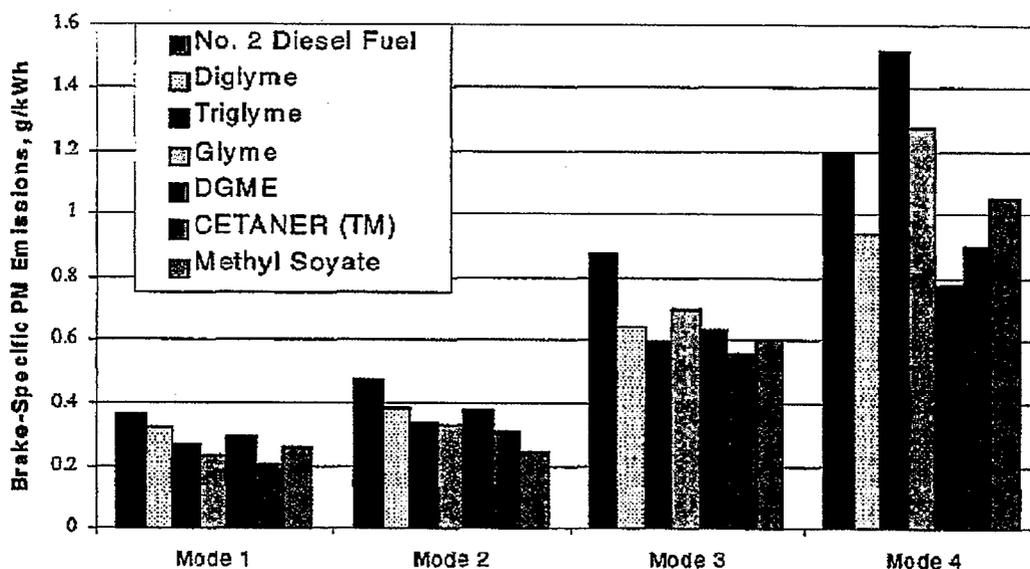


Figure 3. Brake-Specific Particulate Emissions, g/kWhr.

Table 4. Total Brake-Specific Particulate Emissions, g/kWhr.

	% wt Oxygen in Blend	BS PM, g/kWhr	% change from baseline
Baseline BP No. 2 Diesel Fuel	---	0.612	---
Triglyme	3.91	0.538	-12.1%
Glyme	3.89	0.505	-17.5%
Diglyme	3.21	0.494	-19.3%
DGME	4.26	0.457	-25.3%
Methyl Soyate	3.90	0.423	-30.9%
CETANER™	3.92	0.411	-32.8%

reducing the glyme content of CETANER™, which can alleviate the flashpoint concern.

The methyl soyate blend also showed excellent reduction of particulates, at 30.9% below the baseline when blended with No.2 Diesel fuel. It has the advantage that it is a renewable resource and is economically viable. However, the cloud point of the blend was found to be 8°F. Further research in the use of cloud and pour point depressants to enhance the cold weather properties is recommended.

The DGME blend resulted in a 25.3% particulate emission reduction, while maintaining an acceptable density, cloud point and flash point. Of the oxygenate blends evaluated, DGME currently appears to be the most viable method of

reformulating Diesel fuel; however, CETANER™ and methyl soyate both showed potential in oxygenate fuel blends, given further optimization.

The diglyme blend resulted in a 19.3% particulate reduction. It is important to note that the blend was completed at a level slightly above 3 wt% oxygen, due to a calculation error realized after completion of the experimental work. Had diglyme been blended in order to yield 4 wt% oxygen in the fuel blend, it is felt that the particulate matter emissions would have been reduced ever further.

DEVELOPMENT OF A DIMETHYL ETHER (DME)-FUELED SHUTTLE BUS DEMONSTRATION PROJECT

Introduction

This project is driven by Air Products' interest in the development of markets for the Liquid Phase Dimethyl Ether process technology and the state of Pennsylvania's interest in development of transportation fuel usage from Pennsylvania resources (e.g., coal). The project is being funded under the Pennsylvania Department of Environmental Protection (DEP) Alternative Fuels Incentive Grant (AFIG) program. The program manager is Susan Summers. In this project we (Penn State Energy Institute and Air Products and Chemicals, Inc.) will determine how to effect the conversion of a shuttle bus equipped with a Navistar T444E turbodiesel engine to operation on Dimethyl Ether (DME). To accomplish this goal, we will examine the co-firing of the engine on Diesel fuel and dimethyl ether, using the Diesel fuel as a lubricating agent to protect the fuel pump and fuel injection system from excessive wear. Dimethyl ether has no natural lubricity, making it antagonistic to fuel system components [2-6].

Project Plan

The work consists of two parallel efforts. One is an evaluation of the performance, emissions and efficiency of a shuttle bus equipped with a Diesel engine and operated on dimethyl ether. That work will rely on the bus testing facilities and portable emissions analysis equipment of the Pennsylvania Transportation Institute (PTI). The other is the development of a conversion process to operate a Diesel engine on dimethyl ether using conventional fuel injection equipment. PTI will evaluate the in-service performance, emissions and efficiency of a shuttle bus (Champion "Defender" model) that serves as a faculty/staff shuttle on the University Park campus. Initially, the bus will be operated on Diesel fuel to provide baseline information. Tests will be performed after break-in of the vehicle and at several intervals before the conversion to dimethyl ether operation.

Meanwhile, a dimethyl ether fueling station will be constructed on the University Park campus. Tanker trucks will deliver fuel to this station from the Alternative Fuels Development Unit (AFDU) in LaPorte, Texas. This fuel grade dimethyl ether (a mixture of DME and methanol) will be blended with Diesel fuel either on-site in LaPorte for transport to State College, at the University Park fueling station, or on-board the vehicle.

During the baseline operation period of the shuttle bus, we will determine how to perform the conversion of a Navistar T444E turbodiesel engine to DME through laboratory testing with a stand-alone engine. This work will be accomplished in a new engine test cell that is under construction at the Penn State Energy Institute. This cell consists of a 400 hp Eaton eddy current dynamometer, a Nicolet FTIR spectrometer, an HP 6890 Gas Chromatograph, Horiba on-line emissions analyzers, an R&P Series 5100 Diesel Particulate Analyzer, a Sierra Instruments BG-1 Microdilution test stand, and in-cylinder pressure sensing equipment for emissions and combustion analysis. The objective of the laboratory testing is to determine the compositions of fuel and additive blends that will permit long term operation of the T444E engine on dimethyl ether. Three additives will be considered, a Lubrizol lubricity agent, an Ethyl Additives lubricity agent and methyl soyate. Fuel blends will range from very low DME composition in the initial phase of tests, to as high a DME content as the engine can tolerate. Wear of the fuel injection system components will be used to judge the tolerance of the engine to DME fueling and to judge the effectiveness of the additives and Diesel fuel for protection of the fuel system components.

Fuel Systems and Fuel Properties Studies

Recent reports on DME in Diesel fuel systems have demonstrated that the challenges of working with DME are much more substantial than may have been anticipated when DME was first considered as a replacement Diesel fuel. James McCandless of AVL Powertrain Engineering, Plymouth, MI, has reported that development of a completely fuel flexible injection system called NFIS (Novel Fuel Injection System) had made progress but still faces challenges with regard to durability [20]. Spencer Sorenson of the Technical University of Denmark reported that the physical and thermodynamic properties of DME (low critical pressure and low viscosity) create anomalies during fuel injection including: fuel system pressure oscillations that can cause "after-injections"; and loss or degradation of needle lift function due to increased compressibility of the fuel at higher injection pressures [21].

The earlier studies of DME as a replacement Diesel fuel (e.g., Ref. 2-6) demonstrated substantial emissions reductions with DME but problems with durability arose in the fuel injection system. Some of these earlier studies included a Lubrizol lubricity additive in the DME to attempt to protect the fuel system from excessive wear. This

did not prove to be sufficient to allow long term use of DME in a Diesel engine with a conventional fuel system. We suspect that the problem in these earlier tests may have been that because the fuel injection pressures exceeded the critical pressure of DME, a supercritical mixture of fuel and additive was formed. In the supercritical phase, the additive may not have been miscible with DME and consequently, the additive could no longer provide adequate lubricity to the fuel.

We intend to study both the phase behavior of mixtures of DME, Diesel, and lubricity additives and examine the viscosity and lubricating quality of these mixtures. These tests will rely on an existing but idle piece of equipment in the Tribology Laboratory in the Department of Chemical Engineering at Penn State. The work will be done in collaboration with Prof. J.M. Perez. This high pressure viscometer apparatus can permit studies of viscosity and lubricating quality at temperatures and pressures that are relevant to the fuel injection system on a Diesel engine. With this apparatus, we will examine viscosity and wear rates, using standard lubricant testing procedures, for mixtures of fuel ranging from high Diesel/low DME content to low Diesel/high DME content. The additives that we will consider include lubricity agents from Lubrizol, and Ethyl additives, as well as, methyl soyate. Methyl soyate is a primary constituent of transesterified soybean oil and provides bio-Diesel fuel with a higher lubricity than conventional Diesel fuel possesses.

As a consequence of these experiments, we will determine the range of fuel blend compositions that provides adequate lubricating quality to protect the fuel injection system. Also, as a consequence we will be able to deduce conditions under which the fuel blends are likely to exhibit phase separation. We expect to also build into the experiment a capability to directly determine whether phase separation has occurred. Determination of the miscibility of supercritical fluids is an important consideration in supercritical fluid processing technology, and in that literature there are a number of relatively simple strategies described for determination of phase separation. Many of these techniques rely on scattering of a low power laser beam passed through a pressurized cell. If possible, we will configure the viscosity experiment to provide optical access so that a direct determination of phase separation can be made during the viscosity and wear rate measurements. If this is not possible, then we will design and construct a small cell for making these measurements. This portion of the research study is receiving support from the U.S. D.O.E.

Federal Energy Technology Center. The program manager at D.O. E. is John Winslow.

Expected Outcomes and Project Timeline

Two expected outcomes of the laboratory testing are determination of the maximum DME concentration that can run in conventional engine hardware and what additives and additive concentrations are necessary to ensure fuel system integrity. The goal will be to maximize DME utilization, without sacrificing long term durability of the fuel system. Once this information is in hand, Air Products and Penn State will develop fuel system hardware for use on the shuttle bus and install the converted engine into the shuttle bus. The conversion is expected to occur 18 months after start of the project. Then PTI will perform the emissions, performance and efficiency tests on the converted vehicle at several intervals over another 18-month period. The Diesel engine that originally was mounted in the bus will be converted to DME operation in the laboratory for continuing studies of fuel system durability.

Thus, the project timeline covers three years, with the first 18 months involving baseline bus testing and fuel conversion development. This will be followed by 18 months of shuttle operation on DME fuel blends and continuing durability analyses in the laboratory.

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the project and has agreed to provide technical guidance during the laboratory studies. Navistar International and Champion Motor Coach have agreed to cost share on the purchase of the shuttle bus for the on-road demonstration phase of the project.

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A STUDY OF THE COMPATIBILITY OF SEVERAL METHANOL FUELS AND ENGINE LUBRICANTS

J. M. Perez and A. L. Boehman
The Pennsylvania State University

ABSTRACT

Two laboratory methods developed to simulate crankcase and fuel injection systems were used to evaluate the compatibility of several alternative fuels with two commercial engine oils. Six alternative fuels evaluated include M100 and five fuels containing additives or fuel mixtures. Changes in the performance of the lubricants were evaluated following simulated fuel injector and crankcase interaction of fuel and lubricant. Changes in the oxidation stability and deposit forming tendencies following extraction of additives by the fuels were measured using the Klaus Penn State Micro-Oxidation (PSMO) and isothermal differential scanning calorimetry (DSC). A electrochemical method was used to determine the extent of the extraction of the additives. The study examines the effect of chemical structure of the base fluid and the additives on the extraction process and changes in performance of the lubricant.

Keywords: Lubricants, Oxidation, Thermal Analysis, Alternative Fuels, Thin-film Methods

INTRODUCTION

Environmental issues have resulted in the use of alternative fuels such as methanol in trucks, busses and cars. With the exception of formaldehyde, the alcohol fuels produce less chemically reactive emissions than gasoline. Renewed interest in methanol fuels resulted in revisiting some of the issues regarding the used of alternative fuels. As part of an overall study on alcohol fuels (1), the effect of several modified methanol fuels on the lubricant is reported in this paper.

During the oil crisis in the early 1980's, there was a considerable effort to increase the use of alcohol fuels in modified heavy duty diesel truck engines and automotive engines (2). Diesel fleet tests surfaced problems with injector plugging and increased friction and wear in some engines (3,4).

In a diesel engine, the crankcase lubricant is used to lubricate the bearings, piston-ring and liner components and the fuel injector system. Problems identified in the field tests included injector plugging and increased wear. In the crankcase, blow-by products resulted in fuel contamination and condensed methanol fuel was found to exceed 20 percent in some engines. In the fuel injector, there is interaction between large quantities of fuel and a small amount of lubricant and tip plugging deposit formation was occurring.

Klaus and others researched the problem (5,6) and found that the alcohol preferentially extracted additives from the lubricant leaving the remaining raffinate more susceptible to oxidation. In the fuel injector, deposits were forming on the injector tips as a result of loss of additives resulting in increased oxidation. In the crankcase, additives were similarly extracted causing both increased oxidation and wear in the system.

Two bench methods were developed to simulate the diesel engine problems with the alcohol fuels. The two simulation methods were used to study the alternate fuels in this paper. The study involves an evaluation of six methanol fuels and two commercial lubricants. An evaluation of the effect of the fuels on the lubricants was performed using the two simulation tests.

Pressurized differential scanning calorimetry (PDSC), the Penn State Micro-oxidation Test (PSMO) and the Remaining Useful Life Evaluation Routine (RULERTM) methods were used to evaluate the changes in the lubricant performance.

ALTERNATIVE FUEL-LUBRICANT STUDY

Fuels

A total of six fuels were evaluated, Table 1. The fuels evaluated included methanol (M-100) and methanol with additives. Two additives were commercial additives used to reduce carbon deposit formation. Gasoline,

light naphtha or isopentane were added to methanol and were the remaining fuel mixtures evaluated.

FUEL	DESCRIPTION
M-100	METHANOL
M-100+0.06% Add A	COMMERCIAL
M-100+0.12% Add B	COMMERCIAL
M92 RF-A	8% GASOLINE
LN M92	8% Lgt NAPHTHA
IP M95	5% ISOPENTANE

Lubricants

A commercial synthetic 10W30 Flex Fuel automotive engine oil, designated PRL 4723, and a commercial low ash 40wt HDD (heavy duty diesel) engine oil, designated PRL 4713, were used in the study. Most work is with PRL 4713 due to difficulties in separating the emulsions formed with the synthetic oil.

Experimental Methods

The methods used to research the properties of base fluids and additives include: Pressurized Differential Scanning Calorimetry (PDSC), Thin-film Microoxidation (PSMO) tests and Remaining Useful Life Evaluation Regime (RULER™).

PDSC. This method is widely used and one of the earliest applications to lubricant research was reported by Walker et al (7). PDSC applications are run either in an isothermal or a programmed temperature mode. There are a number of modifications of the methods in use. Variations include sample size, flow rates, temperature sequence and type of sample pan.

The PDSC has also been used to study oxidation stability of engine oils (8,9). A correlation of the PDSC and the Thin-Film Oxygen Uptake Test (TFOUT) used to screen lubricants for ASTM IIID and IIIE automotive tests is reported in the literature (10,11).

PSMO. The Klaus Penn State Microreactor is described in the literature (12-15). The PSMO test is a thin film test using as little as 20 ul of test fluid in which volatility loss, oxidized product formation and deposits can be measured. In this study, 20 ul samples were oxidized in an air atmosphere at 225°C for 30 minutes and the volatility and deposit formation measured.

RULER™. This is an electrochemical voltammetric method that was used in this study to confirm the findings of the PDSC and PSMO. The method was developed by Kaufmann to predict the remaining useful life of aircraft turbine lubricants and is described in the literature (16,17). Basically, a small, 200 ul, sample is dissolved in a solvent containing an electrolyte. The additive response is determined by use of a controlled voltage ramp through an electrode inserted into the mixture. This results in a peak at the oxidation potential of the additive evaluated. The peak height is related to the concentration of the additive in the sample.

Simulation Test Methods

The analytical test methods were essentially the same as those described above. The samples analyzed were prepared using the two fuel contamination simulations developed by Klaus et al (5,6). These are designated as the fuel injector simulation (FIS) and the crankcase contamination simulation (CCS).

FIS. To simulate the fuel injector system situation in the laboratory, a 1000:1 fuel to oil mixture in a large flask was kept at 25 °C in a water bath for a week with occasional mixing. Then, the extract layer was carefully decanted and the alcohol removed by distillation. The remaining oil residue was transferred to a vacuum flask and any remaining fuel stripped off under vacuum with slight heating (70°C).

The raffinate layer remaining in the flask, along with a small emulsion layer and about 200 mls of fuel, were also decanted and most of the remaining fuel distilled off. The sample was then poured into a vacuum flask and any remaining fuel stripped off.

The FIS results in an extraction fraction and a raffinate fraction that contains base oil and remaining additives from the original lubricant. All samples were weighed to determine sample recovery.

CCS. It was found from an evaluation of field samples that the crankcase dilution would often exceed 20 percent by weight and could go as high as 30 %. The crankcase simulation (CCS) developed by Klaus et al was to add 25 g of alcohol fuel to 100 g of the crankcase lubricant in a 500 ml Erlenmeyer flask. The flask was stoppered, the mixture swirled for a couple of minutes by hand, and then place on a wrist action mechanical

shaker where it was shaken for an hour two times a day for seven days.

The CCS mixture was decanted into a separatory flask and the layers allowed to separate. Normally, three layers were present. The raffinate or lubricant layer was carefully drawn off the bottom of the flask into a tared vacuum flask containing a magnetic stirrer. This was placed under vacuum with stirring and heated (70 °C) until all dissolved fuel was removed.

The 25 cc fuel layer on the top was then carefully decanted or aspirated from the flask. The fuel layer was then carefully evaporated under vacuum with slight heating. The residue from this extract layer contained mostly additive.

The remaining layer in the flask was an emulsion layer that does not readily break after standing for days unless heated. The emulsion was drained from the flask and placed under a vacuum with slight heating to remove any excess fuel. This layer contained a high level of additives.

EXPERIMENTAL RESULTS

FIS Fractions

Some typical FIS simulations are found in Table 2. The total recovery of the sample is shown. Earlier work (6) indicated at lower oil:fuel ratios, the extraction was not at its maximum. The 1:100 ratio test appears to verify with this oil.

In the FIS method, the fuel additives do affect the extract-raffinate split and the removal of the fuel under vacuum. This is due to the relatively large amount of additive present at the high fuel to oil ratio. Even at a 0.1% concentration, the additive level in the fuel is about equal to the amount oil used in the test.

CCS Fractions

Typical CCS data are found in Table 3. The recovery is better than that found in the FIS due to the smaller quantity of fuel and larger oil sample used in the CCS. The CCS tests were run in duplicate. The average recovery of the oil was about 98%. The extraction layer was small and the effect on the additives was difficult to determine. However, the fuel and synthetic oil formed a very stable emulsion. This was probably due to relative solubilities of the additives in the

more polar base stock and the methanol. Unless heated, the emulsion formed with the synthetic oil was stable for 3-4 months.

To determine the effect of the heating and vacuum stripping steps on the processing of the new oil, a sample of PRL 4717 was placed under vacuum and heated for six hours. The 10.00 gram sample lost only 0.02g or 0.2% by weight in the test.

ANALYSIS OF SIMULATION SAMPLES

The fractions obtained from the FIS and CCS simulations were evaluated using thermal and electrochemical methods previously described. The objective of the testing was to compare the fractions against the original lubricant to determine any change in stability.

PDSC

A fresh sample of PRL 4713 was evaluated at a programmed temperature rate of 10°C per minute using approximately 2 mg of sample under 150 psi of air. The lubricant. Based on the results of the test, an isothermal temperature of 190 °C was selected for the remaining evaluations. At this isothermal temperature condition, the new oil had an oxidation induction period of about 28 minutes, Figure 1. The samples from the evaluations were similarly tested. Typical examples of the thermograms from a CCS are found on Figure 2 and 3. The data are typical in that the raffinate fraction, Figure 2, contained most of the oil. Some of the additives in the raffinate oil fraction were extracted. This results in a shorter oxidation induction time (OIT) than the original oil. The emulsion layers and most extraction layers contained exhibited equal or higher OITs indicating an increase in oxidation stability due to an increase in additive concentration.

A summary of the CCS samples are found on Figure 4. The OIT of the raffinate samples were lower than the original oil indicating extraction.

PSMO

If there is a depletion of additives including the anti-oxidants than the deposit forming tendency of the extracted lubricant should increase. The volatility of the fractions may also vary depending on the nature of the additives extracted. The volatility of the CCS fractions, Figure 5, indicate increased volatility for the raffinate and correspondingly heavier deposits. The deposits formed at 225

°C in 30 minutes are summarized on Figure 6. The emulsion layers contain extracted additives and exhibit lower volatility and lower deposits indicating higher concentrations of antioxidants. The data show a significant increase in the deposit forming tendencies of the raffinate and a decrease for the emulsion fraction. The increase in the volatility of the raffinate samples is due to an increase in volatile oxidation products and some residual fuel in the sample. The emulsion layer was less volatile than the original oil suggesting that the extracted additives in the emulsion layer may also contain less volatile, higher molecular weight dispersant or detergent molecules.

RULER

This method is used to determine changes in additives in used oil samples and has been used to study extended drain tests (18). In this alternate fuel study, the method was used to give some appreciation for the magnitude of the changes in the extracted samples. A typical set of curves is found on Figure 7. The method compares the additive signal obtained for the original sample or new oil with the signal obtained from the extracted fraction. To evaluate the additives quantitatively requires a knowledge of the lubricant formulation. Different additives also require different electrolyte solutions. The lubricant formulation was not known but for this type of engine oil usually zinc dithiophosphate (ZDTP) antioxidants are present in the formulation. Analysis of the fractions for ZDTP were conducted.

Data for the FIS samples obtained using the ruler method are found on Figure 8. The CCS data are summarized on Figure 9. The antioxidant additive in the extract increased several hundred percent while the raffinate are reduced. The high values are due to the relative sizes of the sample fractions. The extracted fractions, after removing the fuel, contains mostly additive and in some cases some oil. The raffinates are mostly the original oil stripped of additives and in some cases containing traces of fuel.

CONCLUSIONS

- Alcohol fuels can significantly deplete the additives in a lubricating oil by extraction.
- Thermal analysis methods are useful in identifying changes.
- The RULER method gave an indication of the extent of the extracted antioxidants.

It is a useful tool for the analysis of additives in oils.

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