

PERFORMANCE ASSESSMENT OF NOVEL SUBSTITUTE GASOLINE COMPONENTS

S. Stournas, E. Lois and P. Polyssis
Fuels and Lubricants Laboratory, Department of Chemical Engineering
National Technical University, 106 82 Athens, Greece

INTRODUCTION

During the last several years there has been an increasing interest in the European Economic Community in the savings of crude oil through the use of substitute fuel components in gasoline, which was officially expressed by EEC regulation 536/1985 and other regulations that are currently in effect. When this regulation was initially conceived in 1982, the principal impetus was concern over the availability of imported crude oil in the Community; as time went by, however, environmental considerations assumed major importance. Given this interest, which is also manifest in other parts of the world, it is important to obtain an accurate understanding of the effects of the substitute fuel components on engine efficiency and pollution abatement. The major difference between traditional gasoline and the substitute fuels under consideration lies in their chemical structure and particularly the oxygen content of the latter.

The first problem that must be solved in testing for increased fuel performance in gasoline engines is the nature of the base fuel to which the additives and extenders will be blended. Most of the research work that has been reported [1-6] employs full range, unleaded gasoline or specific refinery streams, such as reformates [7]. The physical characteristics of these fuels (such as vapor pressure, RON, MON, distillation behavior, proportion of saturates, olefins and aromatics) are usually specified; nevertheless, this does not permit exact duplication or extension of the reported work because it is impossible to procure the exact fuel that was initially employed. To overcome this problem, API-45 [8] used a 60:40 mixture of iso-octane and n-heptane as a base fuel, whereas other workers [9] employed either pure iso-octane or 80 octane PRF. This latter method does permit duplication of experiments but suffers from unrealistic (usually too high) BRON estimates, because of the dissimilarity of the base fuels to actual gasoline. As an example of the disparities that can be encountered, the case of MTBE may be mentioned, whose BRON is listed as 148 in API-45 [8] although in actual practice [10] it ranges between 110 and 120 for most types of gasoline.

Our approach in this matter has been to prepare a series of base fuels which are blends of pure hydrocarbons so as to have reproducible compositions, but which at the same time are complex enough to approach actual gasoline in behavior. It should be remembered, of course, that the high cost of pure hydrocarbons places an economic limit on the complexity of the mixture and the choice of components.

Table 1 contains the compositions and octane numbers of all base fuels that were prepared and tested during the course of this work, along with the RON and BRON values of the individual

constituents, as reported in API-45 [8].

In order to be able to evaluate the results quickly, a relative effectiveness scale was introduced, by which all fuels were compared to the performance of MTBE, both on a molar and on a weight basis; the effectiveness of the latter was taken as unity. The results so far are encouraging, since some useful conclusions can be drawn following this systematic approach.

NOVEL FUEL COMPONENTS: SYNTHETIC ASPECTS

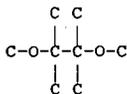
The aim of the chemical synthesis component of the research program is to make available, for testing and correlation purposes, structures that appear promising but at the same time can be easily prepared from readily available starting materials; exotic compounds and intricate synthetic procedures are considered to be outside the scope of our current effort.

In this vein, the procedures that were selected included the Leuckart reaction (preparation of substituted amines), acid catalyzed additions (preparation of ethers and dioxolanes) and simple condensation of amines with formic acid (preparation of substituted formamides), along with classical etherification and Mannich condensation.

An intriguing molecule, which in principle should be an effective oxygenate component in gasoline, is pinacol dimethyl ether (PDME); it is structurally similar to MTBE, except that it contains two of each of the active molecular centers (tertiary carbons and methyl ethers) per molecule:



MTBE



PDME

Another attractive feature of PDME is that it can in principle be derived from acetone via the pinacol reduction and trapping of the intermediate di-anion. Attempted formation of PDME by methylation of the magnesium salt of pinacol that is formed under the classical conditions [13] failed because of the extreme lack of solubility of the salt. In a second attempt, the more soluble aluminum salt [14] was employed instead, but again very little of the desired product was formed. Very recently, PDME was finally prepared by the Williamson etherification of the di-sodium salt of preformed pinacol, but its antiknock activity has not yet been measured.

NOVEL FUEL COMPONENTS: ANTI-KNOCK PERFORMANCE AND STRUCTURE-ACTIVITY CORRELATIONS

Comparison of activity of oxygen atom with nitrogen atom in the same molecular environment

From the results that are depicted in Table 2 it can be seen that aliphatic amines are definitely more active anti-knock additives than the equivalent alcohols; this holds true as long as there is at least one hydrogen attached to the amine nitrogen. On

the contrary, tertiary amine groups have a very strong pro-knock effect; an extreme example is N,N,N',N'-tetramethylethylenediamine, whose two tertiary nitrogens transform it into what is probably the most pro-knock simple amine. An even more striking performance is displayed by the commercially available tetrakis-dimethylaminoethylene, whose four tertiary nitrogens lower its BRON to a value of about -1000. This behavior of aliphatic tertiary amines is in sharp contrast to that of aromatic amines; thus, in the benzene series, tertiary amines (e.g. N,N-dimethylaniline) have no effect on the octane rating of the fuel [11] and in the fulvene series compounds like 6-dimethylaminofulvene are among the most active non-metallic antiknock additives that have been described so far [4]. Another interesting observation from the results in Table 3 is that the known anti-knock activity of the tert-butyl group is matched or in some cases surpassed by that of the iso-butyl group.

In the case of cyclic structures, whose performance is shown in Table 4, the contrast between secondary and tertiary amines is again quite remarkable; the replacement of pyrrolidine by N-methylpyrrolidine at the same concentration (3%) in the same fuel reduces the octane rating by a full 8 RON units! It was also decided to test these two groups in direct comparison and a molecule that contains both of them, N-methyl piperazine, was selected. The effect of the tertiary nitrogen was stronger and N-methylpiperazine displayed proknock behavior.

Other conclusions that can be drawn from the data on Table 4 are that heterocyclic five-membered rings are better performers than equivalent six-membered rings; this is in agreement with the higher activity of cyclopentane (API BRON 141) when compared with cyclohexane (API BRON 110). In addition, the presence in the molecule of the oxymethylene group C-O-CH₂-C leads to pro-knock behavior. This again is in agreement with the reported [5] pro-knock activity of compounds that contain the oxy-methylene group, such as methylal and dimethyl ether; by contrast, antiknock ethers such as MTBE and TAME are devoid of this structural feature.

Furan derivatives

The furan moiety has been known [8,14] to be an antiknock molecular feature. Furfuryl alcohol is one of the most readily available and inexpensive furan derivatives which, upon testing, displayed high antiknock performance, having a higher BRON rating than MTBE and being about 50% more effective on a weight and molar basis. It is noteworthy that furfuryl alcohol is the only alcohol tested thus far that has a higher antiknock performance than its equivalent amine (cf. results in Table 5). The other advantage of this material is its derivation from non-petroleum sources, i.e. from renewable agricultural by-products. Its major drawback lies in its limited solubility in hydrocarbon fuels (maximum solubility in BF-1 is about 1.5% by volume). The next higher homolog, α -methyl furfuryl alcohol, possesses much higher solubility while retaining the anti-knock performance.

It is noteworthy that the methyl ether of furfuryl alcohol, which was also synthesized and tested, displayed proknock behavior, having a BRON of only 66. In hindsight this result should have been expected, given that furfuryl methyl ether, unlike its parent alcohol, possesses the strongly proknock structural feature C-CH₂-O-C. Another furan derivative that was tested was benzofuran, which was also found to possess significant antiknock activity.

Finally, a novel additive was designed and synthesized; this was N-t-butylfurfurylamine (NTBF), which was expected to possess good activity since, in addition to the furan ring, it incorporates a secondary amine and a tert-butyl group. Indeed, as can be seen in the data of table 5, this easily accessible compound possesses one of the highest blending octane numbers among non-aromatic amines and is about six times as effective an additive as MTBE on a molar basis.

Substituted Phenols and Derivatives

Substituted phenols have long been known to possess antiknock activity. Their effectiveness increases by having them undergo the Mannich reaction, which adds an aminomethyl moiety at the ortho position, thus transforming them to 2-hydroxybenzylamines (HBA). The very high activity of the HBA's (and even more so of their salts) was observed by one of us several years ago [5] and was later extensively investigated by Burns [1,15]. As shown in Table 5, the improvement in performance that occurs in going from the parent phenol to the corresponding HBA is highest among di-substituted phenols (xylenols). Creosote, a phenolic mixture that is derived from wood tar, displays an antiknock activity similar to that of MTBE. Upon transformation to the corresponding HBA mixture via the Mannich reaction, a large BRON increase is observed, which is consistent with the high xylene content of creosote.

POLLUTANT EMISSIONS AND ENGINE PERFORMANCE

The effect of oxygenate additives on pollutant emissions from gasoline engines has been extensively studied, and it is generally accepted that they offer tangible benefits on CO and hydrocarbon emissions, while not significantly affecting NOx emissions; the aldehyde content in the exhaust, however, is usually higher. When any nitrogen-containing material is added to the fuel, there is concern that NOx emissions may increase.

Tests that were run on the CFR engine showed that NOx emissions were independent of fuel nitrogen content but dependent on air-fuel ratio. However, we do not consider these results as representative because the CFR engine has a single cylinder and operates under relatively mild conditions when compared to actual automobile engines.

A parallel research project that is being conducted at the Department of Mechanical and Process Engineering of Sheffield University [16] is looking into the performance and emissions of standard spark-ignition engines that run on gasoline that incorporates oxygen and/or nitrogen containing additives. The engine which is used at Sheffield is a fully instrumented four-cylinder standard production unit, which is coupled to an appropriate dynamometer. The additives that have been tested were blended with unleaded premium gasoline and included MTBE, methanol, furan, furfuryl alcohol, anisole, and t-butylamine among several others. Fuel economy on an energy basis was improved by amounts that ranged from 3.5% (furfuryl alcohol) to 0.9% (anisole); representative results are shown in Table 6.

As far as exhaust emissions were concerned, oxygenates generally tended to follow the pattern mentioned above, except that materials containing the furan ring appeared to lower NOx emissions. Additionally, it was observed that one of the factors

that influence the NOx content of the exhaust gases was the concentration of the additive; small amounts of additives actually decreased NOx emissions in comparison to the base gasoline. After a certain concentration threshold was reached, however, NOx emissions increased. Nitrogen-containing additives behaved in similar fashion, except that threshold concentrations were lower than those of oxygenates.

The novel additive NTBF was also tested in the engine under similar conditions but to a limited extent because of the small quantities that were available. Preliminary results show that this material improves fuel economy to an extent similar to other additives that contain the furan ring; a single test showed that, at a concentration of 1%, NOx emissions were lower than those of the base gasoline. Furthermore, it was observed that NTBF lowers the aldehyde content of the exhaust gases, which is a rather unexpected behavior for an oxygen-containing material.

CONCLUSIONS

The screening of over one hundred blends of base fuels with potential additive candidates allows the following conclusions to be made regarding the relation of molecular structure with anti-knock activity:

- a. Amines are usually more effective anti-knock additives than the equivalent alcohols.
- b. The presence in the molecule of a tertiary nitrogen atom imparts a strong pro-knock effect.
- c. The presence of five-membered rings leads to better performance than six-membered rings.
- d. The structural group C-O-CH₂-C is a pro-knock feature in the molecule.
- e. The biomass derived phenolic mixture known as creosote has good antiknock activity, which is greatly enhanced by its transformation to HBA via the Mannich reaction.
- f. Molecules designed on the basis of the activity of their constituent groups can lead to superior anti-knock performance. (e.g. N-t-butyl furfurylamine)

ABBREVIATIONS AND DEFINITIONS

API-45	American Petroleum Institute Research Project 45 (see ref.8)
BF1-BF5	Base fuels for octane number determinations (for compositions refer to Table 1)
BRON	Blending Research Octane Number
HBA	Hydroxy Benzyl Amine
MON	Motor Octane Number (according to ASTM D-2700)
MTBE	Methyl tert-Butyl Ether
NTBF	N-t-butyl furfurylamine
PRF	Primary Reference Fuel
RON	Research Octane Number (according to ASTM D-2699)
TAME	tert-Amyl Methyl Ether
THF	Tetrahydrofuran

BRON is defined by the formula: $B = [M-F(1-V)]/V$ where:

- B = BRON of a given fuel component
- M = RON of the fuel blend
- F = RON of the base fuel
- V = Concentration of the component in the blend (vol/vol)

ACKNOWLEDGEMENT

Financial support for the performance of this work has been provided by a grant from Directorate-General XII for Science, Research and Development of the Commission of the European Communities under contract no. EN3E-0053-GR.

REFERENCES

1. L.D. Burns, U.S.Patent 4,378,231 (1983)
2. L.D. Burns and R.M. Parlman, U.S.Patent 4,444,567 (1984)
3. G.M. Singerman, U.S.Patent 4,312,636 (1982)
4. S.Stournas et al., U.S.Patent 3,706,541 (1972)
5. E.I. Heiba and S. Stournas, U.S.Patent 3,770,397 (1973)
6. E.I. Heiba and S. Stournas, U.S.Patent 3,771,979 (1973)
7. R.Mackinven, "A Search for an Ashless Replacement for Lead in Gasoline", paper presented at Jahrestagung DGMK, W.Germany October 1974.
8. "Knocking Characteristics of Pure Hydrocarbons Developed under American Petroleum Institute Research Project 45", ASTM Special Technical Publication No. 225, 1958
9. R.L.Tischer et al., Preprints, Div. of Petrol. Chem. ACS, 21, 904 (1976)
10. J.A. Weiszmann et al., Hydrocarbon Processing 65(6), 41 (1986)
11. R.F. Bridger, Mobil R + D Corp., unpublished results
12. L.D. Burns, U.S.Patent 4,339,245 (13-7-1982)
13. R. Adams and E.W.Adams, Org. Syn. Coll. Vol., 1, 459 (1941)
14. A.A.P.Schreibmann, Tetr. Letters, 4271 (1970)
15. L.D. Burns, ChemTech, 744 (1984)
16. J.Swithenbank, M.Papachristos and G.H.Priestman, EEC Research Contract EN3E-0054-UK, Periodic Reports 4 and 5 (1988)

TABLE 1

COMPOSITION OF BASE FUELS
(Compositions given in percent by volume)

COMPONENT	API	BRON	API	RON	BF-1	BF-2	BF-3	BF-4	BF-5
n-Hexane	19		24.8		20	15	25	28.5	19.2
Cyclohexane	110		83.0		-	15	15	19.0	-
n-Heptane	0		0.0		5	15	-	-	4.8
iso-Octane	100		100.0		55	20	20	9.5	52.8
Diisobutylene	168		105.3		-	5	5	-	-
Toluene	124		120.1		15	15	15	28.5	14.4
Xylenes*	144		117.2		5	15	20	9.5	4.8
Methanol					-	-	-	1.7	-
Isopropanol					-	-	-	3.3	-
MTBE					-	-	-	-	4.0
RON					90.5	85.5	93.4	93.3	91.9

* The composition of the xylenes mixture, as determined by vapor phase chromatography, was 3.7% o-xylene, 72.3% m-xylene, and 23.9% p-xylene.

TABLE 2
Antiknock performance of simple alcohols and amines
(Results at 3% vol. concentrations in BF-1)

Compound	Δ RON	BRON	Relative Effectiveness (MTBE=1)	
			Molar	Weight
MTBE (5%)	1.8	126	1.00	1.00
Methyl t-octyl ether (2%)	0.7	125	1.52	0.88
i-Butanol	0.8	117	0.57	0.68
i-Butylamine	2.9	187	2.24	2.71
di-(i-Butyl)amine	1.8	151	2.43	1.65
t-Butanol (5%)	1.2	114	0.53	0.63
t-Butylamine (5%)	2.6	143	1.27	1.53
t-Butyldimethylamine	-0.2	84		pro-knock
t-Octylamine	0.8	117	1.04	0.68
t-Octyldimethylamine	0.1	94	0.15	0.07
N,N,N',N'-Tetramethyl- ethylenediamine	-5.5	-93		pro-knock
Tetrakis-dimethylamino- ethylene (1%)	-11.6	-1070		pro-knock

TABLE 3
Antiknock performance of cyclic oxygen and nitrogen compounds
(Results at 3% vol. concentrations in BF-1)

Compound	Δ RON	BRON	Relative Effectiveness (MTBE=1)	
			Molar	Weight
THF	0.2	97.2	0.12	0.16
Pyrrrolidine	4.9	287.2	3.80	4.70
N-Methylpyrrrolidine	-3.0	-9.5		pro-knock
Piperidine	1.9	154	1.46	1.50
Morpholine	-0.5	73.8		pro-knock
N-Methylpiperazine (2%)	-1.0	40		pro-knock
Trimethylidioxolane (1%)	0.1	101	0.29	0.23

TABLE 4
Antiknock performance of furan derivatives

Compound	BRON	Relative Effectiveness (MTBE=1)	
		Molar	Weight
Furan	190	1.40	1.81
Furfuryl alcohol (1.5%)	170	1.66	1.49
Methylfurfuryl alcohol (2%)	171	1.86	1.71
Furfuryl methyl ether (2%)	66		pro-knock
Benzofuran (1%)	144	1.50	1.13
Furfurylamine**	153	3.29	2.98
N-t-Butylfurfurylamine (1%)	250	6.06	3.49
"best amine"***	174	~3.8	

* Data from API-45

** Data from ref. [12]

*** Data from ref. [7]

TABLE 5
Antiknock performance of substituted phenols
and corresponding HBA's

Compound	BRON	Relative Effectiveness (MTBE=1)	
		Molar	Weight
4-cresol (2%)	221	3.41	2.79
HBA (2.5%)	287	8.37	4.20
4-t-butylphenol(0.5%)	173	2.91	1.76
HBA (1%)	247	8.02	3.34
4-t-octylphenol (1%)	128	1.87	0.80
HBA (0.5%)	176	5.10	1.83
3-cresol (2%)	191	2.62	2.14
HBA (0.5%)	292	8.05	4.30
3,5-xylenol (0.5%)	124	1.01	0.72
HBA (0.5%)	271	7.80	3.84
2,5-xylenol (0.5%)	169	2.32	1.68
HBA (0.5%)	332	10.41	5.16
Creosote (2%)	121	--	0.65
HBA (2%)	234	--	3.06

TABLE 6
Change in fuel economy [energy basis] caused by added components
(Net power test, wide open throttle)

Component	Improvement in fuel economy (%)
MTBE	3.1
Methanol	1.6
Anisole	0.9
Furan	1.4
2-Methylfuran	3.1
Furfuryl alcohol	3.5
tert-Butylamine	2.9

Component concentration: 2% vol.
Base gasoline: unleaded premium
Spark timing: minimum for best torque