An alternative fuel for spark ignition engines

A Hull^{1,4*}, I Golubkov², B Kronberg^{1,4}, T Marandzheva³, and J van Stam⁴

¹Institute for Surface Chemistry, Stockholm, Sweden

² Swedish Biofuels AB, Stockholm, Sweden

³ Tuchkov Most, Sankt-Peterburg, Russia

⁴ Department of Physical Chemistry, Karlstads University, Karlstad, Sweden

The manuscript was accepted after revision for publication on 5 September 2005.

DOI: 10.1243/14680874JER02504

Abstract: Alternative fuels have been developed for standard spark ignition engines. The fuels, which contain generic bio-components, maintain all the advantages of ethanol, i.e. the ability to increase considerably the octane number of gasoline and to reduce the amount of harmful pollutants in the exhaust emissions of engines operating on such blends. In contrast with ethanol the new fuel components do not increase the vapour pressure of gasoline–ethanol blends, have a better tolerance to water, and do not increase the fuel consumption. The bio-component-based fuels also compare favourably with mineral-sourced octane boosters such as methyl *tert*-butyl ether. Additionally reformulation of the base gasoline becomes unnecessary.

Keywords: alternative gasoline fuel, biogasoline, oxygenates, vapour pressure reduction, gasoline engine performance, gasoline engine emissions

1 INTRODUCTION

In 1997, representatives of 105 states signed the Kyoto Protocol [1], whose aim is to reduce the atmospheric emissions of excess carbon dioxide produced in the intensive burning of oil, coal, and fossil gas, and products of their combustion.

The combustion of motor fuels disturbs considerably the carbon dioxide balance in the atmosphere. Moreover, nitrogen and sulphur oxides produced as by-products of motor fuel combustion contribute to the acidification of lakes, which are the source of the water for the vital functions of animals and plants. Finally, solid particulates which are products primarily of the incomplete combustion of aromatic compounds cause cancer in humans and animals.

The use of components derived from renewable raw materials in motor fuel compositions [2], particularly oxygenates [3-8], can reduce the harmful impact of the fuel on the environment through cleaner air, lower net carbon dioxide emissions, the absence of carcinogens, and biodegradability. At the same time it should be noted that over the last few years the position of methyl *tert*-butyl ether (MTBE) as a component for gasolines has weakened considerably [**9**]. Some countries such as the USA and Denmark already prohibit the use of MTBE in gasoline.

In 2003, the European Commission proposed a directive [**10**] encouraging member states to use biocomponents extensively in motor fuels starting from 2005. The plan is to increase the content of biocomponents in all the motor fuel sold on the European market up to 5.75 per cent by 2010.

The existing inventory of vehicles and machinery with standard engines does not allow the use of a motor fuel consisting completely of bio-components within the time frame stipulated by the European Commission. Also the content of the harmful pollutants would have to reach a low level that would require heavy investments from engine manufacturers.

Thus, it is evident that, in the years to come, the role of mixed fuels produced partly from petroleum and partly from a renewable raw material will grow considerably. As examples of this type of fuel, gasoline–ethanol blends for spark ignition engines and diesel mixtures containing methyl ethers of higher fatty acids for use in diesel engines should be mentioned.

^{*}Corresponding author: Institute for Surface Chemistry, Box 5607, Stockholm, SE 114 86, Sweden. email: angelica.hull@ surfchem.kth.se

Many oil companies producing and selling gasoline believe that ethanol is the solution of the problem of alternative fuel for conventional spark ignition internal combustion engines [11]. In Europe there is discussion about allowing up to 10 vol% of ethanol in gasoline instead of 5 vol% permitted by the current EN228 standard. On the other hand, other companies propose that oxygenates should not be used at all [12, 13]. The strategy adopted here is to compromise between these two extremes. This reflects the opinion of those oil companies that are rather critical of the idea of solving the problem of alternative fuel for conventional spark ignition engines either completely without using oxygenates or by using solely ethanol–gasoline blends.

The addition of ethanol to gasoline has substantial advantages. First, the octane number of the gasoline–ethanol blend increases [14]. Second, the amount of harmful pollutants in the exhaust emissions is reduced [8, 15].

At the same time, using ethanol as a component for gasoline has considerable disadvantages. First, the vapour pressure of the gasoline–ethanol blend increases above the limits allowed for the safe handling and storage of gasoline. A higher vapour pressure of a flammable substance increases its potential as a fire and explosion hazard. The solution to the problem in practice requires the extraction of the light hydrocarbon fractions from the base gasoline [16]. Second, the tolerance of the gasoline–ethanol blends to water is reduced [13, 17]. Third, the addition of ethanol to gasoline increases fuel consumption principally because of the lower energy content of ethanol compared with gasoline.

It is known [18] that blending ethanol with gasoline increases the vapour pressure of the blend compared with the vapour pressure of the source gasoline and even more compared with the vapour pressure of ethanol. The results of our study demonstrate that the addition of ethanol increases the vapour pressure of a standard gasoline by more than 10 per cent. This is shown in Fig. 1.

The results in Fig. 1 show that, the lower the vapour pressure of the conventional gasoline, the greater the increase in the vapour pressure of the gasoline–ethanol blend induced by ethanol. This means that, when blending summer-grade gasoline with ethanol, a considerable part of the light fraction of hydrocarbons must be extracted to satisfy the requirements of the standard as regards the vapour pressure [16].

Investigations of the physical chemical properties of alcohol–hydrocarbon mixtures have been the subject of a large number of scientific studies [**19–28**].



Fig. 1 Vapour pressure curves at 37.8 °C with the maximum increases in vapour pressure as indicated for each fuel composition. A92, A95, and A98 refer to 92 octane, 95 octane, and 98 octane automobile gasoline respectively

The main focus has been the vapour liquid equilibria of mixtures of ethanol and various hydrocarbons [29-39]. These investigations have only a limited amount of information about the vapour pressure of relatively dilute mixtures of ethanol and hydrocarbons, i.e. less than 0.1 mol fraction of ethanol. The research reported here shows that there is a substantial increase in the vapour pressure of ethanol hydrocarbon mixtures even at low concentrations of ethanol as well as at low concentrations of hydrocarbon in ethanol. Figures 2 to 4 show the dependence of the vapour pressure of ethanol-containing mixtures on the ethanol mole fraction for a series of hydrocarbons with similar molecular weights but different structures. An analysis of the data shows that the vapour pressure of ethanol and linear hydrocarbon mixtures increases the most at low concentrations of ethanol. The research continues.

There are different methods for adjusting the vapour pressure of gasoline–ethanol blends [**40–45**]. However, none of the known methods solves the problem of the vapour pressure of gasoline–ethanol blends containing less than 20 vol % ethanol. For example, one of the older European patents disclosing a fuel containing lower alcohols [**46**] proposed adjusting the vapour pressure by adding C₄ to C₇



Fig. 2 Vapour pressure curve of ethanol octane blends at 35 °C for various concentrations of ethanol



Fig. 3 Vapour pressure curve of ethanol isooctane blends at 35 °C for various concentrations of ethanol

hydrocarbons. However, these particular patented fuels contain too much water and more than 20 vol % of ethanol, which makes their use in modern engines impossible. Wilson [47] proposed weathering* light hydrocarbons from gasolines having an increased vapour pressure. However, using this method to adjust the vapour pressure of gasoline–ethanol blends means that the first weathered component will be ethanol. Zudkevitch *et al.* [48] proposed adding MTBE or ethyl *tert*-butyl ether (ETBE) to gasoline–ethanol blends. The vapour pressure of these fuels is lower than the vapour pressure of the corresponding gasoline–ethanol blends, but this method fails to reduce the vapour pressure to the level of the source gasoline. It also does not comply with the requirements of the standard concerning the overall oxygen content.

2 KEY RESULTS

After several years of intensive research the present authors have invented a method for adjusting the vapour pressure of gasoline–ethanol blends [**49**] avoiding all the problems mentioned in the introduction. In particular, it allows the formulation of alternative fuels using standard gasolines as the base, the starting point. This is in direct contrast with the

^{*}The term weathering refers to the exposure of the fuel to the atmosphere causing the evaporation of precisely those substances with the higher vapour pressures.



Fig. 4 Vapour pressure curve of ethanol *o*-xylene blends at 35 °C for various concentrations of ethanol

current practice of making gasoline–ethanol blends from reformulated gasoline, which is gasoline with the light hydrocarbon fractions removed.

The alternative fuel compositions which have been developed contain, apart from 0.1-20.0 vol %ethanol, other oxygen-containing compounds and certain hydrocarbons. Specifically included are higher alcohols, ethers, esters, ketones, hydroxyketones, ketoesters, and heterocyclic compounds in the proportion of 0.05-15.0 vol %, and C_6 to C_{12} hydrocarbons. The latter family is made up of isooctane, isononane, isodecane, and unsaturated compounds, including cyclic and aromatics. C_6 to C_{12} hydrocarbons can be used either individually or in fractional mixtures boiling within the range 100-200 °C.

The dramatic vapour-pressure-lowering effects of the invention are shown in Fig. 5. The various blends, produced according to the invention, are referred to as biological gasoline booster (BGB). This name reflects the properties of the new gasoline components, which are as follows.

- 1. They may be produced from raw material of a biological origin.
- 2. They are designed for use in gasoline compositions.
- 3. They increase the octane number of the base gasoline.

Starting from the same base gasolines as shown in Fig. 1, all formulations exhibit vapour pressures lower than the base gasoline at all concentrations of the blends.

The compositions of the additives for the gasoline– ethanol blends of Fig. 5 are presented in Table 1.

Adjusting the vapour pressure of gasoline-ethanol



Fig. 5 Vapour pressure curves at 37.8 °C showing vapour pressure reductions of gasoline–ethanol mixtures with BGB additives. See caption of Fig. 1 for explanations of the terminology

Components of the additives	Additive 1 content (vol%)	Additive 2 content (vol %)	Additive 3 content (vol %)	Additive 4 content (vol %)	Additive 5 content (vol %)
Ethanol <i>Tert-</i> pentanol	40.0	33.3 33.3	35.0	35.0	40.0
Isopentanol			5.0	1.0	
Naphtha, 100–170 °C			60.0	43.8	
Isobutanol				0.2	
Isopropyltoluene				20.0	
Methyl benzoate	30.0				
3,3,5-trimethylcyclohexanone					20.0
Naphtha, 130–170 °C	30.0	33.4			20.0
<i>Tert</i> -butyltoluene					20.0

Table 1 Components of the additives for gasoline-ethanol blends shown in Fig. 5

blends by adding oxygen-containing compounds and C_6 to C_{12} hydrocarbons allows the use of almost any non-reformulated gasoline as a source gasoline for the blend, as shown in Fig. 5. In addition, gasoline–ethanol blends consisting of oxygen-containing compounds and C_6 to C_{12} hydrocarbons have low vapour pressure and an oxygen content that does not harm the performance of a standard engine.

Table 2 shows experimental data demonstrating the performance properties of gasoline–ethanol blends formulated according to the invention for vapour pressure adjustment.

The compositions of the blends 2001–2008 are as follows.

- 1. Blend 2001 consists of commercial 96 Shell gasoline containing 2.75 vol % MTBE.
- 2. Blend 2002 consists of 83.3 vol % 96 Shell + 10.0 vol % ethanol + 6.7 vol % MTBE.
- 3. Blend 2003 consists of 92.4 vol % 96 Shell + 5 vol % ethanol + 2.6 vol % MTBE.
- 4. Blend 2004 consists of 89.0 vol % 96 Shell + 5 vol % ethanol + 3.5 vol % isobutyl acetate + 2.5 vol % MTBE.
- 5. Blend 2005 consists of 78.8 vol % 96 Shell + 7.5 vol % A80 + 8.0 vol % ethanol + 3.5 vol % isoamyl acetate + 2.2 vol % MTBE.

- 6. Blend 2006 consists of 73.0 vol % 96 Shell + 9.0 vol % naphtha, 100–130 °C + 10.0 vol % alkylate + 5 vol % ethanol + 1.0 vol % diisoamyl ether + 2.0 vol % MTBE.
- 7. Blend 2007 consists of 78.8 vol % 96 Shell + 9.0 vol % naphtha, 100–130 °C + 4.0 vol % alkylate + 5.0 vol % ethanol + 1.0 vol % isoamyl alcohol + 2.2 vol % MTBE.
- 8. Blend 2008 consists of 73.0 vol % 96 Shell + 9.0 vol % naphtha, 100–130 °C + 10.0 vol % alkylate + 5 vol % ethanol + 1.0 vol % tetrahydrofurfuryl alcohol + 2.0 vol % MTBE.

The gasoline compositions were prepared using the volume method and were tested for compliance with the standard requirements under ASTM methods [**50**] at the SGS Sweden AB laboratory.

Testing of the gasolines was carried out at AVL MTC AB in Sweden under the standard method [**51**] on Volvo 245 model 1987, over 63 000 km without any modifications to the engine. The standard method referred to concerns the emission tests. All the tests were performed under conditions as constant as possible. The test cycle used was the EU2000 test cycle. The test was performed according to the normal cold-start procedure (22 °C). The day before the first test, the vehicle was conditioned on the first

Table 2Performance properties of gasoline–ethanol blends consisting of oxygen-containing compounds and C_6 to
 C_{12} hydrocarbons

Blend composition	Dry vapour pressure equivalent (kPa)	O ₂ (% w/w)	Motor octane number	Research octane number	CO (g/km)	Hydrocarbons (g/km)	NO _x (g/km)	CO ₂ (g/km)	Fuel consumption (10 ⁻² km)
2001	87.4	0.5	85.5	96.9	2.39	0.30	0.27	227.0	9.724
2002	93.0	4.7	86.6	98.0	1.89	0.27	0.31	226.7	10.067
2003	93.9	2.1	86.0	97.0	2.03	0.28	0.30	229.5	9.985
2004	92.3	3.2	85.4	97.8	2.18	0.27	0.31	230.8	10.085
2005	91.0	4.0	85.7	97.6	1.68	0.26	0.31	227.8	10.039
2006	89.9	2.2	86.2	97.3	2.07	0.27	0.29	229.5	10.096
2007	90.1	2.3	85.7	96.2	1.88	0.27	0.29	228.7	10.035
2008	89.3	2.1	84.6	97.3	1.80	0.25	0.32	230.4	10.001

test fuel at 90 km/h for 10 min and then with a full EU 2000 test and soaked overnight. The analysis was performed as three-bag analyses with several welldefined cycles. The exhaust gases were separately analysed for regulated emissions of carbon monoxide, carbon dioxide, unburnt hydrocarbons, and nitrogen oxides. Every day, two tests were run on every fuel and the vehicle was force soaked to 22 °C for $4\frac{1}{2}$ h after the morning test. After the second test on a specific fuel, the engine was briefly halted, the fuel inlet was connected to the next test fuel, the return line was connected to the waste, and the engine was started and run for about 2 min to flush the fuel system. The engine was again stopped and the return line was connected to the test fuel tank. The vehicle was then run at 90 km/h for 10 min and then with a full EU 2000 test. It was then soaked overnight at 22 °C before the first test on the next day.

The results demonstrate that adding ethanol to gasoline together with other oxygen-containing compounds and C_6 to C_{12} hydrocarbons not only keeps the vapour pressure of such a gasoline within the requirements of the standard but also increases the octane number and reduces the content of harmful pollutants in the exhaust emissions.

Comparative tests [**52**] of gasoline blends consisting of known octane-boosting additives and gasoline–ethanol compositions prepared using the invention for adjusting the vapour pressure demonstrated that the known octane boosters perform considerably better when used in combination.

Compositions of the blends 1–14 are as follows.

- 1. Blend 1 consists of 100 vol% of the commercial Haltermann gasoline.
- 2. Blend 2 consists of 96.8 vol % Haltermann gasoline + 3.2 vol % ethanol.

- 3. Blend 3 consists of 95.0 vol% Haltermann gasoline + 5.0 vol% ethanol.
- 4. Blend 4 consists of 88.0 vol % Haltermann gasoline + 12.0 vol % ETBE.
- 5. Blend 5 consists of 90.0 vol% Haltermann gasoline + 10.0 vol% isooctane.
- 6. Blend 6 consists of 78.0 vol % Haltermann gasoline + 12.0 vol % ETBE + 10.0 vol % isooctane.
- 7. Blend 7 consists of 84.8 vol % Haltermann gasoline + 3.2 vol % ethanol + 12.0 vol % ETBE.
- 8. Blend 8 consists of 83.0 vol % Haltermann gasoline + 5.0 vol % ethanol + 12.0 vol % ETBE.
- 9. Blend 9 consists of 86.8 vol % Haltermann gasoline + 3.2 vol % ethanol + 10.0 vol % isooctane.
- 10. Blend 10 consists of 85.0 vol % Haltermann gasoline + 5.0 vol % ethanol + 10.0 vol % isooctane.
- 11. Blend 11 consists of 74.8 vol % Haltermann gasoline + 3.2 vol % ethanol + 12.0 vol % ETBE + 10.0 vol % isooctane.
- 12. Blend 12 consists of 73.0 vol % Haltermann gasoline + 5.0 vol % ethanol + 12.0 vol % ETBE + 10.0 vol % isooctane.
- 13. Blend 13 consists of 76.8 vol % Haltermann gasoline + 3.2 vol % ethanol + 10.0 vol % ETBE + 10.0 vol % isooctane.
- 14. Blend 14 consists of 75.0 vol % Haltermann gasoline + 5.0 vol % ethanol + 10.0 vol % ETBE + 10.0 vol % isooctane.

The data in Table 3 convincingly demonstrate the advantages of the oxygen-containing gasolines prepared using the invention. The component obtained by combining ethanol with appropriate oxygen-containing compounds [**49**] and C_6 to C_{12} hydro-

Blend composition	Dry vapour pressure equivalent (kPa)	O ₂ (% w/w)	Motor octane number	Research octane number	CO (g/km)	Hydrocarbons (g/km)	NO _x (g/km)	CO ₂ (g/km)	Fuel consumption (10 ⁻² km)
1	58.3	0.0	85.6	97.0	7.67	1.01	2.63	239.5	10.62
2	65.0	1.114	86.0	98.0	7.33	1.0	2.7	247.2	10.91
3	65.6	1.74	86.4	98.5	7.36	0.94	2.68	247.6	10.91
4	55.7	1.884	87.1	97.9	7.84	0.99	2.64	245.1	10.88
5	56.4	0.0	87.1	97.4	7.80	0.97	2.56	241.2	10.78
6	58.3	1.884	87.5	98.3	7.60	0.97	2.67	244.8	10.93
7	61.6	2.998	87.3	98.9	7.34	0.96	2.64	248.0	10.95
8	61.8	3.624	87.6	99.1	7.25	0.97	2.50	240.2	10.61
9	61.1	1.114	87.0	98.3	7.69	1.0	2.54	240.8	10.74
10	61.3	1.74	87.3	98.8	7.39	0.98	2.54	240.9	10.71
11	57.1	2.998	88.3	99.3	7.29	0.97	2.52	241.6	10.76
12	57.4	3.624	88.4	99.3	7.03	0.94	2.46	238.9	10.61
13	57.6	2.684	88.1	98.8	7.16	0.96	2.58	239.8	10.66
14	57.8	3.31	88.2	98.9	7.25	0.94	2.56	239.1	10.62

 Table 3
 Results of comparative tests of gasolines containing various octane-boosting additives

carbons can be blended with any commercial gasoline. A remarkable aspect of the oxygencontaining gasoline components according to the invention is that all its constituents can be produced from renewable raw materials. Thus there is a real possibility of introducing to the fuel market an alternative oxygen-containing gasoline containing not more than 25 vol% of bio-component and suitable for use in conventional spark ignition engines.

In the following the properties of alternative fuels consisting of BGB are shown to satisfy the requirements concerning conventional gasolines [53]. As a preview of the results obtained, the biological component BGB increases the octane number of the petrochemical base gasoline by 3–4 units (see section 2.2). It reduces the vapour pressure of the petrochemical base gasoline by 3 kPa (see section 2.3). It does not affect the fuel consumption (see section 2.4) and there are considerable improvements in the exhaust emissions (see sections 2.5 to 2.8).

The results shown below relate to two commercial gasolines: Shell A92 and Preem reformulated gasoline (RFG) A92. The alternative gasoline consisted of 14.5 vol % BGB and 85.5 vol % base gasoline Shell A92. The other blends tested consisted of 85.9 vol % base gasoline Shell A92 and 14.1 vol % MTBE and also 95 vol % base gasoline Shell A92 and 5 vol % ethanol. Preem RFG A92 and an ethanol blend consisting of 90 vol % base gasoline Preem RFG A92 and 10 vol % ethanol were also tested.

2.1 Oxygen content

The oxygen content of the base gasolines was 0 wt % (Fig. 6). As mentioned previously, the base gasolines used for the tests are commercial grades of gasoline; that is why it was important to verify that there is no oxygen. The oxygen content in the alternative gasoline prepared using a standard gasoline and BGB is

somewhat higher than that of the gasoline–ethanol blend containing 5 vol % of ethanol and less than that of the blends containing MTBE. The blend of RFG and 10 vol % ethanol cannot be used in Europe because of its high oxygen content (3.5 wt %) but can be used in some of the states of the USA.

2.2 Octane number

The octane number of the alternative gasoline comprising BGB is 95.6, i.e. 3.8 higher than the octane number of the non-reformulated base gasoline A92, which was 91.8 (Fig. 7). In this case the composition of the alternative gasoline was chosen to obtain a gasoline with an octane number of at least 95.

The octane number of the alternative gasoline containing BGB is higher than the octane number of the gasoline consisting of MTBE and gasoline–ethanol blends. The increase in the octane number of the base gasoline, A92, caused by BGB is (95.6-91.8)/91.8 = 4.1. Also the difference between the octane numbers of the alternative fuel containing BGB and gasoline–ethanol blends should be noted.

2.3 Vapour pressure

The alternative gasoline containing BGB affects dramatically the degree of the vapour pressure reduction. The results shown in Fig. 8 relate to the summer-grade gasoline. The effect of the presence of ethanol in gasoline–ethanol blends, namely a considerable increase in the vapour pressure in comparison with that of the base gasoline, is shown in Fig. 8. For example in these tests the increase is 100(76.5-69.5)/69.5 = 10 per cent. However, the alternative gasoline containing BGB shows a reduction in the vapour pressure in comparison with that of the base gasoline by 100(69.5-66.5)/69.5 = 4.9 per cent. Comparing the two alternatives,





Fig. 8 Vapour pressure of the gasolines tested

A92 + ethanol and A92 + BGB, shows a net reduction due to the BGB components of 100(76.5-66.5)/76.5 = 13 per cent. In this case, it may mean that the base gasoline contains additional light hydrocarbons, which could provide additional economic benefit.

2.4 Fuel consumption

The fuel consumption of the gasoline blends containing oxygen-containing compounds is in general higher than that of the base gasolines (Fig. 9). The reason for this is the lower energy content of MTBE and ethanol. However, alternative gasoline containing BGB demonstrates excellent fuel consumption, better than that of the base gasoline itself.

2.5 Carbon monoxide emissions

The carbon monoxide emissions of the alternative gasoline containing BGB are even better than that of the base gasoline, being 25 per cent lower (Fig. 10). This is better than for the blend of gasoline and 5 vol% of ethanol and for the blend of gasoline and MTBE. For the blend of RFG base gasoline and 10 vol% ethanol this property is marginally, by 4 per

cent, better than that of the alternative fuel containing BGB, but this can be explained by a lower carbon monoxide emission of the RFG base gasoline compared with the carbon monoxide emissions of nonreformulated base gasoline. In fact the reduction in carbon monoxide emissions for the blend of RFG and 10 vol % of ethanol is 21 per cent, which is somewhat lower than the reduction for the blend of BGB and non-reformulated gasoline.

2.6 Nitrogen oxide emissions

The alternative gasoline containing BGB shows a considerable reduction in nitrogen oxides (NO_x) emissions (Fig. 11).

The reductions in NO_x emissions for the alternative gasoline containing BGB are as follows:

- (a) 16 per cent compared with the non-reformulated base gasoline;
- (b) 10 per cent compared with the blend of nonreformulated base gasoline and 5 vol % ethanol;
- (c) 7 per cent compared to the blend of non-reformulated base gasoline and MTBE.

In cases where reformulated gasoline is used as the base gasoline for preparing alternative gasoline the





Fig. 10 Carbon monoxide content in the exhaust emissions of the gasolines tested





same level of NO_x reduction can be expected. It should be noted that gasoline–ethanol blends do not produce similar reducing effects on NO_x emissions.

2.7 Emissions of non-combusted hydrocarbons

The alternative gasoline containing BGB reduces also the emissions of unburnt hydrocarbons (Fig. 12). The reductions in unburnt hydrocarbons emissions for the alternative gasoline containing BGB are as follows:

- (a) 8 per cent compared with the non-reformulated base gasoline;
- (b) 11 per cent compared with the blend of nonreformulated gasoline and 5 vol % ethanol;



Fig. 12 Unburnt hydrocarbon content in the exhaust emissions of gasolines tested

(c) 4 per cent compared with the blend of non-reformulated gasoline and MTBE.

The blend of reformulated base gasoline and 10 vol% of ethanol also shows a reduction in hydrocarbon emissions by 8 per cent compared with the reformulated gasoline. However, as already mentioned the gasoline blends containing 10 vol% of ethanol have limited application and are not allowed for use in Europe.

2.8 Emissions of non-methane hydrocarbons

Evaluation of the emissions of non-methane hydrocarbons shows that the alternative gasoline consisting of non-reformulated gasoline and BGB performs better than non-reformulated gasoline containing 5 vol % ethanol or MTBE (Fig. 13).

Various biologically sourced products can be used for the production of BGB components. Amongst these are terpen hydrocarbons, which are a byproduct of woodpulp production, biogas, which is obtained during the recycling of organic waste, and also the waste products from ethanol production. A new method has been developed for producing highmolecular-weight oxygen-containing hydrocarbon compounds and high-molecular-weight hydrocarbons based on the fermentation of carbohydrates [**54**]. It has the advantage of using 1.5 times less carbohydrate for the production of the same amount of fuel components and can use existing ethanol production facilities.

3 CONCLUSIONS

The results of the research show that the generic biocomponent BGB maintains all the advantages of ethanol, i.e. the ability to increase considerably the octane number of gasoline and to reduce the amount of harmful pollutants in the exhaust emissions of engines operating on such blends. In contrast with ethanol it does not increase the vapour pressure of gasoline–ethanol blends, has a better tolerance to water, and does not increase the fuel consumption.



Fig. 13 Content of non-methane hydrocarbons in the exhaust emissions of the gasolines tested

ACKNOWLEDGEMENTS

The authors appreciate the assistance of AVL MTC AB and SGS Sweden AB for extensive tests carried out during this work. The authors are grateful for financial support from Swedish Biofuels AB for the conduction of parts of this work.

REFERENCES

- 1 *Kyoto protocol to the United Nations framework convention on climate change*, 1997 (United Nations, New York).
- **2** Hull, A. and Marandzheva, T. Prospective diesel fuel from renewable raw material. In *New fuels with additives*, Proceedings of the Second Conference on Fuel Additives, St Petersburg, Russia, 2002, pp. 250– 259.
- **3 Wrage, K. E.** and **Goering, C. E.** Technical feasibility of diesohol. Transactions of the ASAE, 1980, 1338–1343.
- 4 Unzelman, G. H. Value of oxygenates in motor fuels. *Proc. Am. Petrol. Inst., Refining Dep.*, 1981, **60**, 107–124.
- Johnson, R. T. and Stoffer, J. O. Performance of stabilized diesel fuels containing alcohols and water in single and multicylinder direct injection engines. SAE Special Publication S.P. 542, 1983, pp. 91–104 (Society of Automotive Engineers, New York).
- **6 Mathur, H. B., Babu, M. K. G.,** and **Reddy, B. P.** Effect of methanol supplementation on exhaust emissions from swirl chamber diesel engine. *J. Thermal Engng*, 1988, **2**(3), 63–72.
- **7 Haschimoto, K.,** *et al. J. Jap. Petrol. Inst.*, 1996, **39**(2), 166–169.
- 8 Gouli, S., Lois, E., and Stournas, S. Effects of some oxygenated substitutes on gasoline properties, spark ignition engine performance, and emissions. *Energy fuels*, 1998, **12**, 818–924.
- **9** California Environmental Protection Agency, http: //www.calepa.ca.gov/programs/MTBE/ EOTasks.htm, 2001.
- 10 Directive of the European Commission Proposal for a Directive of the European Parliament and of the Council on the promotion of the use of biofuels for transport, Brussels, 7 November 2001, Nr COM (2001) 547 final. http://europa.eu.int/eur-lex/en/ com/pdf/2001/en_501PC0547_01.pdf
- 11 Lugar, R. G. and Woolsey, R. J. The new petroleum. *J. Foreign Affairs*, January–February 1999.
- 12 Perander, J., Rantanen, L., Pentikäinen, J., Aakko, P., and Jäntti, A. No major backsling in air quality when replacing MTBE with Isooctane in CARB gasoline. SAE technical paper 2001-01-3588.
- **13 Hodge, C.** Ethanol use in US gasoline should be banned, not expanded. *Oil gas J.*, 9 September 2002.
- 14 Cox, F. W. The physical properties of gasoline– alcohol automotive fuels. In Proceedings of the Third International Symposium on *Alcohol fuels*

technology, University of Santa Clara, Asilomar, California, USA, 29–31 May 1979, pp. 1–14.

- **15 Rajan, S.** Water–ethanol–gasoline blends physical properties, power, and pollution characteristics. *J. Engng Gas Turbines Power*, **106**(4), 841–848.
- 16 Berger, J. E. Ethanols as fuel: options, advantages, and disadvantages. *Encyclopedia of chemical processing and design*, Vol. 20, pp. 1–11 (Dekker, New York).
- 17 Palz, W., Chartier, P., and Hall, D. O. Energy from biomass. In Proceedings of the International Conference on Biomass, Brighton, 4–7 November 1980, pp. 928–933 (Applied Science Publishers Ltd, London).
- 18 Kirk-Othmer *Encyclopedia of chemical technology*, 3rd edition, Vol. 11, p. 653 (John Wiley, New York).
- 19 Goral, M., Oracz, P., and Warycha, S. Vapour–liquid equilibria. XIV. The ternary system cyclohexane– methanol–hexane at 293.15 K. *Fluid Phase Equilibria*, 2000, 169, 85.
- **20** Alekseeva, M. V. and Moiseenko, M. F. Experimental investigation and calculations of liquid–vapour equilibria in the system *n*-propanol–*n*-decanol–hexane. *Khim. Termodinamika Rastvorov (Leningrad)*, 1982, **5**, 179–196.
- 21 Zielkiewicz, J. (Vapor+liquid) equilibria in (propane-1-ol+n-hexane+n-heptane) at the temperature 313.15 K. *J. Chem. Thermodynamics*, 1991, 23, 605–612.
- 22 Zielkiewicz, J. (Vapor+liquid) equilibria in (propane-1-ol+heptane+octane) at the temperature 313.15 K. *J. Chem. Thermodynamics*, 1992, 24, 455–462.
- **23** Zielkiewicz, J. (Vapor+liquid) equilibria in (heptane+propan-2-ol or 2-methyl propan-2-ol or pentan-1-ol) at the temperature 313.15 K. *J. Chem. Thermodynamics*, 1994, **26**, 919–923.
- 24 Berro, C. and Peneloux, A. Excess Gibbs energies and excess volumes of 1-butanol-n-heptane and 2-methyl-1-propanol-n-heptane binary systems. *J. Chem. Engng Data*, 1984, **29**, 206–210.
- **25 Kogan, V. V., Fridman, V. M.,** and **Romanova, T. G.** Phase equilibria in systems formed by paraffin hydrocarbons and aliphatic alcohols. *Zh. Fiz. Khim.*, 1959, **33**, 1521–1525.
- **26 Machova, I., Linek, J.,** and **Wichterle, I.** Vapor– liquid equilibria in the heptane-1-pentanol and heptane 3-methyl-1-buthanol systems at 75, 85 and 95 °C. *Fluid Phase Equilibria*, 1988, **4**, 257–267.
- 27 Bernatova, S., Linek, J., and Wichterle, I. Vapor– liquid equilibria in the butyl alcohol-n-decane systems at 85, 100 and 115 °C. *Fluid Phase Equilibria*, 1992, **74**, 127–132.
- 28 Rhodes, J. M., Bhethanabotla, V. R., and Campbell,
 S.W. Total vapor pressure measurements for heptane + 1-pentanol, + 2-pentanol, + 3-pentanol,
 + 2-methyl-1-butanol, + 2-methyl-2-butanol,
 + 3-methyl-1-butanol, and + 3-methyl-2-butanol at 313.15 K. J. Chem. Engng Data, 1997, 42, 731–734.
- 29 Dahlhoff, G., Pfennig, A., Hammer, H., and VanOorschot, M. Vapor–liquid equilibria in quat-

ernary mixtures of dimethyl ether + n-butane+ ethanol+water. *J. Chem. Engng Data*, 2000, **45**, 887–892.

- **30 Ishii, N.** The volatility of fuels containing ethyl alcohol. V. Total and partial vapor pressures of mixtures of ethyl alcohol with methylcyclohexan. *J. Soc. Chem. Industry Japan*, 1935, **38**, 659–661.
- **31 Reimers, J. L., Bhethanabotla, V. R.,** and **Campbell, S. W.** Total pressure measurements for pentane+ methanol+ethanol at 303.15 K. *J. Chem. Engng Data*, 1992, **37**, 127–130.
- **32 Kudryavtseva, L. S.** and **Susarev, M. P.** Vapour– liquid equilibrium of the system acetone-hexane and ethyl-hexane alcohol at 35, 45, 55 °C and 760 mm Hg. *Zh. Prikl. Khim. (Leningrad)*, 1963, **36**, 1471–1477.
- **33 Wolff, H.** and **Goetz, R.** The association of various deuterium ethanols in n-hexane (using vapour pressure measurements). *Z. Phys. Chem. (Frank-furt)*, 1976, **100**, 25–36.
- 34 Janaszewski, B., Oracz, P., Goral, M., and Warycha, S. Vapour–liquid equilibria. I. An apparatus for isothermal total vapor pressure measurements: binary mixtures of ethanol and t-butanol with n-hexane, n-heptane and n-octane at 313.15 K. *Fluid Phase Equilibria*, 1982, 9, 295–310.
- **35** Zhang, L.-Z., Chen, G.-H., Cao, Z.-H., and Han, S.-J. New double circulation apparatus for vle determination: establishment and applications in the determination of isobars, isotherms, and isopleths. *Thermochim. Acta*, 1990, **169**, 247–261.
- **36 Van Ness, H. C., Soczek, C. A.,** and **Kochar, N. K.** Thermodynamic excess properties for ethanol-nheptane. *J. Chem. Engng Data*, 1967, **12**, 346–351.
- **37 Ronc, M.** and **Ratcliff, G. A.** *Can. J. Chem. Engng*, 1976, **54**, 326.
- **38 Berro, C., Rogalski, M.,** and **Peneloux, A.** A new ebulliometric technique. Vapour–liquid equilibria in the binary systems ethanol-n-heptane and ethanol-n-nonane. *Fluid Phase Equilibria*, 1982, **8**, 55–73.
- **39 Boublikova, L.** and **Lu, B. C.-Y.** Isothermal vapor– liquid equilibrias for the ethanol n-octane system. *J. Appl. Chem.*, 1969, **19**, 89–92.
- **40 Robertson, A. E.** Motor fuels. US Pat. 2365009, 44/53, 1944.
- **41 Muller, H.** and **Keim, K. H.** Motor fuels. US Pat. 4801305, C10L, 1989.
- **42 Talbert, W. L.** Hydrocarbon fuel systems. US Pat. 5015356, C10L, 1991.
- **43 Paul, S. F.** Alternative fuel. US Pat. 5697987, C10L, 1997.

- 44 Lopez, A. F., Orio, A., Herroro, E. R., Perez, C. F., and Anunziata, O. A. Stabilizers for hydrated ethanol–gasoline mixtures. *Lat. Am. Appl. Res. (English)*, 1990, **20**(3–4), 183–187.
- 45 Erwin, J. Vapor pressure interactions of ethanol with butane and pentan in gasoline. *Am. Chem. Soc., Div. Fuel Chemistry*, 1994, **39**, 310–315.
- 46 Mueller, H. and Keim, K. H. Motor fuels based on lower alcohols. Pat. Bundesrepublik Deutschland Offenlegungsschrift DE 3422506 A1, C10L, 1984.
- **47 Wilson, E. J. A.** Liquid fuels for internal combustion engines and process and apparatus for making same. US Pat. 5208402, C10L, 1993.
- **48 Zudkevitch, D., Murthy, A. K. S.,** and **Gmehling, J.** Thermodynamics of reformulated automotive fuels. *Hydrocarbon Processing*, 1995, **74**(6), 93–99.
- **49 Hull, A.** and **Golubkov, I.** European Patent No. 1 252 268 B1. Method of reducing the vapour pressure of ethanol-containing motor fuels for spark ignition combustion engines. Priority data 2000.01.24, publication of application Bulletin 2002/44, publication and mention of the grant of the patent Bulletin 2005/21.
- **50 Laveskog, A.** ASTM *Methods for testing gasoline,* CASTM, Pennsylvania.
- **51 Laveskog, A.** Testing of ethanol-containing gasolines. Report on Research and Development Work for Svenska Technoferm AB, MTC AB, Sweden, 2000.
- 52 Laveskog, A. Testing of ethanol-containing gasolines. Report on Research and Development Work for Svenska Technoferm AB, MTC AB, Sweden, 2003.
- **53** Gasoline Standard, Svensk Standard SS-EN228, Motorbränslen-Oblyad bensin. *Krav och provningsmetoder*, 31 March 2001 (Swedish Institute for Standards, Stockholm).
- **54 Golubkov, I.** Method for producing oxygencontaining compounds from biomass. Sverige Pat. No. 526 429, Reg. date 13 September 2005.

APPENDIX

Notation

A92	92 octane	automobile	gasoline
-----	-----------	------------	----------

- A95 95 octane automobile gasoline
- A98 98 octane automobile gasoline
- BGB biological gasoline booster
- ETBE ethyl *tert*-butyl ether
- MTBE methyl *tert*-butyl ether
- THFA tetrahydrofurfuryl alcohol