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synopsis

CONSEQUENCES OF LIMITING BENZENE CONTENT OF MOTOR GASOLINE

CONCAWE Report No. 13/83

This report considers current motor gasoline benzene levels and the consequences of limiting benzene contents because of possible health effects.

Current legislation in Europe is limited to five countries; Austria, Norway, Sweden and Switzerland have a 5 vol% maximum limit and the Netherlands 7.5 vol%. The analysis of the benzene contents of 356 marketed gasolines sampled during 1980/81 shows that regular gasolines in Western Europe contain less benzene than premium grades and that premium gasoline benzene contents are unlikely to exceed 5 vol%, except for a limited amount of production in Germany caused mainly by the usage of undebenzenised steam cracker gasoline.

Variation in benzene contents of gasolines is due to process differences between refineries, crude oil used, grade of gasoline, lead content and, particularly, the quantity of high benzene content steam cracker gasoline. It is expected that more steam cracker gasoline will have benzene extracted from it in the future and, as a consequence, a smaller proportion of gasoline production is likely to have greater than 5 vol% benzene content.

The benzene contents of motor gasoline components show a wide variation. Catalytic reformate, which is a major gasoline component, may have a benzene content ranging between 1 and 11 vol%, depending upon feedstock, crude source and boiling range, and octane number of reformate.

The impact of benzene limitations on the production of motor gasolines has been assessed through a series of refinery schemes. These fall into two groups: the first considers the benzene levels which might be achieved with existing process routes, without extraction of benzene from components. The second considers meeting a 1 vol% benzene content maximum limit, necessitating extraction of benzene from catalytic reformate and with production of surplus benzene which may exceed the quantity which the chemical industry could absorb. Within these groups two lead levels are considered, 0.15 gPb/l and zero, for three refinery types; crude input varies between 100% North Sea type and 100% Middle East.

Without any restrictions the average benzene content of European premium gasoline (97 RON) with 0.15 gPb/l would be 3.2 vol% and of regular (92 RON) 1.1 vol%. Wide variations between refineries are expected. The more numerous cracking/reforming refineries would produce premium gasoline with benzene content of about 5 vol% from North Sea crude and 2.5-3 vol% from Middle East. The same premium gasoline produced by simple hydroskimming refineries would contain 6-8 vol% when processing North Sea crude and 3-3.5 vol% from Middle East crude. The unleaded gasoline situation has also been assessed, assuming one grade of gasoline of 92 RON.

Apart from any repercussions in the chemical industry, purely within the oil refinery sector the cost of reducing benzene to 1 vol%, with gasoline containing 0.15 gPb/l, is estimated to be in the range $US 20-35/t of gasoline (1982 money), depending upon refinery type, crude oil processed and values of products. Assuming 100 million t/year of gasoline production in Europe, the total cost would be about $2800 million/year.

The investment in new processes, because of different refinery circumstances, ranges from $14 to $52 per tonne of gasoline produced per year, averaging at about $30-40. Thus a typical refinery, processing about 5 million t/year crude and producing about 1 million t/year of motor gasoline, would, on the basis of these figures, require to invest $30-40 million to achieve 1 vol% benzene maximum. On the same basis, total European investment would be about $3,000 - 4,000 million. Up to five years would be needed for the planning and construction of new plants.

The energy penalty in the 0.15 gPb/l case in terms of additional crude required would be approximately 5 million t/year for total Western Europe to balance the loss of extracted benzene and to provide additional process fuel. For unleaded gasoline, assuming that the octane number is reduced to 92 RON from current levels, the penalties would be slightly lower. However, if higher octanes were required the benzene contents, and hence the problems and costs for reducing them, would significantly increase, as indicated in CONCAWE report no. 11/83.

At least two million t/year of benzene would have to be extracted. This is expected to exceed the amount which could be absorbed by the chemical industry and in itself would cause a serious environmental hazard, even if only used as fuel.

December 1983

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the oil companies' european organisation
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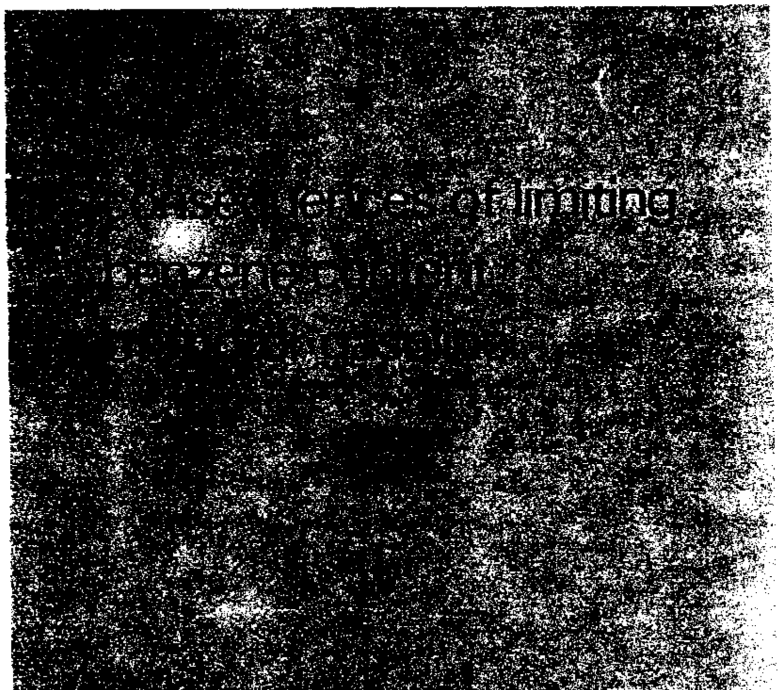
report no. 13/83



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consequences of limiting benzene content of motor gasoline

Prepared by CONCAWE's Ad Hoc Group
on Effects of Limitations on Gasoline Benzene Content

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ABSTRACT

This report considers current motor gasoline benzene levels, related legislation in Western Europe and the consequences of limiting the benzene content of gasoline. The report first reviews the sources of benzene in gasoline and summarises the existing legislation on allowable levels. It then surveys the benzene levels in current motor gasolines and analyses the causes of variations. Means of reducing benzene contents, either by adjusting existing processing routes or by extracting benzene from gasoline blending components, are considered. The impact of benzene limitations on the production of motor gasolines are assessed in terms of the costs involved and the energy penalties incurred. Finally, the report looks at the potential problem of the disposal of extracted benzene.

Dit rapport bespreekt het gangbare benzeengehalte in autobenzine, de hierop betrekking hebbende wetgeving in West-Europa, en de consequenties die het reduceren van het benzeengehalte in benzine met zich meebrengt. In het rapport wordt eerst de oorsprong van benzeen in benzine besproken en de bestaande wetgeving over het toegestane gehalte samengevat. Vervolgens wordt een overzicht gegeven van de benzeengehaltes in gangbare autobenzines en de oorzaken van afwijkingen geanalyseerd. Het aanpassen van bestaande procesgangen en het extraheren van benzeen uit de mengcomponenten van benzine worden overwogen als middelen tot verlaging van het benzeengehalte. De consequenties van lagere benzeengehaltes voor de produktie van autobenzine worden beoordeeld uit het oogpunt van de kosten die hiermee gemoeid zijn en het energie-offer dat moet worden gebracht. Tenslotte wordt in het rapport het potentiële probleem van het opruimen van de geëxtraheerde benzeen besproken.

Dieser Bericht behandelt die derzeitigen Gehalte von Benzol im Benzin, die einschlägigen gesetzlichen Bestimmungen in Westeuropa und die Konsequenzen der Begrenzung des Benzolgehalts von Benzin. Zunächst werden die Quellen des Benzols im Benzin besprochen und die heutigen Vorschriften in bezug auf den zulässigen Höchstgehalt dargestellt. Danach werden die Benzolgehalte der heutigen Benzinqualitäten betrachtet und die Ursachen der Abweichungen betrachtet. Es werden die Möglichkeiten zur Verringerung des Benzolgehalts durch verfahrenstechnische Veränderungen oder durch Benzolextraction behandelt. Die damit verbundenen Kosten und Energieeinbussen werden erörtert. Zum Schluss wird das mit dem Benzolentzug möglicherweise entstehende neue Problem der Entsorgung behandelt.

Le présent rapport examine les niveaux de benzène actuellement présents dans les essences, la législation y afférente en Europe occidentale et les conséquences d'une limitation de la teneur en benzène dans l'essence. Le rapport examine en premier lieu les sources de benzène dans l'essence et récapitule la législation existante sur les niveaux autorisés. Il examine ensuite les niveaux de benzène dans les essences courantes et analyse les raisons des fluctuations. Sont également étudiés les moyens de réduire les taux de benzène, soit par modification des procédés existants, soit par extraction du benzène des composants utilisés dans le mélange d'essence. L'impact des limitations en benzène sur la production d'essence pour moteurs est évalué en termes de coûts et de pénalités encourues du point de vue énergétique. Enfin, le rapport aborde le problème potentiel de l'élimination du benzène extrait.

Este informe considera los niveles de benceno actuales en la gasolina, la legislación correspondiente en la Europa Occidental y las consecuencias de limitar el contenido de benceno en la gasolina. Se refiere en primer lugar a las fuentes de benceno en la gasolina y da un resumen de la legislación existente en cuanto a los niveles admisibles, examinando a continuación los niveles en las gasolinas actuales y analizando las causas de las variaciones. Considera también los medios para reducir el contenido de benceno, ya sea alterando los procesos existentes o extrayendo benceno de la mezcla de la gasolina. Se evalúa el impacto de limitar el benceno en la producción de gasolinas, en cuanto a los costes y penalidades energéticas resultantes. Finalmente, el informe examina el problema en potencia de desembarazarse del benceno extraído.

Il rapporto esamina gli attuali livelli di benzene nella benzina, la relativa legislazione nell'Europa Occidentale e le consequenze della limitazione del tenore in benzene della benzina. Fa innanzi tutto una rassegna delle fonti di benzene nella benzina e dà un sommario dell'attuale legislazione sui livelli permessi, esaminando successivamente i livelli di benzene nelle benzine attuali ed analizzandone le cause delle variazioni. Presenta inoltre una trattazione dei mezzi per ridurre il tenore in benzene, sia modificando gli attuali trattamenti e lavorazioni che estraendo il benzene dai componenti delle miscele di benzina. Valuta pure le consequenze delle limitazioni del benzene sulla produzione delle benzine in termini dei costi comportati e dell'onere energetico. Per ultimo il rapporto esamina il problema potenziale dello smaltimento dei benzene estratto.

CONTENTS

1. INTRODUCTION

In view of the interest in the possible effects on health of benzene present in motor gasoline, CONCAWE has undertaken an investigation into the consequences for gasoline production of limiting benzene content.

2. FORMATION OF BENZENE

The formation of benzene during the manufacture of gasoline is unavoidable with the crude oils and processes available to the oil refining industry. The most important process for making high octane number motor gasoline components, catalytic reforming, produces benzene as part of the reaction to increase the octane number of the naphtha used as feedstock. The reformate from this process contains from 1 - 11% volume benzene. Also, benzene occurs naturally in small quantities in crude oil.

A minor amount of motor gasoline component is obtained as a by-product of the petro-chemical industry. In the steam cracking of the naphtha fraction of crude oil to make ethylene, steam cracker gasoline (or pyrolysis gasoline) is produced which has high benzene content (20 - 50%).

These are the main sources of benzene in gasoline. Another major gasoline component, naphtha from the catalytic cracking process, contains only a small amount of benzene (<1%). There is a popular misconception that benzene is added to motor gasoline. This is not so. In the past coal tar benzene from the gas-making industry was added, but with the change from manufactured gas to natural gas, coal tar benzene is no longer available. Nowadays benzene for manufacturing chemicals is obtained by extraction from reformates or steam cracked gasoline.

It should be noted that most of the benzene in vehicle exhaust emissions is formed by the combustion of compounds other than benzene. Technology exists however to reduce benzene in exhaust gases.

3. LEGISLATION

The benzene content of gasoline is not limited in the majority of European countries. Existing legislation is summarised in Table 1 below:

Table 1 Existing benzene legislation

Country	Max benzene content (liquid volume %)	Date of implementation
Austria	5.0	Oct. 1983
Netherlands	7.5	1977
Norway	5.0	1983
Sweden	5.0	1978
Switzerland	5.0	1972

4. BENZENE CONTENT OF CURRENT MOTOR GASOLINES

Over 90% of current motor gasolines in Western Europe have benzene contents below the 5% volume maximum limit set by the countries listed above.

4.1 SURVEY OF MARKETED GASOLINES

From analyses of 356 samples, taken in 1980-81, it was concluded that:

- regular gasolines in all European countries contain less benzene than premium grades;
- premium gasoline benzene contents in the four major gasoline consuming European countries - UK, Italy, France and Germany - are unlikely to exceed 5% volume, except for a limited amount of production in Germany. There, some 20% of premium gasoline contained greater than 5% volume benzene and about 10% greater than 6% benzene;
- no very significant changes since 1976-8 are indicated by these data;
- on average for Europe, in 1980-81, 50% of the premium grade samples contained 2.7% volume or less of benzene and 80% contained 3.7% or less. Corresponding figures for regular are 1.8% and 2.8%.

4.2 CAUSES OF BENZENE CONTENT VARIATIONS

There are many reasons for the wide variations:

a) the specifications, particularly octane numbers, of the gasolines and the ratio of premium/regular grades;

b) the lead alkyl content allowable;

c) the crude oil type(s) available;

d) the type of process plant used for gasoline production in the refinery;

e) the proportion of motor gasoline in the total refinery product make;

f) import/export of motor gasoline components;

g) extracted benzene to be sold as such.

4.2.1 Octane number and lead content

Benzene is one of the highest octane components in motor gasoline. It is present in catalytically reformed naphtha (reformate). A higher octane number requirement for a motor gasoline will generally result in a greater proportion of reformate in the blend and hence a higher benzene content. This explains why most premium grade gasolines have higher benzene contents than regular grades.

The use of lead as an octane booster permits a lesser use of the higher octane number hydrocarbon components and hence, if the higher octane material is reformate, a lower benzene content. Conversely, decreasing lead use will tend to result in higher benzene contents if the gasoline octane number required is unchanged.

4.2.2 Crude oil type

The type of crude oil processed in a refinery is most important since this, together with the boiling range of the feedstock, determines the quantity of low octane naphtha compounds in the catalytic reformer feed which will turn into benzene during processing. When processing some of the North Sea crudes, motor gasolines of around 8% volume benzene content may be produced, whilst the same refinery might produce gasoline of around 3% benzene content from Middle East crudes.

4.2.3 Processes available and proportion of motor gasoline

Refineries differ considerably in the combination of processes they use. The most significant difference in the present context is whether or not they include a catalytic cracker. The majority of refineries are required to meet fuel oil product demands lower than the amount naturally occurring in crude oil. Catalytic cracking is the conversion process most commonly used to reduce the proportion of fuel oil and almost all refineries will use this type of processing in the future. This process converts heavy fractions, only suitable otherwise for fuel oil blending, into a range of lighter components, in particular a high proportion of gasoline blending components with low (<1%) benzene content.

These catalytic cracker gasoline blending components dilute the high benzene content of the reformate in motor gasoline and hence refineries including catalytic crackers will produce lower benzene content gasolines, other factors remaining unchanged. However, catalytic cracking cannot be regarded as a tool for reducing benzene content since the octane numbers of the gasoline components it produces are lower than reformate and the extent of its use is controlled by the ratios of the demands for the whole range of refinery products.

Thus the proportion of motor gasoline in the total product demand will determine the amount of fuel oil conversion used and, if this is by catalytic cracking, then it will influence gasoline benzene content.

Other processes used to convert fuel oil components to lighter components produce low octane gasoline which is usually catalytically reformed to improve its octane number, resulting in a high benzene content product.

Processes which produce high octane iso-paraffins (eg. alkylation and isomerisation) may be used to yield virtually benzene-free components for motor gasoline. Their use is, however, severely restricted since they require special feedstocks which a refinery can only produce in limited amounts.

4.2.4 Imports of components

The most significant import into a refinery, as far as benzene content is concerned, is steam cracker gasoline. Undoubtedly, the highest benzene content gasolines observed in the German samples will have contained steam cracker gasoline. An increasing proportion of benzene is being extracted from steam cracker gasoline and then used for manufacture of chemicals. It is anticipated that only a very few refineries will be using undebenzenised steam cracker gasoline in the future. It follows that, for them, any benzene content restrictions would be far more difficult to meet than for other refineries.

4.3 MEANS OF REDUCING BENZENE CONTENT

Some reduction in gasoline benzene content can be achieved by adjustments to refining, notably to the operation of the catalytic reformer. However, this process cannot be considered in isolation; changes to its feedstock or operating conditions may be used to lower benzene contents but these will automatically affect the other processes and products in the refinery. Since the problem is quite complex, an outline of catalytic reforming, and to a lesser extent other processes, is given in the following sections.

To improve upon the reduction achievable by modifying reformer operation or feedstocks it would be necessary to extract benzene from the reformate. This would result in a lower motor gasoline octane quality and reduced production from a given quantity of crude, together with benzene as a by-product. Installation of such a process would require investment in new plant and increase operating costs.

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4.3.1 Catalytic reformate

Benzene levels in catalytic reformate can range from about 1% volume to 11%. The fundamental variables which determine this level are:

- benzene precursor level (i.e. benzene-forming compounds) in the naphtha feed to the reformer;
- reformer severity (i.e. reformate octane number) and conditions.

4.3.1.1 Feedstock quality

The level of benzene precursors in the naphtha feed is a function of its boiling range, in particular its initial boiling point (IBP), and also the crude oil from which it originates.

Benzene itself, and the major benzene precursor cyclohexane, boil at 80 and 81°C respectively. If the initial boiling point of the naphtha feedstock is set above this level the content of benzene in the reformate is substantially reduced. Undesirable consequences to increasing the IBP are that the amount of reformer feed is restricted and the amount of light straight run gasoline (the fraction boiling below the naphtha) is increased in quantity and its octane number reduced. The means of overcoming these disadvantages will depend upon the particular refinery configuration. In any event, they contribute to an increase in consumption of crude oil and increased costs in order to reduce benzene content.

Naphthas from North Sea crudes generally have higher naphthene plus aromatic content, i.e. benzene precursors, and these result in a higher benzene content in their reformates.

The variations in reformate benzene content due to feed boiling range and crude oil type are illustrated in Table 2 below:

Table 2 Benzene content of 98 RON reformate (vol%)

Crude oil:	North Sea	Middle East
Feed boiling range (C°)		
70 - 150	8.4	5.2
90 - 150	6.5	3.8
70 - 185	5.7	3.6
Average/typical	7	4

4.3.1.2 Reformate octane number

Variation of reformer severity, as measured by reformate octane number, affects the benzene content of the reformate. The octane number of the reformate which has to be produced is determined not only by the octane number and lead level of the gasoline to be made but also by the quality of the other components available. Therefore, reducing severity to reduce benzene is not a likely route to meeting benzene content restrictions.

In the refinery cases referred to later, the option to change reforming severity was allowed, and if alternative high octane components could be made then some reduction in reforming severity or quantity could occur. The feedstock changes referred to in section 4.3.1.1 are, however, far more effective for reducing benzene.

4.3.2 Steam cracker gasoline

The benzene content of steam cracker gasoline is dependent on the ethylene production with which it is associated and is outside the control of the gasoline manufacturer. However, as pointed out in section 4.2.4, the increasing extraction of benzene from steam cracker gasoline to meet the external benzene requirements will reduce the potential problem for all but a few refiners.

4.3.3 Gasoline components of low benzene content

The benzene content of reformate or undebenzenised steam cracker gasoline may be diluted by greater use of low benzene content blending components. The major one is catalytic cracker gasoline but, as explained above, catalytic cracker operation influences all other products in the refinery.

4.3.4 Benzene extraction

The only effective method of achieving major reductions is to physically remove benzene from reformate and steam cracker gasoline. This is technically feasible, but costly. Benzene can be extracted by distillation and/or solvent extraction techniques. Apart from the cost of building extraction plant, there would be a problem of disposing of the extracted benzene and substantial additional costs in replacing the benzene with other gasoline components.

4.4 IMPACT OF BENZENE LIMITATIONS ON PRODUCTION OF MOTOR GASOLINES

In order to assess plant changes, investments and crude oil requirements which would arise if benzene limitations were imposed, 31 refinery cases were prepared by various CONCAWE members. These fall into two groups with:

a) lead content 0.15 gPb/l and current octane numbers (97 RON premium, 92 RON regular);

b) unleaded gasoline. Further details about octane numbers and benzene levels are given in CONCAWE report no. 11/83 (1).

In each group total European refining industry cases were prepared; these included cases for hydroskimming refineries with reformate as the only available high octane component, compared with conversion refinery cases including both catalytic cracking and reforming.

The benzene levels which might be achieved by existing process techniques, without extraction of benzene components, were estimated and then the means of meeting a 1% volume maximum benzene content by extracting benzene was considered.

4.4.1 <u>0.15 gPb/l leaded gasoline</u>

For the total European refining industry, if no limit is placed on benzene, it has been estimated that the average benzene content of premium gasoline (97 RON) with 0.15 gPb/l would be 3.2% volume and for regular grade (92 RON) 1.1%. Wide variations about the average are to be expected. This is borne out by the cases and the survey of marketed gasolines in <u>section 4.1</u> above. Most gasoline is produced by conversion refineries; in these, if crudes are processed in blocked-out operation, premium gasoline would contain about 5-6% benzene if only North Sea crude was processed but 2.5-3% if 100% Middle East crude was used. The less common hydroskimming refinery would be expected to produce premium grade containing 6-8% benzene when processing North Sea crude or 3-3.5% with Middle East crude.

4.4.2 <u>Unleaded gasoline</u>

Assuming a single grade of gasoline of 92 RON, the benzene situation would be slightly easier than in the 0.15 gPb/l cases, but with similar variations due to crude and refinery type.

However, if higher octane numbers were required for unleaded gasoline (1) the benzene contents, and hence the problems and costs of reducing them, would significantly increase.

4.4.3 Reduction in benzene content with existing processes

The option to change reforming severity was studied, and if alternative high octane components could be made then some reduction in reforming severity or quantity could occur. The feedstock changes referred to in Section 4.3.1.1 would, however, be far more effective for reducing benzene. Processes having less interaction with other products are more likely to be used, e.g. alkylation or isomerisation. The amount of feedstock for these processes is limited and product quality considerations (octane number and volatility) may also inhibit their use.

4.4.4 Cost of achieving 1% volume benzene by extraction

Apart from any repercussions in the chemical industry, purely within the oil refining industry, the cost of reducing benzene to 1%, with gasoline containing 0.15 gPb/l, is estimated to be in the range \$20 - \$35 per tonne (1982 money) depending upon refinery type, crude oil processed and product values. The average for the industry is estimated at \$28/t. Assuming 100 million t/year of gasoline produced in Europe, the total cost would be \$2800 million/year.

The investment in new processes ranges from \$14 to \$52 per tonne of gasoline produced per year, averaging about \$30 - \$40. The wide variation above is a reflection of the considerable differences between producers' gasolines and the benzene contents of their base gasolines.

A typical refinery processing 5 million t/year of crude oil and producing 1 million t/year of motor gasoline would require to invest \$30 - \$40 million to achieve 1% benzene maximum. On the same basis, European investment would be \$3,000 - \$4,000 million. Up to five years lead time must be allowed for the construction of new plants.

4.4.5. Additional crude oil

In the case of 0.15 gPb/l gasoline some 5 million t/year extra crude would be required to make up the volume of benzene extracted and to meet additional fuel requirements if 1% volume benzene maximum was imposed.

5. DISPOSAL OF EXTRACTED BENZENE

To produce all European gasoline at a benzene content of 1% volume would require at least 2 million t/year of benzene to be extracted. Disposal of this benzene would present a problem. It is expected to exceed by far the amount that could be absorbed by the chemical industry. In itself, benzene can cause a serious environmental hazard. Conversion to other chemicals is technically possible, but existing technology does not produce any material of sufficient value to pay for the extra processing. Use as a fuel is a possibility, but the possible health risk would appear to rule this out unless strict handling precautions are taken.

6. CONCLUSIONS

1) An average benzene content of 2.5 - 3% volume is expected for future European motor gasolines assuming either current octane numbers and 0.15 gPb/l or unleaded gasoline of 92 RON.

2) Considerable higher figures than the mean are to be expected from a very small number of gasoline producers.

3) Little reduction in benzene content can be achieved by modifications to existing operations.

4) To reduce benzene substantially would require extraction of benzene from components, particularly from catalytic reformate.

5) The additional cost of reducing benzene content to 1% volume for current quality 0.15 gPb/l gasoline would be in the range \$20 - \$35/t, depending on the refinery type and the crude oil it processes. On average about \$28/t is expected or \$2,800 million/year for Europe.

6) Investments for new plant are estimated at \$3,000 - \$4,000 million for 0.15 gPb/l gasoline.

7) Some 2 million t/year benzene would need to be extracted. No satisfactory, safe, economic method of disposal is known.

8) Lead at zero and a benzene restriction would result in an overall shortage of high octane components, and would further limit supplies of high octane gasoline compared with zero lead alone.

Remark:

As reported in another CONCAWE Report "Benzene emissions from passenger cars" (2) most of the benzene in vehicle exhaust emissions is formed by the combustion of compounds other than benzene in the engine. If exhaust emission legislation is made more restrictive and leads to a requirement for on-board vehicle control devices such as catalytic converters, the total benzene emissions from vehicles could be reduced by nearly 90% while total debenzenisation of gasoline alone would only reduce benzene emissions by about 50%.

7. REFERENCES

1. CONCAWE (1983) Assessment of the energy balances and economic consequences of the reduction and elimination of lead in gasoline. Report 11/83. The Hague: CONCAWE.

2. CONCAWE (1983) Benzene emissions from passenger cars. Report 12/83. The Hague: CONCAWE.