THE EFFECT OF BLENDING OF MTBE IN GASOLINE ON REDUCING LEAD CONTENT

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ABSTRACT

There are two basic incentives nin blending MTBE in gasoline for a country like Indonesia, i.e. to improve the octane quality and to reduce the lead content in gasoline. Changes in physical and chemical properties of gasoline will also occur, accompanying the improvement of the octane number. The blends used in this study were made in four concentrations, viz. 3, 6, 10 and 15 volume percent MTBE in unleaded gasoline. The test results were compared to the Indonesian specification of premium gasoline.

I. INTRODUCTION

Research activities on the use of MTBE blended with gasoline have developed so well that some countries have even begun its use in automotive vehicles. MTBE is a relatively new component for the petroleum refinery. Because its blending characteristics are close to those of hydrocarbons, methyl tertiary-butyl ether (MTBE), which is synthesized from methanol and isobutylene, is now used to enhance, the octane number of motor gasoline. In the USA, the use of MTBE (up to 7% volume) in finished unleaded gasoline was approved by EPA in February 1979. Later the limit was raised to a maximum oxygen content of 2 volume %, allowing approximately 11 vol. % MTBE in unleaded gasoline. MTBE was first manufactured commercially in Europe by Chemische Werke Hüls in West Germany and by Anic in Italy (Ref. 2). Indonesia is now actively involved in conducting research on the use of MTBE blended with unleaded gasoline. The purpose of this research is to reduce the TEL content in gasoline and to increase the octane rating of premium grade gasoline.

The paper presents the results of laboratory test on a series of MTBE gasoline blends. The blends were made in four concentrations (viz. 3), 6, 10 and 15 vol.% MTBE in unleaded gasoline). The test results were compared to the Indonesian spesification of premium gasoline. From the analysis of laboratory test results it will be possible to determine the volume percent of MTBE, which can be maximally blended into gasoline, and the reduction in TEL addition in the resulting gasoline, which still agrees with the Indonesian gasoline specification.

II. INDONESIAN MOTOR GASOLINE SPECIFICATION.

In 1986 Indonesia has produced around 29,75 million bbl (1bbl = .159m^3) of motor gasoline using ca 2.000 MT of TEL-B. Indonesia is producing two grades of motor gasoline, viz. premium grade and super grade. Super grade is the higher octane number gasoline of the two with 98 RON, while the premium grade has 87 RON. The production of super grade is only 4,77% of the total gasoline consumption.

III. QUALITY OF INDONESIAN MOTOR GASOLINE

Gasoline characteristics have influence on engine performance and engine smooth operating conditions. Some of the characteristics are as follows :

- Ignition quality
- Volatility
- Corrosivity
- Stability.

Ignition quality of gasoline is usually expressed by means of the octane number and calorific value. Volatility of gasoline is usually indicated by ASTM distillation and Reid Vapour Pressure.

The above mentioned characteristics can influence engine performance and engine operating conditions such as :

- Combustion efficiency
- Cold starting
- Engine acceleration
- Warm-up period
- Carburation icing tendencies
- Vapour lock
- Dilution
- Distribution
- Engine clogging
- Engine wear
- Fuel economy, etc.

Indonesian petroleum refineries produce motor gasoline of two different grades, namely super grade with 98 RON and premium with 87 RON. The Indonesians specification allows a maximum TEL content of 2.50 cc/USG for premium gasoline and 3.00 cc/USG for super grade, although in actual practice the refineries rarely use more than 2.00 cc/USG and 2.50 cc/USG for the premium and super grades, respectively. Indonesian imported automotive vehicles mostly from Japan; consequently the Indonesian octane number requirement for the majority of Indonesia's car population is around 92 RON (Ref. 1).

Besides studies on octane number requirement the Indonesian government supported research activities for the improvement of the motor gasoline quality produced by Pertamina refineries, among other things by studies on increasing the octane number and reduction of TEL content and the use of detergent additives in motor gasoline. Typecal motor gasoline quality produced by Pertamina refineries can be seen in Table 2.

IV. MTBE

MTBE (Methyl Tertiary Butyl Ether) is already used as an octane booster in competition with toluence, alkylates, and reformates. MTBE has several advantages, among which is the octane number of its blends, its miscibility with gasoline in all proportions, and its high calorific value. MTBE containing gasoline is not so hygroscopic as other oxygenated gasoline blends.

Table 1
Indonesian specification for motor gasoline

Characteristics	Premium (87 ON)	Super 98
Octane Number F1	min. 87	min. 98
TEL (ml/USG)	max. 2.50	max. 3.00
Distillation		
10% evap. (°C)	max. 74	max. 74
50% evap. (°C)	88 – 125	88 – 125
90% evap. (°C)	max. 180	max. 180
End Point (°C)	max. 205	max. 205
20% – 10% evap. temp (°C)	min. 8	min. 8
Residue (% vol.)	max. 2.0	max. 2.0
RVP at 100°F (psi)	7.0 – 9.0	max. 9.0
Existent Gum (mg/100 ml)	max. 4.0	max. 4.0
Induction Period	min. 240	min. 240
Sulphur Content (% wt)	max. 0.2	max 0.2
Copper Strip 3h, 122°F	max. No. 1	max. No. 1
Doctor Test or Alternative		
Mercaptan	negative	negative
Sulphur (% wt)	max. 0.015	max. 0015
Colour	yellow	yellow
Dye Content :		
Yellow (g/100 USG)	0.5	0.5
Odour	marketable	marketable

Notes : 1 USG = 3.785 dm^3 100°F = 37.8°C
122°F = 50°C 1 psi = 6.9 kPa

Table 2
Typical test figures of commercial motor gasoline

Analyses	Premium	Super
Specific Gravity 60/10F	0.7434	0.748
Distillation		
10% vol. evap (°C)	72	69
50% vol. evap. (°C)	107	114
90% vol. evap. (°C)	142	154
End Point (°C)	179	186
20% – 10% evap. (°C)	10	15
Octane Number, F–1	86.5	97.1
Octane Number, F–2	80.7	83.6
Lead Content (g/l)	0.6	0.7
TEL Content (ml/USG)	1.8	2.33
Existent Gum (mg/100 ml)	1.4	3.6
Sulphur Content (% wt)	0.007	–
Copper Strip Corrosion	ASTM No. 1	ASTM No. 1
Colour, Visual	Yellow	Yellow
Odour	marketable	marketable

Note : 1 USG = 3.785 dm^3

Produced by the reaction of isobutylene and methanol, it is one way to indirectly use methanol in motor fuel without the problems associaed with a light alcohol as a belnding component. Gasoline containing MTBE are compatible with the present gasoline distribution systems due to their low water sensitivity. The characteristics of MTBE ocygenated compounds are shown in the following table (Table 3).

Table 3

Characteristics of MTBE oxygenated compounds

Properties	MTBE
Specific Gravity 20/4°C	0.7405
R V P (bar)	0.610
Boiling Point @ 760 mm Hg (°C)	55.2
Freezing Point (°C)	− 108.6
Blending ON :	
RON	116
MON	98
Heating Valeu, Lower (kcal/kg)	8.395
Solubility in Water at 20°C (g/100 g solution)	4.8
Azeotrope Formation with Hydrocarbon	
Stoichiometric Air/Fuel Ratio (%-wt)	11.8 : 1

Notes : 1 bar = 100 kPa
1 kcal = 4.187 kJ
1 mm Hg = 133 Pa

V. SAMPLE PREPARATION FOR LABORATORY TESTS

In order to conduct laboratory tests to study the changes in physical and chemical properties and its knock rating, as a consequence of mixing MTBE in unleaded gasoline, a series of blends were prepared. Unleaded gasoline used was produced by Indonesian refineries, while MTBE was imported from West Germany.

The blends prepared for the laboratory tests were as follows:

- Unleaded gasoline consisting of 70% vol. reformate and 30% vol. naphta (UG)
- 3% vol. MTBE blend in unleaded gasoline (MGB-3)
- 6% vol MTBE blend in unleaded gasoline (MGB–6)
- 10% vol. MTBE blend in unleaded gasoline (MGB–10)
- 15% vol. MTBE blend in unleaded gasoline (MGB–15)
- 3% vol. MTBE blend in unleaded gasoline with TEL (MGBT–3)
- 6% vol. MTBE belnd in unleaded gasoline with TEL (MGBT–6)
- 10% vol. MTBE blend in unleaded gasoline with TEL (MGBT–10)
- 15% vol. MTBE blend in unleaded gasoline with TEL (MGBT–15)

Notes: UG = Unleaded Gasoline
MGB = MTBE Gasoline Blend
MGBT = MTBE Gasoline Blend with TEL-B

VI ANALYSIS OF LABORATORY TEST RESULTS

The laboratory test results of MTBE blended gasoline (MGB as well as MGBT) are found in Tables 4, 5, and 6.

VII. KNOCK RATING OF MGB

The test results of MGB in a CFR engine, as shown in Figure 1, indicate increasing octane numbers of MGB with increase of MTBE content. 15% vol. MTBE in unleaded gasoline yielded an octane number of 87 with a fuel sensitivity of 6.2 ON. If 3% vol. MTBE is blended with unleaded gasoline, the octane number increases from 80.9

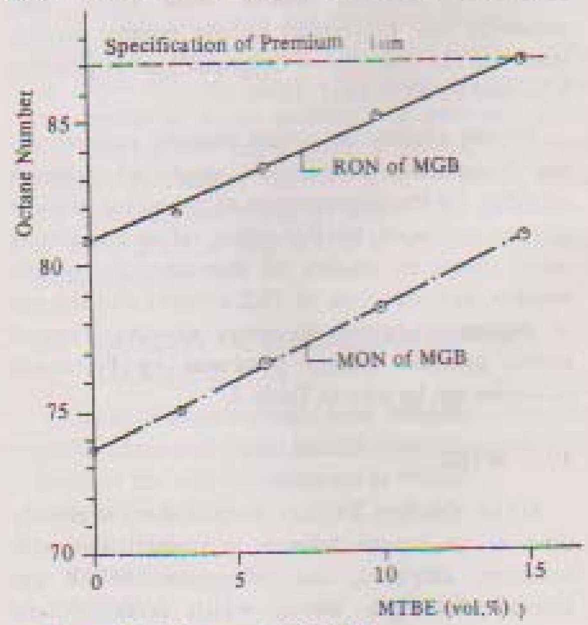

Figure 1 . Influence of MTBE in Unleaded Gasoline on Octane Number

RON to 81.9 RON, 6% vol. MTBE raised it up to 83.3 RON, and 10% vol. MTBE raised it up to 85.1 RON.

VIII. REDUCTION OF TEL CONTENT IN GASOLINE

From the laboratory test results, as shown in Figure 2, it can be seen that an increase in MTBE content was causing a decrease of TEL content in MGBT, while increasing its fuel sensitivity.

With 3% vol. MTBE for an octane number of 87 RON (MGBT) a decrease of TEL content from 0.85 to 0.65 cc/USG was achieved (i.e. a decrease of 0.20 cc/USG).

With 15% vol. MTBE unleaded gasoline an octane number 87 RON was achieved with zero TEL content, while an octane number of 92 RON requires the addition of 0.68 cc TEL/USG.

IX. DISTILLATION OF MGBT

From the laboratory test results, as shown in Figure 3, it can be seen that increasing MTBE contents were causing greater deviation below the required minimum 50% volume recovery temperature. This will be of influence in its use as an automotive fuel.

For MTBE contents in gasoline greater than 10% vol. the increased volatility becomes such that blends must be considered off-spec for Indonesia.

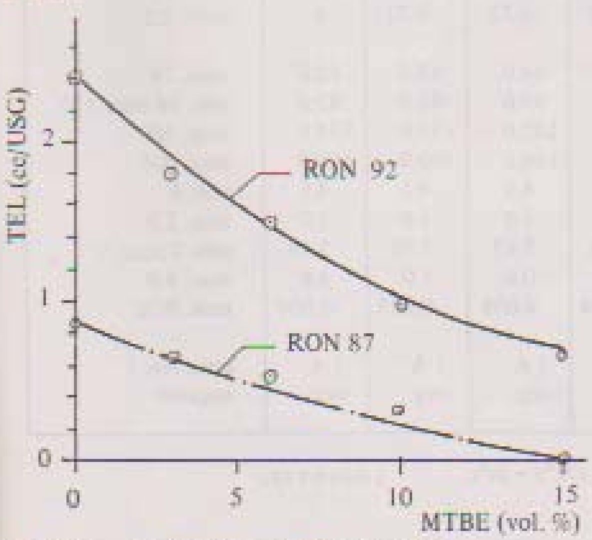

Figure 2 . Influence of MTBE in gasoline on TEL content

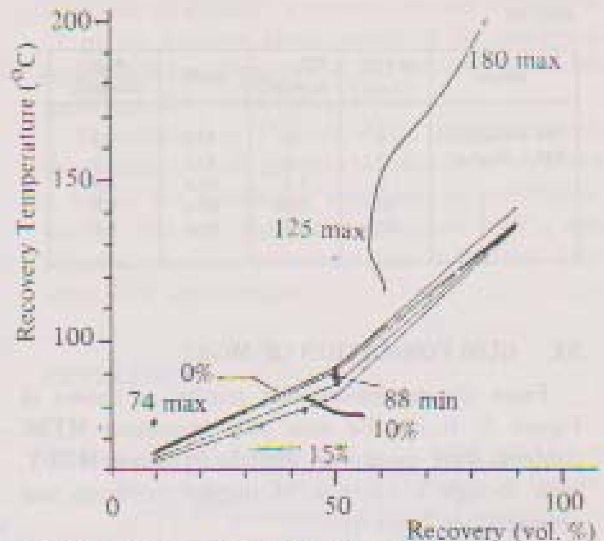

Figure 3 : Distillation of MTBE blend in gasoline (MGBT 87 RON)

X. REID VAPOUR PRESSURE FOR MGBT

From the laboratory test results, as shown in Figure 4, it can be seen that up to 15% vol. of MTBE in gasoline with 87 RON, the RVP, while increased by the MTBE addition, was still below the Indonesian premium specification (minimum RVP is 7 psi or 48,3 kPa.

Table 4
Influence of MTBE in unleaded gasoline on octane number

Sample	MTBE (% vol.)	RON	MON	Fuel Sensitivity
Unleaded gasoline (70% Reformate + 30% L. Naphta)	0	80.9	73.7	7.2
	3	81.9	75.0	6.9
	6	83.3	76.6	6.6
	10	85.1	78.4	6.7
	15	87	80.8	6.2

Table 5
Influence of MTBE gasoline on TEL content
RON 87

Sample	MTBE (% vol.)	TEL (cc/USG)	MON	Fuel Sensitivity
70% Reformate + 30% L. Naptha	0	0.85	83.5	3.5
	3	0.65	83.1	3.9
	6	0.53	83.8	3.2
	10	0.31	83.3	3.7
	15	0	80.8	6.2

RON 92

Sample	MTBE (% vol.)	TEL (cc/USG)	MON	Fuel sensitivity
70% Reformate + 30% L. Naptha	0	2.4	87.9	4.1
	3	1.8	87.2	4.8
	6	1.5	87.6	4.4
	10	0.98	87.6	4.4
	15	0.68	87.6	4.4

XI. GUM FORMATION OF MGBT

From the laboratory test results, as shown in Figure 5, it can be seen that increasing MTBE contents were causing an increase of gum in MGBT, even though a decrease of sulphur contents was observed (see Table 6).

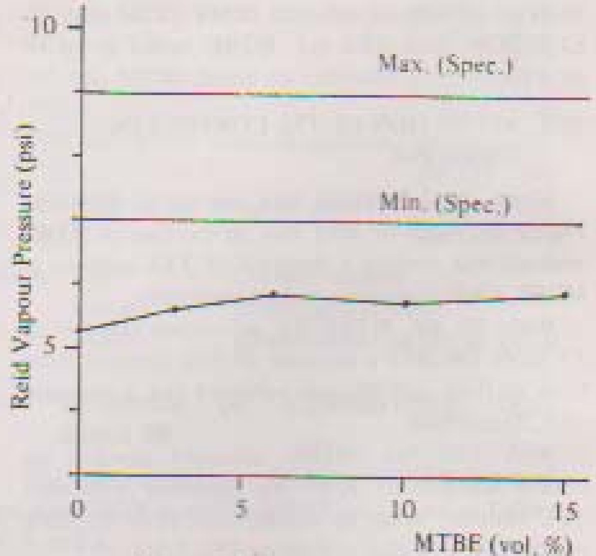

Figure 4 . Vapour pressure of MTBE blend in gasoline (MGBT 87 RON)

Table 6
Laboratory test results
Influence of M TBE in gasoline on physical and chemical properties

Characteristics	Unit	0	3	6	10	15	Indonesian Premium Specification
Knock Rating FI	ON	87	87	87	87	87	Min. 87
TEL Content	cc/USG	0.85	0.65	0.53	0.31	0	max. 2.5
ASTM Distillation							
10% vol evap.	^oC	64.5	64.0	64.0	63.0	62.0	max. 74
50% vol. evap.	^oC	90.5	90.0	89.0	86.0	82.0	min. 88 max. 125
90% vol. evap.	^oC	135.5	140.5	135.0	135.0	134.0	max. 180
End Point	^oC	161.0	161.0	160.0	160.0	160.0	max. 205
20% – 10% vol. evap.	^oC	6.5	7.0	4.5	4.5	4.5	min. 8
Residue	% vol.	0.8	1.0	1.0	1.0	1.0	max. 2.0
RVP at 100^oF	psi.	5.25	5.60	5.87	5.76	5.89	min. 7 max. 9
Existent Gum	mg/100 ml	0.2	0.2	0.6	1.0	1.4	max. 4.0
Sulphur Content	% wt	0.062	0.048	0.038	0.033	0.030	max. 0.20
Copper Strip Corrosion	3 h/ 122^oF	1 A	1 A	1 A	1 A	1 A	max. No. 1
Doctor Test	–	neg.	neg.	neg.	neg.	neg.	negative

Notes : 1 USG = 3.785 dm^3 $100^oF = 37.8^oC$ $122^oF = 50^oC$ 1 psi = 6.9 kPa.

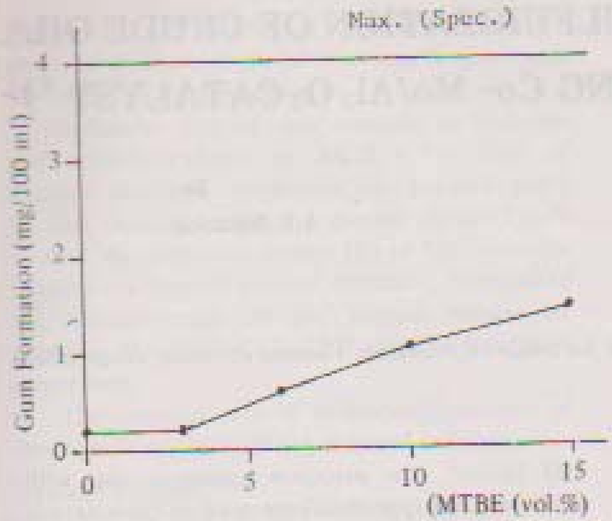

Figure 5 . Gum formation of MTBE blend in gasoline (MGBT 87 RON)

XII. CONCLUSION

The experimental results confirm the positive effects of MTBE as an octane booster of gasoline. An increase of octane number of 6.1 (RON) was observed for an addition of 15% vol. MTBE to an Indonesian unleaded gasoline blend. Such an increase would reduce the TEL requirement of the gasoline by 0.85 cc TEL/USG.

An addition of 15% vol. MTBE would be sufficient to produce a research octane number of 87 in the gasoline blend, which is the minimum octane number stipulated in the current Indonesian specification for premium gasoline.

The addition of 15% vol. MTBE, however affects the volatility of the gasoline blend such as to reduce it below the distillation specification, particularly for the 50% vol. distilled temperature. RVP is also affected, reaching pressure values below the minimum RVP specification

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