AN OPTIMIZED ALTERNATIVE MOTOR FUEL FORMULATION: NATURAL GAS LIQUIDS, ETHANOL, AND A BIOMASS-DERIVED ETHER

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ABSTRACT

A multi-component, liquid, non-petroleum, alternative motor fuel for spark ignition engines has been developed. The fuel is composed of approximately equal volumes of: (1) medium-molecular weight alkanes, isoalkanes, and cycloalkanes (C_5 - C_8) which are extracted in the course of coalbed gas or natural gas production and/or processing, (2) anhydrous fermentation ethanol, and (3) 2-methylTHF, a biomass-derived heterocyclic ether. The ether serves as a co-solvent that reduces the volatility of the ethanol/hydrocarbon blend. The formulation can be adjusted to vary the fuel characteristics over a range similar to winter/summer and regular/premium gasoline grades: 87 - 94 octane; 0.74 - 0.78 specific gravity; and a 6.5 - 13.5 psi Reid vapor pressure. This fuel contains little or no sulfur, phosphorous, aromatics, olefins, or high-boiling-point hydrocarbons, but does contain 11 - 19% oxygen (by weight), with a corresponding reduction in heat content (100,000 - 106,000 BTU/gal). This fuel has been tested in 1996 and 1997 Ford Taurus ethanol-Flexible Fuel Vehicles which automatically adjust the air/fuel ratio over a wide range. Emissions testing (USEPA's FTP protocol) show the following differences in the tailpipe exhaust characteristics (compared to conventional gasoline): 40 - 50% less unburned hydrocarbons, 20% less CO, no significant change in NO_x, 4% less CO_2, 40% less ozone-forming potential, and 2 - 3 times less toxicity.

BACKGROUND

Natural gas liquids (NGL's) and coalbed gas liquids (CGL's) are underutilized alternatives to crude oil as hydrocarbon sources for spark ignition engine motor fuels. NGL's are recovered from natural gas wells as a gas-saturated liquid condensate.[1] The quantity of hydrocarbons with higher molecular weight is typically about 4 - 5%. Coalbed gases have long been recognized because of explosions that have occurring in the course of coal mining. In New Mexico and Europe, coalbed gas can contain significant amounts of heavier hydrocarbons, with C_{2+} fractions as high as 70%.[2] The liquids are classified by the Gas Processors Association [3] and the American Society for Testing and Materials (ASTM) according to carbon chain length as ethane, propane, n-butane, isobutane and "pentanes plus." Pentanes plus is further subdivided into iso-pentane and "natural gasoline". Pentanes plus are not generally desirable as gasoline is because they have low (65 - 70) octane and a 10 - 13 psi Reid Vapor Pressure (RVP) [4] which results in high evaporative losses and, in severe cases, engine vapor lock in warm weather.

Ethanol (EtOH) is a biomass-derived, octane-increasing motor fuel additive. While neat ethanol has a 2.3 psi RVP, when blended alone with gasoline, the resulting fuel has an RVP much higher than the ideal linear blending-RVP of gasoline ethanol mixtures.[5] This has been analyzed and explained as being a result of the strong dipole moment of ethanol.[6] EtOH's hydrogen bonding reduces its vapor pressure far below that expected from its molecular weight. But when mostly diluted in a non-polar substance such as gasoline, the attractive van der Walls force between the EtOH and the hydrocarbon dominates and is much weaker than the attraction due to hydrogen bonding. The maximum RVP is reached at 5-10% EtOH and is typically 1 psi above the base gasoline.

The situation is considerably more severe in NGL's. The high partial pressures of the low-carbon-number species in gasoline are the main contributors to the RVP. However, the deviation from ideal mixing a function of the heavy hydrocarbons contained in the fuel.[7] The ideal vapor liquid equilibrium ratio is largely determined by the individual vapor pressure of the diluents and the vapor-phase fugacity coefficient. Non-ideal mixing effects alter the ideal vapor-liquid equilibrium and are parameterized in the activity coefficient. For EtOH, the activity coefficient is a stronger function of the composition of the heavy hydrocarbons than of carbon number. For a carbon number of 7, the activity coefficient for paraffins and napthtenes ranges from 25 - 35, for olefins it is ≈ 18, and for aromatics, ≈ 11. For pentanes, the primary constituent in pentanes-plus, it is ≈ 40. Therefore the aromatic content, absent in NGL's, serves as a co-solvent for mixing EtOH in gasoline.

In the search for a non-toxic, renewable solubilizing agent to replace the aromatics, the solubility of the proposed solvent in both hydrocarbons and EtOH was considered. In general, hydrocarbons are more tolerant of ethers that contain non-polar groups. And ethers are quite tolerant of EtOH: the activity coefficients of EtOH in TAME, ETBE and MTBE are 10, 6.5 and 3.7 respectively. Because of its high density, low solubility in water, and low flashpoint, 2-methyl-tetrahydrofuran (MTHF) was selected as the primary candidate. It is produced from waste cellulosic biomass materials such as corn husks, corn cobs, straw, oat/rice hulls, sugar cane stocks, low-grade waste paper, paper mill waste sludge and wood wastes. It has been considered as a fuel additive to gasoline [8,9]. MTHF has been proposed as a low-cost, low-octane alternative oxygenate to EtOH in conventional gasoline [10]

METHODOLOGY

A fuel composition was prepared by blending 32.5% pentanes-plus, 35% 200 proof anhydrous EtOH, and 32.5% MTHF. The EtOH was pre-blended in the MTHF in order to avoid evaporative loss of the EtOH upon contact with the natural gasoline. The EtOH and MTHF were cooled to 40 °F prior to blending to further minimize evaporative losses. The pentanes-plus were cooled to 40 °F to minimize evaporative losses was poured into a cooled steel mixing tank. The blend of ethanol and MTHF was then added to the pentanes-plus while gently stirring for 5 seconds until a uniform, homogeneous blend was obtained.

The fuel characteristics were obtained in accordance with ASTM Standards.[6] To maintain the ability to test for exhaust emissions on both gasoline, E85 and/or this fuel without any manual engine adjustment, a 1996 Ford Taurus Flexible Fuel Vehicle (ethanol calibration) was used as the test vehicle. This engine includes a fuel sensor that, by measuring the dielectric constant of the fuel, enables it to calculate the concentration of ethanol. The vehicle was not modified between tests.

RESULTS

Hydrocarbon speciation of the NGL's (supplied as C_5^+ from a natural gas processing plant) was measured using a gas chromatograph shows that the composition of the NGL's was ≈ 46% pentanes, ≈ 33% hexanes, ≈ 14% heptanes, and ≈ 3% octanes. The vapor pressure resulting from diluting EtOH in NGL's is shown in Figure 1. Unlike when blending with gasoline, the concentration of EtOH must exceed 50% to return the RVP down to 10.8 psi, the RVP the NGL's alone. The non-ideal mixing is very apparent in the curvature of the RVP plot. To achieve the 7 - 8 psi requirements of reformulated gasoline, 80- 85% EtOH would have to be blended. This is in distinct contrast to blending MTHF in NGL's, also shown in Figure 1. The RVP decreases in a nearly ideal fashion from the 10.8 psi RVP of the NGL's to the neat RVP of MTHF at 3.2 psi. Also, the MTHF blends with the EtOH, but there is a stronger decline when the EtOH concentration exceeds 60%. While the solubility seems good, MTHF alone could not be a substitute for the aromatics, because the measured research octane number (RON) is only 86. The motor octane number (MON) is 72, 10 points below the minimum standard for regular fuel and the (R+M)/2 anti-knock index is 79, 9 points below the *minimum* standard. The low octane of the NGL's (67 measured in this case), means that substantial quantities of EtOH with a RON of 112 and a MON of 96 need be included.

After repeated experimentation, a blend of roughly equal parts of NGL's, EtOH, and MTHF was formulated as described in the methods section. The resulting fuel characteristics are shown in Table 1. The specific gravity, octane, RVP, and heat content are all within ranges detailed by ASTM specification for gasoline, D439-86. However, the distillation properties are quite different. The T_{90} value indicates the amount of "heavy-end" components (polyaromatics, etc.) fuels. These components are considered to be a source of unburned hydrocarbons during the cold start phase of engine operation. The lower values for the EtOH/MTHF/NGL blends compared to gasoline (T_{90} is ≈ 350°F for gasoline) should reduce HC emissions.

After having been operated for 5,000 miles to age the vehicle's catalyst, the car was tested using the Federal Test Protocol (FTP), the transient driving cycle developed by the USEPA as specified in 40 CFR 86. The vehicle's engine block heater was not used to preheat the engine in any of these tests. The composite weighted results averaged over several (3-10) tests are shown in Table 2. For all the controlled pollutants, all the fuels emit 25-75% less than present federal standards (Tier I) allow at 50,000 miles.

Both the NGL/EtOH/MTHF blend and the CA RFG meet TLEV standards for NMHC. The CA RFG had the lowest NMHC emissions, and nearly met LEV standards, but in one of the three tests, .080 g/mi of NMHC was emitted. E85 emitted nearly 50% more NMHC than indolene, but all of the increase was during the cold-start phase. The low combustion temperature and high heat of vaporization of ethanol results in a longer warm-up period. Despite the 35% ethanol content of the NGL/EtOH/MTHF blend, it showed a 30% reduction in NMHC compared to indolene. reduction in adiabatic flame temperature. During the hot-stabilized portion (phase II) of the FTP, NMHC emissions from the NGL/EtOH/MTHF blend were 78% less than that of indolene.

Carbon monoxide emission was much more comparable among the fuels and was less than Tier I/TLEV/LEV standard of 3.4 g/mi. The NGL/EtOH/MTHF blend, Fed RFG and CA RFG emitted less than the 1.75 g/mi ULEV standard. The NGL/EtOH/MTHF blend emitted 7% less CO than indolene but the measurement error showed that this was not significant. In the stabilized portion (phase II) of the FTP, CO emissions from the summer blend were 49% less than that of indolene.

NO_x emissions for all fuels were less than half the Tier I/TLEV 0.4 g/mi standard and easily met the LEV/ULEV standards at 0.2 g/mile. The fuels containing ethanol had the higher NO_x emissions, though the increase was not proportional to the ethanol content. E85 exhibited an 7% increase in NO_x over indolene. The NGL/Et/MTHF blend showed a 30% increase and Federal RFG showed a 27% increase. During the stabilized portion of the FTP, NO_x emissions from the summer blend showed no change from indolene.

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FIGURE 1.

Variation of RVP in 3 mixtures: EtOH in NGL's, MTHF in NGL's, EtOH in MTHF.

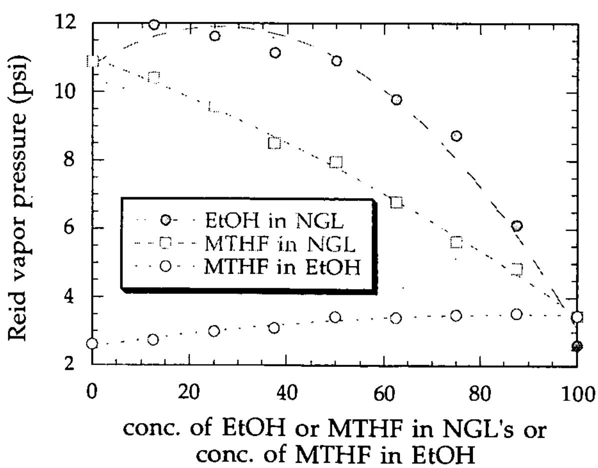

TABLE 1.

ASTM test results for NGL/EtOH/MTHF alternative fuel:

TEST	METHOD	RESULT	UNITS
API GRAVITY	ASTM D4052	52.1	60 DEGS F
COLOR	VISUAL	UNDYED	
DISTILLATION	ASTM D86		DEGS F
IBP		107.0	
10 PCT EVAPORATED		133.2	
50 PCT EVAPORATED		161.8	
90 PCT EVAPORATED		166.9	
FBP		195.5	
PCT RECOVERED		99.5	WT. %
PCT RESIDUE		0.3	WT. %
PCT LOSS		0.2	WT. %
RVP, PSI	ASTM D5191	8.10	
LEAD	ASTM D3237	<0.01	gm/gal
RESEARCH OCTANE NO.	ASTM D2699	96.8	
MOTOR OCTANE NO.	ASTM D2700	82.6	
R+M/2	ASTM D4814	89.7	
COPPER CORROSION	ASTM D130	1A	3 HRS @ 122I
GUM, (AFTER WASH)	ASTM D381	2.2	mg/100 ml
SULFUR	ASTM D2622	3	PPM
PHOSPHOROUS	ASTM D3231	<0.004	gm/gal
OXIDATION STABILITY	ASTM D525	165	minutes
OXYGENATES -- ETHANOL	ASTM D4815	34.87	PCT VOL
OXYGEN	ASTM D4815	12.48	PCT WT
BENZENE	ASTM D3606	0.15	PCT VOL
V/L 20	CALCULATED	135	DEGS F
DOCTOR TEST	ASTM D4952	POSITIVE	
APPEARANCE	VISUAL	BRIGHT/CLEAR	
AROMATICS	ASTM D1319	0.17/.41	PCT VOL
OLEFINS	ASTM D1319	0.09	PCT VOL
MERCAPTAN SULFUR	ASTM D3227	.0010	PCT WT
WATER TOLERANCE	ASTM D4814	<-65°C	
HEAT CONTENT	ASTM D3338	18,663 BTU/lb	

TABLE 2.

FTP weighted exhaust emissions for several fuels (all figures in grams per mile):

	Tier I Fed Standards	Et/MTHF alt. fuel	indolene	E85	Fed RFG	CA RFG Phase II
NMHC:	0.25	0.085	0.122	0.142	0.136	0.071
CO:	3.40	1.66	1.78	1.82	1.70	1.47
NO_x:	0.40	0.161	0.124	0.132	0.157	0.097

notes:

1) *indolene* is EPA certified emissions testing gasoline (40 CFR 86)
2) *RFG* is reformulated gasoline
3) *NMHC* is non-methane hydrocarbons
4) *CO* is carbon monoxide
5) *NO_x* is oxides of nitrogen
6) *Fed Winter RFG* is blended from 92.5% indolene and 7.5% 200-proof ethanol. It is a premium grade (92 octane) winter fuel.
7) *E85* is blended from 20% indolene and 80% 200-proof ethanol
8) CA RFG Phase II is a premium grade (93 octane) reformulated fuel
9) NGL/Et/MTHF is an 89 octane, 8.1 psi fuel alt. fuel with the following composition: 35% EtOH, 32.5% MTHF, 32.5% NGL's