

# ALKYLATE PETROL

## Environmental Aspects of Volatile Hydrocarbon Emissions

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### ABSTRACT

All hydrocarbons emitted from production and use of petrol are hazardous to human health and the environment, but to a different extent for individual compounds. This thesis compares and characterizes C<sub>2</sub>-C<sub>8</sub> hydrocarbons related to alkylate petrol and conventional petrol. Production of alkylate depends on cat-cracking, and studies linked to fluid catalytic cracking (FCC) are included.

Quantitative proportions and retention data of more than sixty C<sub>5</sub>-C<sub>7</sub> alkenes in conventional petrol and FCC petrol naphtha were assessed by gas chromatography and gas chromatography-mass spectrometry. The naphtha contained about 40% alkenes. Speciated hydrocarbon emissions from the FCC unit consisted of about 15-20% alkenes, 5% or less arenes and 80% alkanes.

Specific hydrocarbons in refuelling vapour and in two-stroke engine exhaust were determined for alkylate and conventional petrol using adsorbent sampling and gas chromatography on an alumina column. About 90% of the amount of hydrocarbons in exhaust from the two-stroke engine was unburnt petrol. Major advantages of the alkylate petrol were found to be low proportions of benzene, alkylbenzenes and alkenes in the fuel. The compositions of fuel alkanes and combustion-formed alkenes differed markedly for the two fuels.

Today almost all alkylate produced worldwide is mixed into petrol for automobiles. A separate study concludes that it would be better to use alkylate as fuel for small engines. The main reason is that hydrocarbon emissions for two-stroke engines are more than one order of magnitude larger per litre petrol consumed. Both in Europe and in the US, the present production of alkylate is large enough to replace conventional petrol in most small engines, without seriously affecting the pool of petrol for automobiles.

**Key words:** Hydrocarbons, alkenes, benzene, 1,3-butadiene, ethene, alkylate, reformulated petrol, reformulated gasoline, small engines, two-stroke engines.

## LIST OF PUBLICATIONS

This thesis is based on work reported in the following articles, referred to by Roman numerals in the text.

- I. **Assessment by Gas Chromatography-Mass Spectrometry of Hexenes Emitted to Air**  
Ramnäs O., Östermark U. and Petersson G. (1993)  
*Journal of Chromatography* **638**, 65-69
- II. **Characterization of Sixty Alkenes in a Cat-Cracked Gasoline Naphtha by Gas Chromatography**  
Ramnäs O., Östermark U. and Petersson G. (1994)  
*Chromatographia* **38**, 222-226
- III. **Characterization of Volatile Hydrocarbons Emitted to Air From a Cat-Cracking Refinery**  
Östermark U. (1995)  
*Chemosphere* **30**, 1813-1817
- IV. **Assessment of Hydrocarbons in Vapours of Conventional and Alkylate-based Petrol**  
Östermark U. and Petersson G. (1992)  
*Chemosphere* **25**, 763-768
- V. **Volatile Hydrocarbons in Exhaust from Alkylate-based Petrol**  
Östermark U. and Petersson G. (1993)  
*Chemosphere* **27**, 1719-1728
- VI. **Better Use of Cleaner Petrol**  
Östermark U. (1996)  
Accepted for publication in *Journal of Cleaner Production*

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ABSTRACT

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## 1. INTRODUCTION

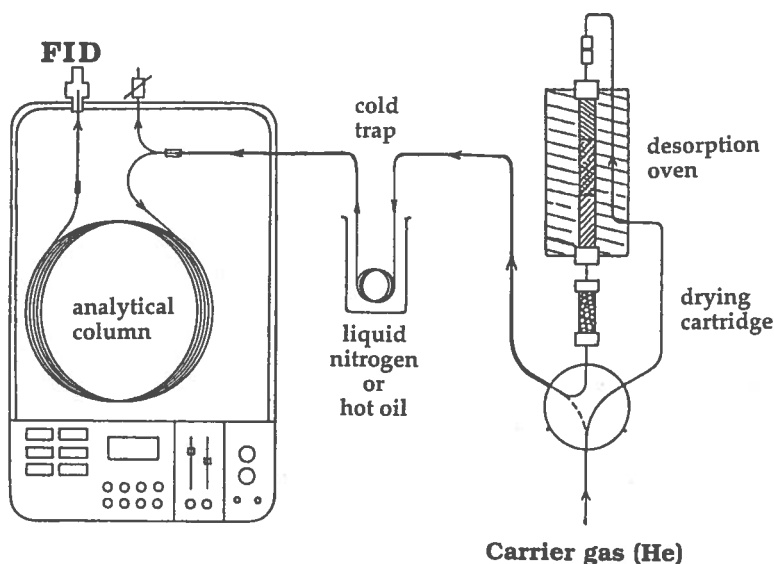
All hydrocarbons emitted from production and use of petrol are hazardous to human health and the environment, but to a different extent for individual compounds. However, hydrocarbons have often been monitored as a group, total hydrocarbons, and discussed as one pollutant. Environmentally related measures taken have rather intended to reduce total hydrocarbon emissions than specific compounds. More recently, petrol reformulation has been discussed as a way of reducing emissions of the most hazardous compounds, but not necessarily all compounds. In order to evaluate changes in the petrol, hazardous emission components must be individually determined. This need was the main reason for starting the work behind this thesis.

Hydrocarbon emissions from alkylate petrol, a markedly reformulated petrol recently marketed in Sweden as fuel for small engines, was especially interesting to compare with conventional petrol. As production of alkylate is linked to cat-cracking, additional studies associated with fluid catalytic cracking were conducted. The results have been published internationally in six articles (I-VI). The first two articles deal with assessment of alkenes in conventional petrol and cat-cracked petrol naphtha (I-II). The third is a study of fugitive hydrocarbon emissions from a cat-cracking refinery (III). In the fourth and fifth articles, hydrocarbons in vapour and exhaust from alkylate and conventional petrol are compared (IV-V). In the final article, the use of alkylate petrol in small engines is compared with use in automobiles (VI).

The work with this thesis was carried out at the department of Chemical Environmental Science during the years 1991-1996. Several projects based on determinations of volatile hydrocarbons have been carried out at the department. Earlier work includes studies of vehicle-polluted ambient air (Barrefors, 1996; Löfgren, 1992), terpenes emitted from forestry (Strömvall, 1992) and emissions from biomass burning (Barrefors, 1996).

## 2. ANALYTICAL METHODS

Adsorbent sampling followed by thermal desorption and gas chromatography is an established technique for assessment of volatile hydrocarbons (Barrefors and Petersson, 1993; Schaeffer, 1989). The gas chromatographic system illustrated in Figure 1 was used in several studies included in this thesis (I–V).



**Figure 1.** The gas chromatographic system with thermal desorption unit.

### 2.1 Adsorbent sampling

Air samples were taken using adsorbent cartridges. The cartridges were made of glass tubings (150 mm x 4mm i.d.) filled with in most cases three adsorbents of increasing strength: Tenax TA (~0.6 ml, 60/80 mesh, Chrompack), Carbotrap (~0.4ml, 20/40 mesh, Chrompack) and Carbosieve S-III (~0.4 ml, 60/80 mesh, Chrompack). After preparation, the cartridges were conditioned at 280°C in a helium gas flow of 30-40 ml/min for more than one hour. Shortly before each sampling they were conditioned at 235°C for about 15 min.

During sampling, a thin aluminium foil was used to protect the cartridges from photolytic degradation of hydrocarbons adsorbed. Before and after sampling, the cartridges were kept in sealed glass tubes placed in brown glass bottles. The air was passed through the cartridges using personal air sampling pumps. For most samples, Accuhaler Model 808 (MDA, Lincolnshire, IL, USA) was used. The sampling rates were in the range 10–100 ml/min, and the sampling volumes 10–1800 ml. Losses by breakthrough and decomposition of reactive hydrocarbons have been studied earlier by colleagues (Barrefors, 1993; Löfgren et al., 1991<sup>a</sup>). These aspects are shortly discussed in the articles (III-V). In most cases, the losses were judged to be negligible.

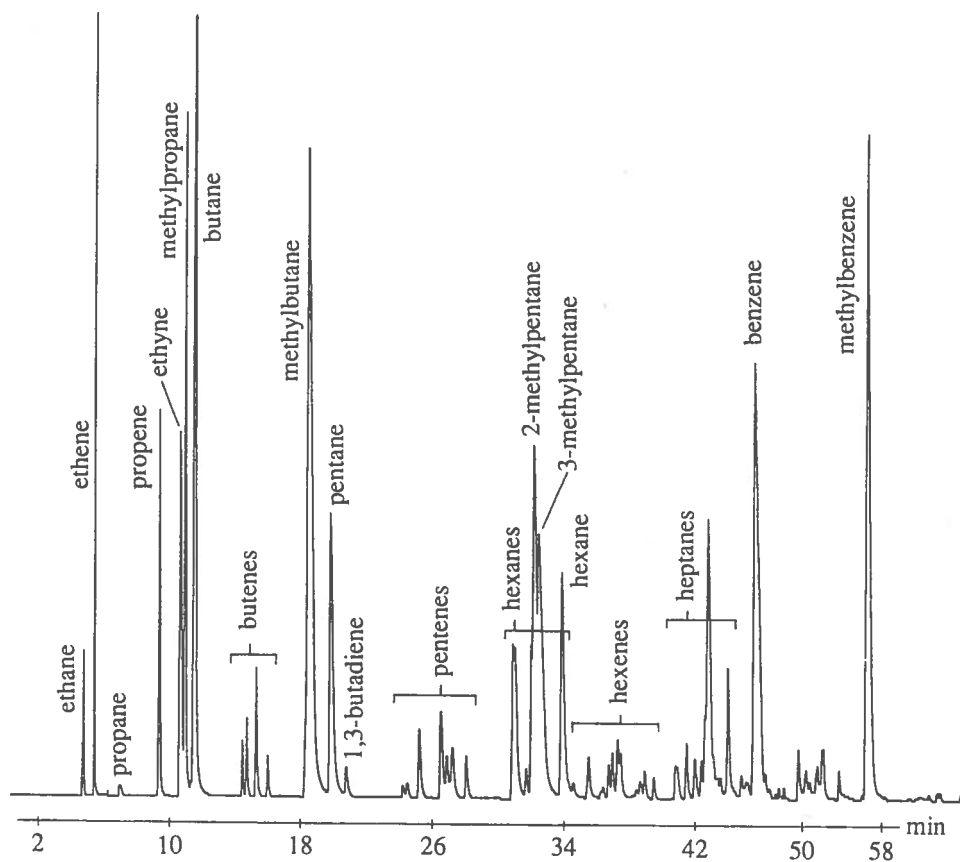
## 2.2 Gas chromatography

In the laboratory, the hydrocarbons were thermally desorbed (235°C, 14 min) in a helium gas flow (20-30 ml/min) and focused in a cold trap consisting of an empty fused silica column (~5 m, 0.32 mm i.d.) in liquid nitrogen (-196°C; Figure 1). After completed desorption, the hydrocarbons were injected by manually transferring the trap into an oil bath (150°C). The cold trap used was somewhat different from the original set-up of the system (Löfgren et al., 1991<sup>a</sup>).

As drying agent, magnesium perchlorate in a glass tubing (100 x 4 mm i.d.) was used. The drying agent was exchanged regularly, and no losses due to the magnesium perchlorate were observed, which is consistent with results of Matuska et al. (1986).

Analytical separations of volatile hydrocarbons were made mainly on an aluminium oxide (5% KCl) PLOT column (50 m x 0.32 mm i.d., Chrompack). It has successfully been used at our department for a long time (Nordlinder et al., 1984) as well as by other researchers (de Zeeuw et al., 1987; Mowrer and Lindskog, 1991; Pelz et al., 1990). Figure 2 illustrates the usefulness of the strongly polar aluminium oxide column. With the temperature program used, a large number of C<sub>2</sub>-C<sub>8</sub> hydrocarbons in petrol exhaust, petrol vapour and refinery emissions were separated (see also chromatograms in V, IV and III respectively). The alkenes favourably eluted as separate groups after the alkanes with the same number of carbon atoms. All four butenes and all seven pentenes were separated. In a study focused upon C<sub>5</sub>-C<sub>7</sub> alkenes, a slower temperature gradient increased the resolution of hexenes and heptenes (II).





**Figure 2. Gas chromatographic separation of C<sub>2</sub>-C<sub>7</sub> hydrocarbons emitted from a two-stroke engine fuelled with conventional petrol (V). Column: aluminium oxide (5% KCl) PLOT column (50 m x 0.32 mm i.d., Chrom-pack). Temperature program: 30°C–110°C (10°C/min), 110°C isothermally (14 min), 110°C–200°C (4°C/min) and 200°C isothermally (maximum recommended temperature).**

Complementary studies were made using a non-polar methylsilicone FSOT column (DB-1, 50 m x 0.32 mm i.d., 1  $\mu$ m phase layer, J&W) in another gas chromatographic system (Varian 3300, split/splitless injection). Liquid samples of different varieties of petrol (V) and cat-cracked naphtha (II) were analyzed. Due to the different elution orders, many hydrocarbons that were not separated on the aluminium oxide column did separate on the methylsilicone column (II). Figure 3 shows the separation of major hydrocarbons in alkylate petrol. Successful use of non-polar columns for analysis of hydrocarbons in other refinery fractions (Estel et al., 1995) as well as motor vehicle exhaust (Kaiser and Siegl, 1994; Zielinska et al., 1996) has recently been reported.

Flame ionization detectors (FID) were used in both gas chromatographic systems. The FID response was basically set equal for all hydrocarbons (Dietz, 1967), with minor corrections in some studies. Calibration was performed using gas standards prepared in the laboratory. Small quantities (in the mg range) of a mixture of a few specific hydrocarbons (usually C<sub>6</sub>-C<sub>9</sub>) were evaporated in a large glass vessel. This method included adsorbent sampling and thermal desorption, and was therefore regarded to be more accurate than an earlier method based on directly injected gas standards (Löfgren et al., 1991<sup>a</sup>).

### *2.3 Gas chromatography-mass spectrometry*

Mass spectrometric studies were made on a Varian Saturn II ion trap GC-MS instrument. Selective ion monitoring and identification by mass spectra made possible assessment of all seventeen acyclic hexenes in conventional petrol (I) as well as a detailed characterization of C<sub>5</sub>-C<sub>7</sub> alkenes in light cat-cracked naphtha (II). In the crack naphtha study, both the polar aluminium oxide column and the non-polar methylsilicone column were used. As mass spectra of several isomers were very similar, retention data for the two gas chromatographic columns were needed for final identifications.

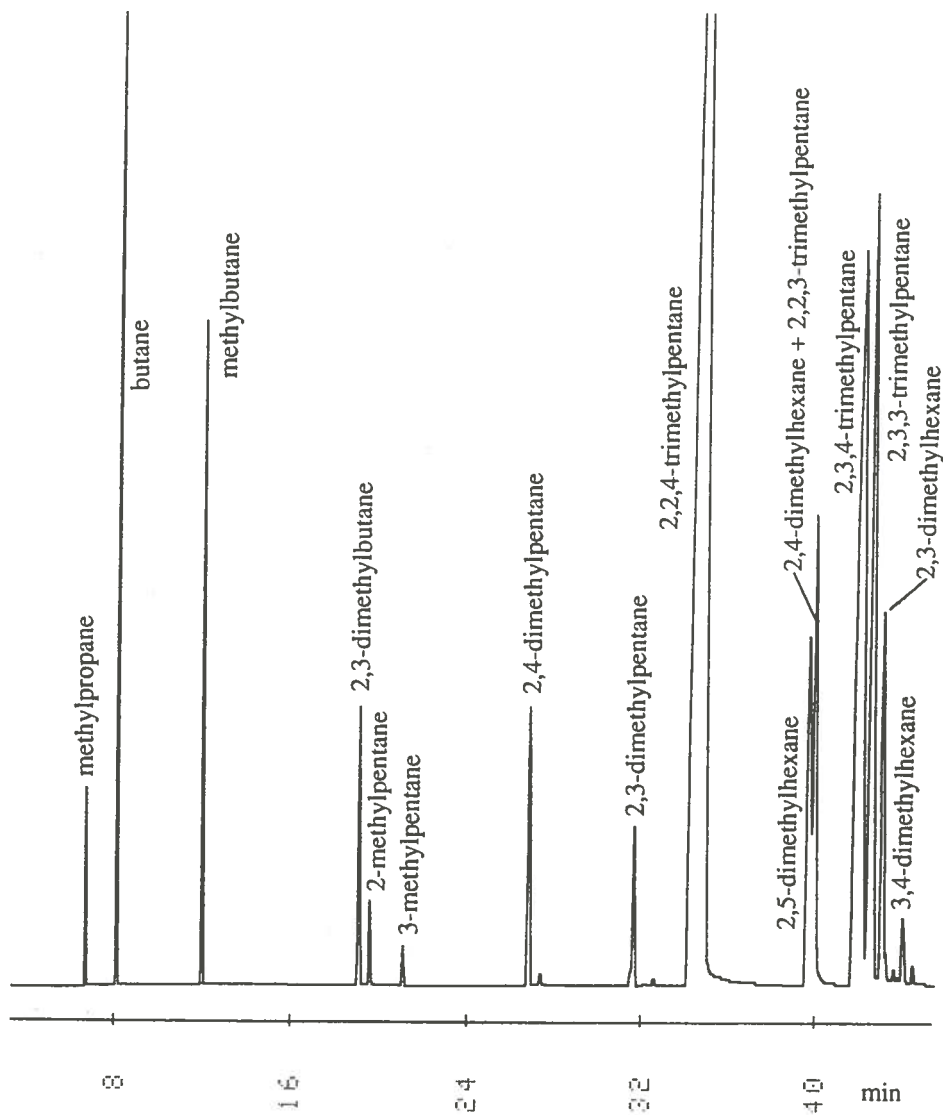


Figure 3. Gas chromatographic separation of  $C_4$ - $C_8$  hydrocarbons in alkylate petrol on a methylsilicone column (DB-1, 50 m x 0.32 mm i.d., 1  $\mu$ m phase layer, J&W). Split injection (1:35) at a column temperature of  $-10^\circ\text{C}$  and then  $+2^\circ\text{C}/\text{min}$ .

### 3. HAZARDS OF DIFFERENT HYDROCARBONS

Petrol consists of a mixture of a large number of hydrocarbons, and during combustion additional compounds are formed. Different hydrocarbons have different impacts on human health and the environment, and the hazards of specific hydrocarbons, or at least groups of hydrocarbons, must be considered. The main hydrocarbon groups in petrol are alkanes (paraffins and naphthenes), arenes (aromatic hydrocarbons) and alkenes (olefines). Beside alkanes, conventional petrol contains a high percentage of arenes and alkenes (Table 1). Alkylate petrol consists almost entirely of alkanes.

#### *3.1 Human health hazards*

Major acute health effects of high exposure to volatile hydrocarbons are effects on the central nervous system. From this aspect, arenes are regarded to be more hazardous than alkanes (Axelson and Hogstedt, 1994). However, as ambient air pollutants, volatile hydrocarbons have been paid most attention as cancer risks (Möller et al., 1994). Table 2 shows two different estimations of cancer risks for individual volatile hydrocarbons. For a discussion of different approaches and results, see Törnqvist and Ehrenberg (1994).

One of the arenes, benzene, is classified as a human carcinogen by the International Agency for Research on Cancer (IARC, 1987). Benzene is contained in petrol as well as formed due to incomplete combustion. The alkenes ethene, propene and 1,3-butadiene are combustion-formed, but not contained in petrol. They are of special toxicological interest due to metabolic formation of genotoxic epoxides (Victorin, 1993). 1,3-Butadiene has proved to be carcinogenic in animal tests. A part of inhaled ethene (~5%) is converted into ethylene oxide (Törnqvist, 1994), which is judged to be a probable human carcinogen (IARC, 1985).

**Table 1. Hydrocarbon composition (% vol) of European conventional petrol and alkylate petrol.**

	European conv. (average) <sup>a</sup>	Alkylate petrol <sup>b</sup>
<b>Alkanes</b>	<b>49</b>	<b>&gt;99</b>
<b>Arenes</b>	<b>40</b>	<b>&lt;0.5</b>
benzene	2.3	<0.05
<b>Alkenes</b>	<b>11</b>	<b>&lt;0.5</b>

<sup>a</sup>(Jarsin, 1996)

<sup>b</sup>(V; Hare and Carroll, 1993; Laveskog, 1995)

### *3.2 Environmental hazards*

Formation of ozone and other photooxidants is considered to be the most serious environmental threat of volatile hydrocarbon emissions (Finlayson-Pitts and Pitts, 1993<sup>a</sup>; Finlayson-Pitts and Pitts, 1993<sup>b</sup>). Photooxidants are secondary pollutants formed in sunlight-initiated reactions primarily involving nitrogen oxides (NO<sub>x</sub>) and volatile organic compounds (VOC= hydrocarbons, aldehydes, etc). In the spring and summer season, when the light-initiated formation is favoured and the highest levels occur, ozone contribute to forest decline and agricultural crop losses (Pleijel, 1993) as well as constituting health hazards (Lippman, 1991). All hydrocarbons contribute to the formation of photooxidants, but alkenes and alkylbenzenes generally form photooxidants more efficiently than alkanes (Altshuller, 1993; Atkinson, 1990; Hough and Derwent, 1987).

Concepts of quantifying specific ozone-forming potentials for different organic compounds have been reported (Andersson-Sköld et al., 1992; Carter and Atkinson, 1989; Derwent and Jenkin, 1991). One concept is used for legislation. The California Air Resources Board (CARB) has incorporated the concept of "maximum incremental reactivities" (MIR; developed by Carter) into their motor vehicle exhaust regulations (Lloyd et al., 1992). Incremental reactivity (IR) is defined as the change in ozone formation resulting from a small addition of an individual species to a polluted airshed, divided by the amount added. Incremental reactivities are dependent on a number of airshed conditions, especially the ratio of VOC to NO<sub>x</sub>. MIR is the peak value of IR, appearing at

**Table 2. Estimations of cancer risks (death) for ethene, propene, 1,3-butadiene and benzene.**

	Individual lifetime risk <sup>a</sup> × 10 <sup>5</sup>		Relative risk (ethene=100)	
	US EPA	Ehrenb. & Törnqv.	US EPA	Ehrenb. & Törnqv.
ethene	0.5 <sup>b</sup>	7	100	100
propene	–	1	–	15
1,3-butadiene	30	30	6000	430
benzene	0.8	4	160	60

<sup>a</sup>The risk factors are given as the risk of cancer death due to lifetime exposure at the concentration 1 µg/m<sup>3</sup> of the substance (Ehrenberg and Törnqvist, 1993; Törnqvist and Ehrenberg, 1994). In the latter reference, somewhat different values are given.

<sup>b</sup>The US Environmental Protection Agency has no risk factor for ethene. In (Ehrenberg and Törnqvist, 1993; Törnqvist and Ehrenberg, 1994) this risk factor was calculated as 5% of the EPA risk factor for ethylene oxide ( $1 \times 10^{-4}$ ).

the NO<sub>x</sub> level where the organic species has the maximum impact on the ozone level. A motive for using the maximum reactivity method is that it is under such atmospheric conditions that VOC control is the most effective strategy for reducing ozone formation (Lowi and Carter, 1990). The MIR-concept tends primarily to focus upon rapid ozone formation on a local scale. In Table 3 MIR-values for some hydrocarbons are given. Although there are uncertainties (Yang and Milford, 1996; Yang et al., 1995), the tendency is for alkenes and most arenes to be regarded as having considerably higher ozone forming potentials than alkanes. The difference is smaller in concepts focusing upon long-range transport (Andersson-Sköld et al., 1992; Derwent and Jenkin, 1991).

**Table 3. Maximum incremental reactivities (MIR) for selected hydrocarbons (Carter, 1994).**

Hydrocarbon species	MIR (g O <sub>3</sub> formed per g HC emitted)	Relative MIR-value (ethene=100)
<b>Alkenes</b>		
ethene	7.4	100
propene	9.4	130
methylpropene	5.3	72
<b>Arenes</b>		
benzene	0.42	6
methylbenzene	2.7	36
dimethylbenzenes	6.5-8.2	88-110
trimethylbenzenes	8.8-10.1	120-140
<b>Alkanes</b>		
propane	0.48	6
methylpropane	1.2	16
2,2,4-trimethylpentane	0.93	13

## 4. PETROL AND REFINERY-PROCESSES

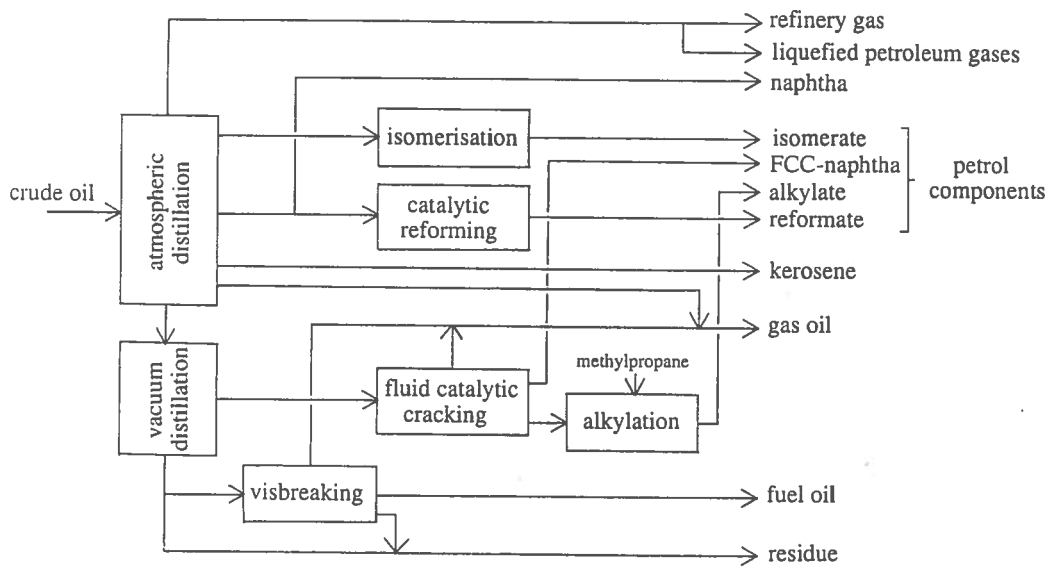
Worldwide, an enormous amount of petroleum oil is continuously recovered, in 1994 more than 10 million m<sup>3</sup>/day (Shell Briefing Service, 1995). About one third of the amount of oil is transformed into petrol in refineries. Figure 4 displays major processes used in a modern petroleum refinery. Depending on different properties of the petrol components produced in each process (Table 4), the components are mixed together to meet several technical, and in some cases, environmental specifications. In order to obtain a fuel functional in petrol-fuelled engines, volatility and octane numbers are important parameters. From an environmental point of view, hydrocarbon composition of the petrol is of vital interest (Lee, 1991; Sawyer, 1993).

### *4.1 Hydrocarbon composition of petrol*

Depending on the refinery processes used, the hydrocarbon composition of the petrol differs significantly. Table 5 shows the present production and composition of the four major petrol components in Europe (EC-countries). Alkylate and isomerate components consist almost entirely of alkanes. Reformate components contain high percentages of arenes, and cat-cracked naphtha contains high percentages of alkenes.

Since more than 50% of the petrol pool in Europe is reformate, European petrol contains on average a high proportion of arenes. So far, European discussions on environmentally related reformulation of petrol have involved arenes, but generally not alkenes (Dreschler, 1995). Due to a more common use of fluid catalytic cracking (FCC), US-petrol generally contains more alkenes and alkanes, and less arenes (Stump et al., 1992). Alkylate petrol is, off course, based on alkylate, usually with some butanes or isomerate added (5-10%), and therefore consists almost completely of alkanes (V; Hare and Carroll, 1993). It is worth noticing that isomerate generally has higher volatility and lower octane numbers than alkylate (Table 4). Isomerate is, however, a useful blending component both in alkylate petrol intended for small engines and in reformulated petrol for automobiles. In some varieties of alkylate-based petrol sold in Sweden (not studied in this thesis), ethanol (~15%) and C<sub>8</sub>-arenes (~5%) are added (Laveskog, 1995).





**Figure 4. Simplified<sup>1</sup> block flow diagram of a modern refinery (Gover and High, 1994; Frisch, 1996).**

#### 4.2 Cat-cracked naphtha and alkylate

A modern petroleum refinery is a complex chemical plant where product streams of many processes are directly or indirectly connected and therefore dependent on each other. In the case of alkylate, alkylation is directly linked to FCC (Figure 4). In the alkylation unit, alkenes in off-gas from the FCC-unit are combined with methylpropane. (Albright, 1990<sup>a</sup>; McPherson and Olive, 1984). The product consists of highly branched alkanes, mainly octanes, with high octane numbers (Table 4). Alkylation reactions are catalyzed by strong acids, hydrofluoric acid (HF) or sulphuric acid. Both acids constitute serious health risks for refinery

<sup>1</sup>In order to give an overall picture of the refinery, especially the placing of the FCC and alkylation units, a number of product streams, hydrotreating, hydrodesulphurization and sulphur recovery plants as well as optional units have been left out.

**Table 4. Examples of technical properties for major petrol components (Gover and High, 1994)<sup>a</sup>.**

Petrol component	RON <sup>b</sup>	MON <sup>c</sup>	RVP <sup>d</sup> (kPa)
Reformate	98-102	86-88	30
FCC-naphtha	90-92	81-82	70
Isomerate	90	89	75
Alkylate	96	94	40

<sup>a</sup>The figures are to be seen as typical values for a refinery run and designed to meet average modern product quality standards. As the running and design of a refinery is elaborated to fit product quality standards at its own market area, significant variations exist in the components produced and/or in the blending of semifinished products. (Frisch, 1996).

<sup>b</sup>Research octane number, measure of anti-knock performance under low speed conditions.

<sup>c</sup>Motor octane number, measure of anti-knock performance under high speed conditions.

<sup>d</sup>Reid vapour pressure, measure of volatility (must be high enough for cold starting, but low enough to avoid vapour locking under hot conditions).

personnel, but HF is considerably more hazardous. Efforts are being made to develop new, less hazardous alkylation technologies (Albright, 1990<sup>b</sup>). Promising pilot plant results from use of a fixed-bed catalyst have recently been reported (Oil and Gas Journal, 1996).

Today, there is no production of alkylate in Sweden. However, the present production of alkylate in Europe constitute about 5% (v/v) of the petrol pool (Table 5). In the US, cat-cracking is more frequently used and hence the production of alkylate is larger, more than 10% of the US petrol pool being alkylate (Albright, 1990<sup>a</sup>; Felten et al., 1994). In today's environmental trend towards petrol reformulation, alkylate is a desirable component, but unfortunately FCC-naphtha is not. There are, however, several options how to deal with the unwanted alkenes of the naphtha. Hydrotreatment, etherification, and alkylation also of C<sub>5</sub>-alkenes are discussed, and in some cases already in use (Birk, 1994; Ignatius et al., 1995; Oil and Gas Journal, 1995; Pescarollo et al., 1993). For further refinery processing, knowledge of alkene proportions of the FCC-naphtha is vital (Alemay and Brown, 1995; Pescarollo et al., 1993; Rajendra et al., 1992). A detailed characterization of a large number of specific C<sub>5</sub>-C<sub>7</sub> alkenes in conventional petrol and FCC-naphtha has been achieved (I, II).

**Table 5. Relative volumes, arene- and alkene content of major petrol components in Europe.**

Petrol component	Percentage of European petrol pool <sup>a,b</sup> (%vol)	Arenes <sup>a</sup> (%vol)	Alkenes <sup>c</sup> (%vol)
Reformate	56	50-75	1-5
FCC-naphtha	20	10-45	10-65
Isomerase	8	<0.5 <sup>d</sup>	<0.5 <sup>d</sup>
Alkylate	5	<0.5	<0.5

<sup>a</sup>(Dreschler, 1995)

<sup>b</sup>(Williamson, 1995)

<sup>c</sup>(Karlsson, 1996; Pescarollo et al., 1993)

<sup>d</sup>(Preem, 1996)

#### 4.3 Refinery hydrocarbon emissions

Refinery emissions often contribute considerably to local/regional air pollution (O'Shea and Scheff, 1988; Pandit and Rao, 1990; Wadden et al., 1986). Elevated ozone levels generated solely from refinery discharges have been reported (Sexton and Westberg, 1983<sup>a</sup>; Sexton and Westberg, 1983<sup>b</sup>). Typical sources of hydrocarbon emissions are fugitive equipment leaks, loading/transfer operations, wastewater treatment and storage tanks (Siegell, 1995). Hydrocarbon emissions downwind of petroleum refineries have been reported to predominantly consist of alkanes and the composition to be highly variable (Sexton and Westberg, 1979; Sexton and Westberg, 1983<sup>a</sup>; Doskey et al., 1992).

The proportions of fugitive emissions from the FCC-unit of a Swedish refinery were found to be relatively uniform (III). The C<sub>2</sub>-C<sub>8</sub> emissions consisted of approximately 15-20% alkenes, 5% or less arenes and about 80% alkanes. The alkene emissions were mainly propene, butenes and pentenes. C<sub>3</sub> and C<sub>4</sub> alkanes were the major components of the FCC-unit emissions. This contrasted with the emissions from the aggregated other processes of the refinery, where varying C<sub>2</sub>-C<sub>6</sub> alkanes were the most prominent. The capacity of the FCC-unit studied was about 15% of the total capacity of the refinery (10 million tonnes of crude oil per year).

## 5. VAPOUR AND EXHAUST EMISSIONS

Since alkylate petrol consists of the least hazardous hydrocarbons, both to human health and the environment, the use of alkylate appears to be advantageous compared with conventional petrol. However, the composition of petrol vapour and exhaust is not identical with the composition of petrol, and consequently emissions from alkylate petrol must be compared with emissions from conventional petrol.

### *5.1 Vapour hydrocarbons*

Petrol is a volatile liquid, and vapour emissions occur for instance due to refuelling and container/engine leaks. In table 6, the composition of hydrocarbons in vapour from refuelling is compared for different petrol varieties (IV). The proportions are governed by the volatility of the specific hydrocarbons and the composition of the fuel. As discussed in chapter four, the composition varies depending on the refinery processes used. It is seen that the proportions of the benzene, alkylbenzenes and alkenes are low for the alkylate fuel. Furthermore, due to a lower vapour pressure<sup>2</sup>, the total emission of petrol vapour during refuelling, and consequently also the amount of hydrocarbons inhaled, should be lower for alkylate compared with conventional petrol.

### *5.2 Exhaust hydrocarbons*

Exhaust hydrocarbons can be classified into two categories: unburnt fuel hydrocarbons and combustion-formed hydrocarbons (not contained in the fuel). A change of the petrol hydrocarbons results in an equal change of the unburnt-fuel part of the exhaust. The situation is more complex for the combustion-formed hydrocarbons.

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<sup>2</sup>According to Swedish standards: maximum 65 kPa (RVP) for alkylate petrol ("Motor fuels—Special gasoline for powered implements"; Swedish standards institution, 1995) maximum 80 kPa summer time and 95 kPa winter time for conventional petrol ("Environmental Class 3").

**Table 6. Hydrocarbon composition (%weight) of refuelling petrol vapour (IV).**

	Basic petrol character		
	Alkylate	Reformate	Cat-cracked
<b>Arenes</b>	<b>0.3</b>	<b>9.1</b>	<b>2.6</b>
benzene	0.1	3.2	0.8
alkylbenzenes	0.2	5.9	1.8
<b>Alkenes</b>	<b>0.5</b>	<b>1.3</b>	<b>16</b>
<b>Alkanes</b>	<b>99</b>	<b>89</b>	<b>81</b>

In Table 7, the hydrocarbon composition of fuel and exhaust is compared for alkylate petrol and a conventional reformate-based motor petrol (V). The exhaust samples refer to a moped during driving. About 90% of the tail-pipe hydrocarbon emissions from the two-stroke engine consist of unburnt fuel hydrocarbons. A similar proportion for a two-stroke utility engine has been reported (Hare et al., 1993). The composition of the exhaust hydrocarbons from two-stroke engines therefore resembles that of the fuel. Prominent combustion-formed hydrocarbons are the short-chain alkenes.

As illustrated in Table 7, alkylate petrol represents progress with respect to health hazards from petrol exhaust. Benzene is almost absent in the alkylate petrol. During combustion, benzene is also formed in smaller amounts than from conventional petrol. The proportion of alkylbenzenes is low in alkylate petrol. The comparison with a Swedish reformate-rich conventional petrol in Table 7 emphasizes the advantages of alkylate petrol regarding arenes. Compared with an average US petrol (containing less arenes and more alkanes and alkenes), a significant advantage is that 1,3-butadiene is formed in lower proportions (VI; Hare and Carroll, 1993).

Alkylbenzenes and alkenes contribute more efficiently than other hydrocarbons to elevated harmful photooxidant levels, especially in the local region near to the emissions. The low content of these hydrocarbons in alkylate petrol is therefore advantageous from an environmental point of view. Combustion-formed alkenes (mainly C<sub>2</sub>-C<sub>4</sub>) contribute to the photochemical reactivity of the exhaust hydrocarbons. Some of these alkenes are formed in

**Table 7. Non-methane hydrocarbon composition (%weight) of fuel and exhaust for a two-stroke engine (motorcycle, 49 cc) (V).**

	Alkylate		Conventional (reformate)	
	fuel	exhaust	fuel	exhaust
<b>Arenes</b>	<b>0.2</b>	<b>0.2</b>	<b>57</b>	<b>54</b>
benzene	0.01	0.1	4	5
alkylbenzenes	0.2	0.1	53	49
<b>Alkenes</b>	<b>0.2</b>	<b>9</b>	<b>5</b>	<b>8</b>
ethene	<0.01	2	<0.01	2
propene	<0.01	3	<0.01	1
1,3-butadiene	<0.01	0.1	<0.01	0.1
<b>Alkanes</b>	<b>99</b>	<b>88</b>	<b>36</b>	<b>33</b>

higher proportions from alkylate petrol than from conventional petrol (V; Hare et al., 1993). However, the total ozone-forming potential of alkylate exhaust from small engines has been reported to be lower (30-50% for two-stroke and 10-30% for four-stroke, using MIR-values) than that of exhaust from an average USpetrol (Hare and White, 1991; Hare and Carroll, 1993; Hare et al., 1993).

### *5.3 Combustion chemistry*

The effects of petrol composition on the composition of exhaust hydrocarbons have recently been studied both for small engines (V; Hare and White, 1991; Hare and Carroll, 1993) and automobiles (Leppard et al., 1992; Perry and Gee, 1994). Laboratory studies using test fuels in research engines have further established fundamental relationships between fuel composition and exhaust (Kaiser et al., 1991; Kaiser et al., 1992; Kaiser et al., 1993; Schuetzle et al., 1994; Kameoka et al., 1994).

A high content of arenes in the petrol has been observed to result in high benzene levels in the exhaust. Part of the benzene is unburnt fuel, but benzene is

also formed during combustion, probably due to dealkylation of alkylbenzenes (Kaiser et al., 1991; Kaiser et al., 1992).

Prominent combustion reactions of alkanes involve alkyl radical and  $\beta$ -scission reactions (Kaiser et al., 1991). A comparative study of 2,2,4-trimethylpentane and octane demonstrates the difference in combustion chemistry and combustion products between highly branched and unbranched alkanes (Dryer and Brezinsky, 1986). Straight-chain alkanes of conventional petrol prominently give rise to ethene as combustion product, whereas major constituents of alkylate petrol prominently give rise to various  $C_2$ - $C_5$  alkenes (V; Kaiser et al., 1991).

Petrol alkenes as well as naphthenes (mainly cyclohexanes) have been found to be important precursors of the combustion product 1,3-butadiene (Kaiser et al., 1992; Kaiser et al., 1993; Perry and Gee, 1994). Alkenes also contribute to the formation of ethene (Kaiser et al., 1993; Kameoka et al., 1994). As for alkanes, alkyl radical and  $\beta$ -scission reactions play important roles in determining the combustion products of alkenes, but cannot explain all hydrocarbons formed (Kaiser et al., 1993).

## 6. OPTIMAL USE OF ALKYLATE

Worldwide, almost all alkylate presently produced is mixed into petrol for automobiles. However, alkylate as fuel for small engines has shown remarkably improved exhausts in several emission studies (V, Hare and White, 1991; Hare and Carroll, 1993; Nilsson, 1988). Considering the fact that alkylate is desirable both as fuel for small engines and as a blending component in petrol for automobiles, it is important to decide which application should have the highest priority.

### *6.1 Hydrocarbon emissions from automobiles and small engines*

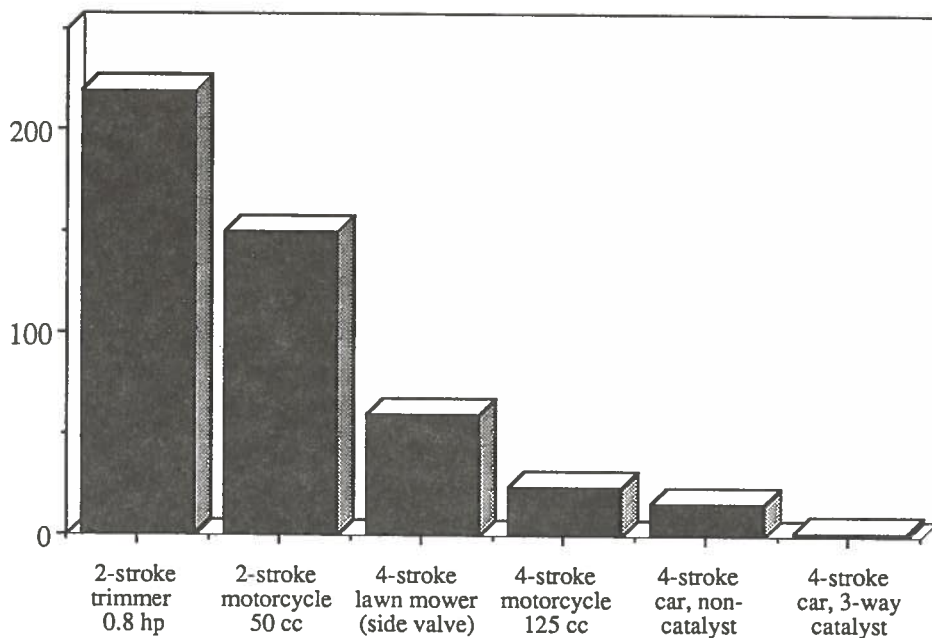
When use of alkylate in automobiles or small engines is discussed, the most obvious difference between the alternatives is the improvement of the hydrocarbon exhaust emissions (VI). In Figure 5, total hydrocarbon emissions (per litre of petrol consumed) from six different engines are compared. Total emissions are more than one order of magnitude larger for two-stroke engines than for automobiles. Emission levels from small four-stroke engines are intermediate.

Alkylate replacing conventional petrol do not decrease the total hydrocarbon emissions, but less hazardous hydrocarbons are emitted (VI). This accounts especially for the fraction of unburnt fuel in the exhaust. For two-stroke engines, about 90% of the hydrocarbon emissions are unburnt petrol, compared with 50-65% (engine-out and tail-pipe) for modern automobiles (Schuetzle et al., 1994). The remaining part is combustion-formed hydrocarbons, which are not equally improved as the petrol is improved (V; Hare et al., 1993; Schuetzle et al., 1994).

Because of the larger hydrocarbon emissions per litre of petrol consumed and the larger fraction of unburnt fuel in the exhaust, it is concluded that the presently produced alkylate should replace conventional petrol in small engines prior to automobiles (VI). The petrol consumption of small engines in Europe (except motorcycles) is estimated to be of the order of 1% (VI), and the production of alkylate is approximately 5% of the petrol pool (Dreschler, 1995; Williamson, 1995). A prompt introduction of alkylate petrol for small engines appears to be possible, at least from a production point of view.



HC (g/l fuel consumed)



**Figure 5. Total emissions of hydrocarbons from selected utility engines and transportation vehicles (Chan et al., 1995; White et al., 1991).**

### *6.2 Location and time of emissions*

Pollutants from small engines are often emitted near to people, which results in high exposure concentrations. For example, before switching to alkylate petrol, Swedish forest workers using conventional petrol for their chain saws were typically exposed to benzene concentrations in the range 300-1800  $\mu\text{g}/\text{m}^3$  (Nilsson et al., 1987). As a comparison, during urban/suburban commuting in Sweden, benzene levels of 30-70  $\mu\text{g}/\text{m}^3$  inside the car have been reported (Barrefors and Petersson, 1993; Löfgren et al., 1991<sup>b</sup>). Similar levels have been reported in US studies (Chan et al., 1991; Lawryk and Weisel, 1996; Wallace, 1989; Weisel et al., 1992). Furthermore, many small engines, such as garden tools and outboard engines, are mainly used during the critical spring and summer photooxidant season. When the location and time of emissions are considered, human health and environmental arguments for using alkylate for small engines are therefore strengthened.

### *6.3 Professional and private use*

Originally, alkylate petrol was introduced in Sweden in 1989 for professional forest workers using chain saws (Nilsson, 1988). Today, it has acquired a solid position within professional forestry. About 90% of the chain saws and most of the swirl cut saws are fuelled by alkylate petrol. Also for small engines used in parks, public places and cemeteries, the use of alkylate petrol is increasing rapidly. On the private market, alkylate petrol is most frequently used by farmers and private forest owners. Alkylate petrol accounts for more than half of their working machines. For garden equipment, the market share is smaller, and for outboard engines and scooters, an ethanol-blended alkylate-based petrol has recently been introduced.

In Sweden, the consumer price is today 1.5-3 times the cost of conventional petrol. For private use, the high price probably constitutes the bottle-neck for increased replacement of conventional petrol with alkylate petrol. In professional applications, the price is often less important. For an employer, the extra cost of more expensive petrol is normally small compared with the total cost for the employee, and there are also Swedish occupational health proclamations supporting the use of the least hazardous fuel.

## 7. THE FUTURE OF ALKYLATE FUELS

Telling the future is a difficult challenge. A variety of unpredictable factors may change the scenario. Nevertheless, in spite of uncertainties, a scenario of the future will hopefully stimulate interesting discussions. Therefore I conclude my thesis with a sketch of the future production and use of alkylate in Europe.

### *7.1 Alkylate for small engines*

In countries with high environmental awareness, the use of alkylate petrol in small engines should gradually replace conventional petrol within the next few years. The health and environmental benefits compared with conventional petrol are convincing and the present production of alkylate appears to be more than high enough to supply most small engines with fuel. As in Sweden, the change is likely to start with professional users of utility engines, primarily because they are heavily exposed and because the high price of the alkylate petrol is not as critical for them as for private users. On the private market, fiscal incentives must probably be used if alkylate petrol is going to replace conventional petrol in more fuel consuming applications such as outboard engines.

### *7.2 Alkylate for automobiles*

Also for automobiles, the use of alkylate as well as isomerate and other less hazardous petrol components is probably going to increase. These components are needed as blending components in petrol when environmentally related governmental demands are gradually issued. It is, however, difficult to state precisely how much of the more hazardous petrol components should optimally be replaced. The use of less hazardous petrol components decreases hazardous vapour and tail-pipe emissions, but unfortunately refinery emissions during the production tend to increase. Furthermore, petrol components made from petroleum oil inevitably cause a net carbon dioxide emission into the atmosphere.

A constructive future vision would be aiming at improving today's environmentally dubious petrol while simultaneously decreasing the consumption of petrol and other fossil fuels. This would contribute to rapidly decreased local/regional environmental problems, as well as to decreased threat

of global warming in the long run. Consequently, the environmental optimum would probably be for a reasonably large part of today's most hazardous petrol components to be replaced by increased production of alkylate and other less hazardous petrol components during the next decade, and for all fossil petrol components to be phased out during the next century.

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