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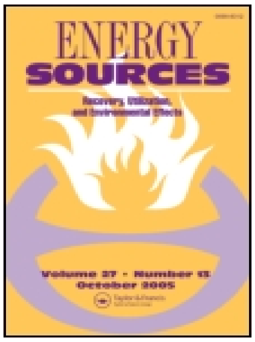

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Low-Temperature Miscibility of Ethanol-Gasoline-Water Blends in Flex Fuel Applications

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Abstract *The miscibility of blends of gasoline and hydrous ethanol was investigated experimentally at −25°C and −2°C. Furthermore, the maximum water content was found for ethanol in flex fuel blends. The results strongly indicate that blends containing ethanol with a water content above that of the ethanol/water azeotrope (4.4% water by mass) can be used as Flex Fuel blends together with gasoline at ambient temperatures of −25°C and −2°C, without phase separation occurring. Additionally, it was shown that the ethanol purity requirement of ethanol-rich flex fuel blends falls with increasing ethanol content in the gasoline-rich flex fuel blend.*

Keywords bioethanol, biofuel, ethanol, flex fuel, flex fuel vehicle, gasohol, gasoline, hydrous ethanol, miscibility, phase separation, ternary phase diagram

1. Introduction

For biofuels to increase their share of the market for transportation fuels, both fuel reliability and production cost are crucial parameters. In both of these regards, the water content of the fuel ethanol has a large significance.

In the northern hemisphere, the ethanol used as a vehicle fuel is generally anhydrous (less than 1% water by mass) in order to guard against the phase separation, which can arise in ethanol/gasoline/water blends at low temperatures. Comparatively, using hydrous ethanol (even with only 5% water) could give significant savings in the production process (Martinez-Frias et al., 2007), both regarding cost and in terms of energy use. However, the successful use of hydrous ethanol depends on the feasibility of avoiding phase separation in the vehicle fuel tank.

Consequently, it seems prudent to identify the exact purity requirements of hydrous ethanol in blends with gasoline. It is not surprising that research has been conducted on this topic previously (Bolt, 1964; Rawat and Khanna, 1979; Rajan, 1984; Letcher et al., 1986; Barton and Tjandra, 1989; Stephenson, 1992; Castro et al., 1994),[1] but due to several recent developments in fuel formulation and use, old miscibility data need to be updated.

One of the reasons is the considerable changes in gasoline specifications over the past decades (primarily, but not only, in the industrialized world). Additives are being phased

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[1] More recently, some miscibility tests of ethanol-gasoline-water have been reported, but only for low-level ethanol blends (<15%) (Peng et al., 1996; French and Malone, 2005; Gramajo de Doz. et al., 2004).

out as others are adopted, and recently the content of aromatics has been lowered in many countries. The impact of such changes on water tolerances has not been addressed in the scientific literature so far.

Second, in the flex fuel vehicle (FFV) concept currently gaining momentum, the question of miscibility becomes somewhat more complicated: it is obviously of no use having half a tank of a stable, ethanol-rich fuel blend if the act of filling up with the vehicle's other specified flex fuel (for example pure gasoline) will cause phase separation in the fuel tank.

In order to identify the purity requirements of ethanol used in an FFV context, a full mapping of the phase separation curves at the relevant temperatures is necessary—data which previous miscibility studies have not provided for the low temperatures encountered in temperate climates, winter temperature of −25°C being common in many countries in the northern hemisphere.

Using new experimental data, this article examines the purity requirements of ethanol in blends with gasoline, incorporating the complexities arising from the use in a flex fuel concept. The temperature range of the miscibility experiments extends as low as −25°C, thereby also providing the miscibility data which is relevant for many areas in the temperate climate zone.

2. Materials and Methods

The phase separation curves were determined at −2°C and −25°C. The experiments were conducted with the following equipment and chemical species:

- Anhydrous ethanol (99.9% water-free), delivered by Kemetyl corporation
- Distilled water
- Gasoline, 95 RON, winter-grade, delivered by Shell Denmark (content of aromatics: 32% maximum; content of olefins: 18% maximum[2]).

As shown in Table 1 below, for each of the two experiment temperatures, ten gasoline/anhydrous ethanol mixtures were prepared with the following compositions:

Table 1
Experimental blends

Sample number	Gasoline content, ml	Ethanol content, ml
1	1.0	9.0
2	2.0	8.0
3	3.0	7.0
4	4.0	6.0
5	5.0	5.0
6	6.0	4.0
7	7.0	3.0
8	8.0	2.0
9	9.0	1.0
10	9.5	0.5

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[2] http://www.shell.com/home/page/dk-da/produkt_og_sikkerhedsdatablade/app_products_0310_1510.html

After preparing the ethanol/gasoline blends, the test tubes were sealed with rubber bungs and placed in a refrigerating bath circulator, until their temperature had reached the specified experiment temperature.

A volume of distilled water was then added, followed by a vigorous shaking of the fuel sample, in order to ensure complete mixing of the fuel components with the water. After a ten-minute waiting period, allowing thermal and phase equilibrium to be reached, the fuel samples were checked for phase separation, signified initially by the blend becoming hazy (the "cloud point"), followed by a gradual formation of two separate liquid layers: a lower ethanol/water layer and an upper gasoline/ethanol layer. If phase separation had not occurred, the process was then repeated until phase separation was reached.

For each of the ten blends, at each of the two temperatures, an initial pilot test was conducted using large incremental additions of water (100 μl) in order to find the approximate phase separation point. In the proper experimental run, these separation points were then approached by smaller increments of water (10–50 μl), in order to increase the accuracy of the data.

In all cases, the point of phase separation was clearly visible, with the phase-separated blend becoming immediately hazy after being shaken, signifying the cloud point.

In all the cases where phase separation had occurred after the period of ten minutes, the fuel sample had already immediately upon shaking become hazy. In other words, the fuel samples seemed to either phase separate immediately or not at all.

3. Results and Discussion

Figure 1 shows the experimental phase separation curves, plotted in a ternary phase diagram. From Figure 1 it can be seen that the miscible zone is somewhat smaller at −25°C (the upper curve) than at −2°C, though not overwhelmingly so.

As shown in Figure 2, the same experimental data can be depicted as the purity requirement of the ethanol as a function of gasoline content in the blend. Figure 2 demonstrates how the ethanol purity demand increases with the gasoline content of the blend, while decreasing with the temperature.[3]

Also, it can be clearly seen that hydrous ethanol with a water content higher than the azeotrope concentration *is* miscible with gasoline down to −25°C, with the possible exception of mixtures with a very high (>95%) gasoline content.

In comparison with the miscibility studies which have been conducted in the past, the present experiments generally found lower ethanol purity limits, as can be seen in Figure 3 (blends with an overall gasoline content of 20%) and Figure 4 (blends with an overall gasoline content of 80%).

It can be seen from Figures 3 and 4 how the oldest studies tend to show a lower ethanol-gasoline-water miscibility, a tendency which might be linked to the higher aromatics content of late-century gasoline (aromatics having been shown to have a higher water tolerance than other gasoline components (Stephenson, 1992)). Still, this theory might be inadequate in explaining the high miscibility found in the present experiments, seeing that the aromatics content of gasoline in the European Union has recently been *lowered* from 42 to 35% maximum.

Overall, there are certain sources of inaccuracy which must be addressed for the experimental results. First, each single blend was not tested again beyond the initial

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[3] The experimental data can be found in Appendix II: Experimental Data.

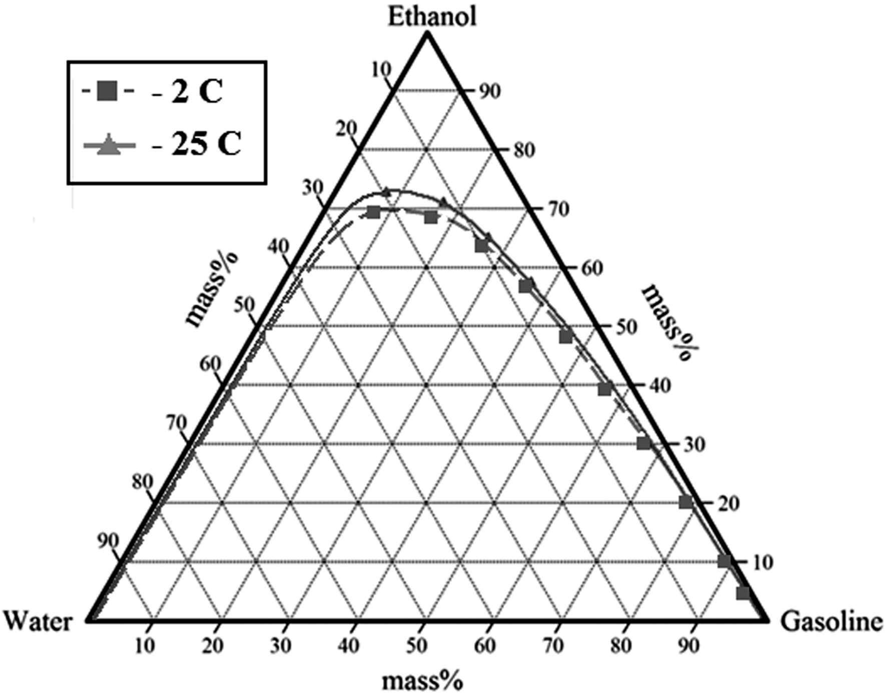

Figure 1. Phase separation curves of ethanol/gasoline/water at −2°C and −25°C.

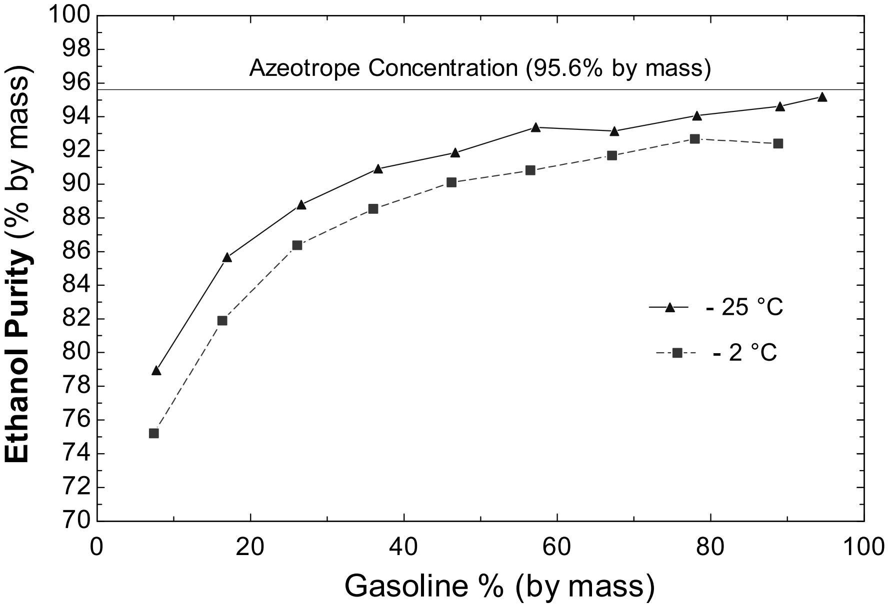

Figure 2. Purity requirement of hydrous ethanol in blends with gasoline.

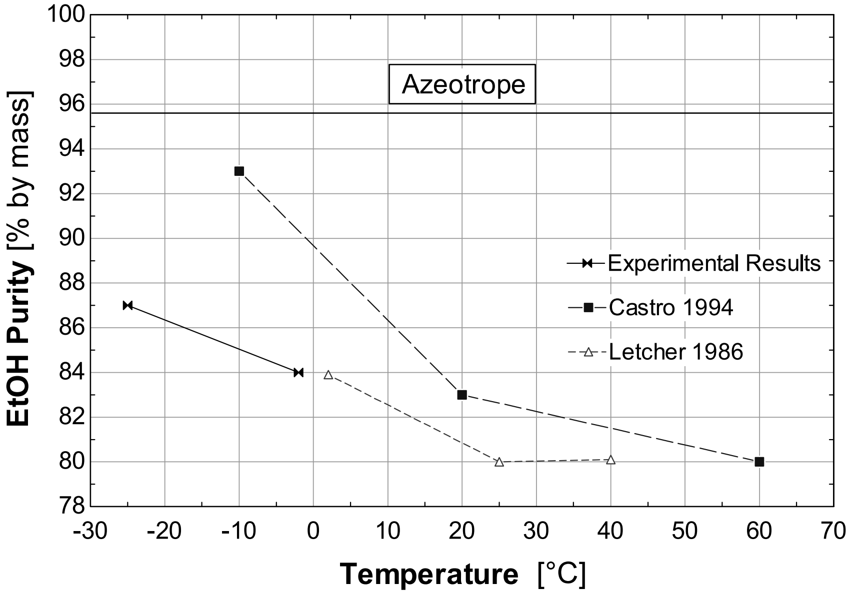

Figure 3. Comparison of experimental results with prior miscibility studies. Data for blends with an overall gasoline content of 20% by mass.

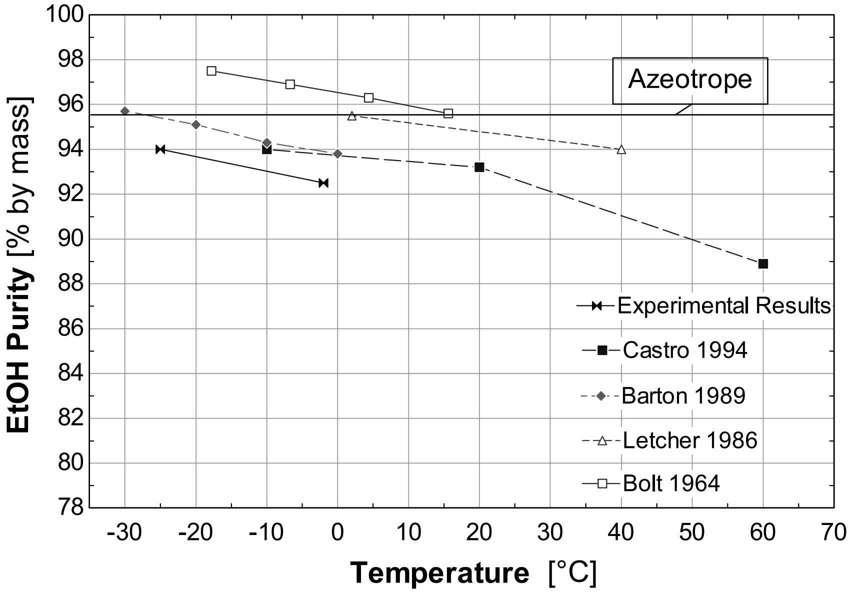

Figure 4. Comparison of experimental results with prior miscibility studies. Data for blends with an overall gasoline content of 80% by mass.

pilot experiment and subsequent “main” experiment. It is clear that a larger number of replicating experiments would give a higher accuracy of the data. Second, experimental uncertainties made it much harder to judge the exact water tolerances of the blends with a very high gasoline content (>95%). Still, the data at hand give a clear indication that ethanol below the azeotropic concentration is miscible with gasoline as low as −25°C, at least at a global gasoline content below 95% by mass in the blend.

Recently, it has been claimed that certain ethanol/gasoline/water blends exhibit *meta*-stability, referring to a phase separated, turbid blend, but without separate liquid layers (in effect, an emulsion) (Keuken et al., 2008). In the present experiments, it was only in a single test sample (a 95/5 gasoline/ethanol blend tested at −25°C) that the haziness of phase separation had not resulted in the formation of separate liquid layers after the ten minute waiting period. It was not examined whether separate liquid layers formed eventually in this blend (beyond the ten minute period), but this seems likely to happen, due to the differences in density of hydrous ethanol and gasoline.

In conclusion, the present experimental data does not indicate that a meta-stability area exists, which is anywhere as large as has been claimed.

4. Flex Fuel Miscibility

The water tolerance issue is complicated somewhat when ethanol/gasoline/water blends are used in FFVs; it is obvious that all mixtures of the flex fuels specified for an FFV must lie within the miscible zone if phase separation is to be avoided.

As opposed to Brazilian FFVs, hydrous ethanol is not used in northern hemisphere FFVs. The current “northern” flex fuels (primarily used in Sweden and parts of the USA) are anhydrous E85 and pure gasoline, thus effectively avoiding the question of ethanol/gasoline/water miscibility.

If hydrous ethanol fuel blends are to be used in northern hemisphere FFVs, knowledge of the phase separation curves in the ternary phase diagram (Figure 1) is needed to find compatible pairs of possible flex fuels.

In the ternary diagram, all the possible blends resulting from mixing two flex fuels can be found along a straight line connecting the coordinates of the two fuel blends. Consequently, if this line is above the relevant phase separation curve, no phase separation will occur in any conceivable mixture of the two fuels.

This concept has been illustrated in Figure 5, showing the connecting line between two purely hypothetical flex fuels—point B designating a 60/40 gasoline/ethanol blend and point A an 80/20 ethanol/water blend. It is clear from the diagram that all mixtures of these two blends would theoretically be free from phase separation.

In order to evaluate in a more formal way, the ethanol purity requirement of ethanol-rich flex fuels, a simple algorithm has been devised which, based on the experimental miscibility data, calculates the required ethanol purity for flex fuel blends (see Appendix I for algorithm details).

As illustrated in Figure 6, the results from using the algorithm show that the required ethanol purity of the ethanol-rich flex fuel not only depends on the temperature, but also very significantly on the amount of anhydrous ethanol in the gasoline-rich flex fuel blend. Figure 6 clearly shows that the ethanol purity requirement decreases with an increasing content of anhydrous ethanol in the gasoline flex fuel blend.

This phenomenon underpins the Brazilian flex fuel concept, in which gasohol (gasoline containing 20% anhydrous ethanol) is used as an FFV blend together with hydrous

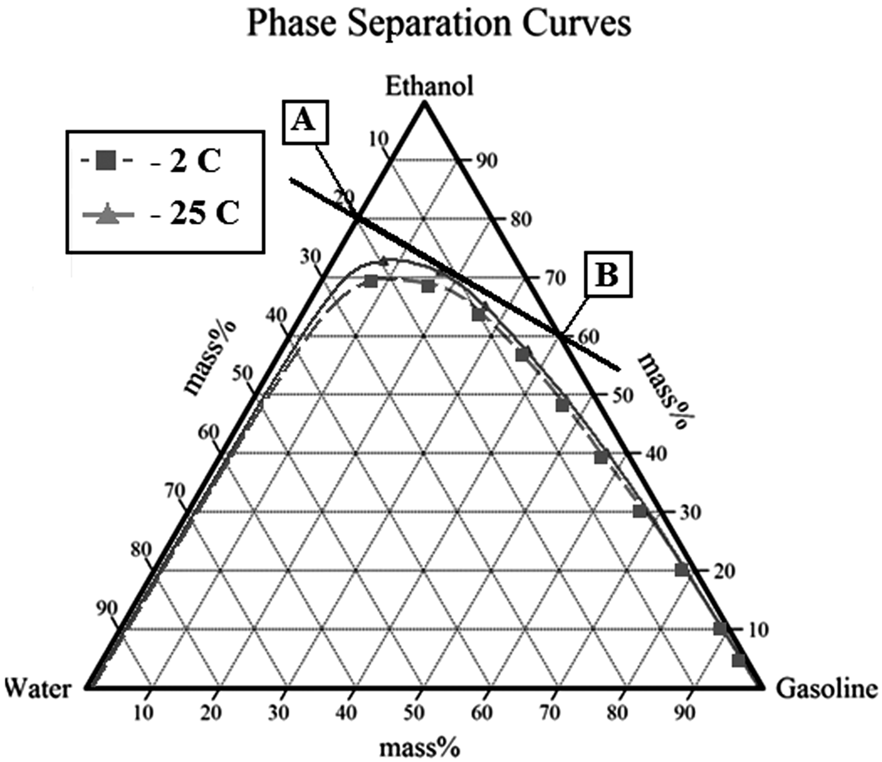

Figure 5. Illustration of flex fuel compatibility.

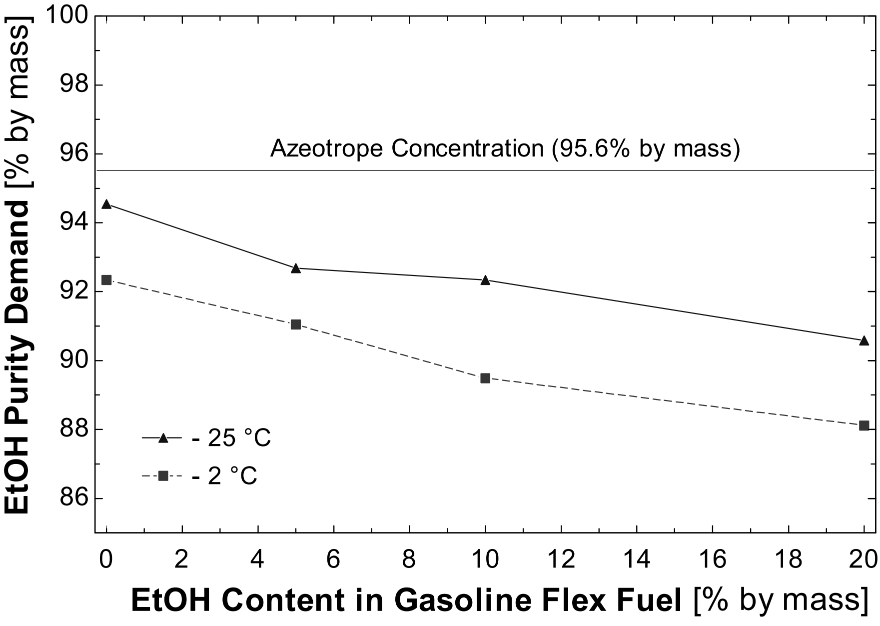

Figure 6. Ethanol purity requirement in ethanol-rich FFV blend.

ethanol containing 7% water. If pure gasoline had been used as the gasoline-rich flex fuel instead of gasohol, there would have been a much larger risk of phase separation at the lowest temperatures encountered in Brazil.

Most significantly, Figure 6 indicates that pure gasoline and E80 with azeotropic ethanol/water *would* be compatible as flex fuels, even in temperate climates. However, using E10 (10% anhydrous ethanol in gasoline) as the gasoline-rich FFV blend (instead of pure gasoline) would clearly leave a larger margin for any additional water contamination of the ternary fuel blend, either from atmospheric absorption or other sources. Though less hygroscopic than anhydrous ethanol, azeotropic ethanol/water will still be susceptible to water absorption.

Currently, E10 blends are being offered in an increasing number of filling stations, and in the near future it is likely that E10 will be widespread enough for it to be an acceptable choice as the gasoline-rich blend for FFVs, thus obviating the present requirement in Sweden and the USA that FFVs must be compatible with pure gasoline.

Overall, the experimental results seem to contradict the conventional wisdom concerning ethanol/gasoline miscibility (see for example, Jeuland et al., 2004), and it indicates that a range of hydrous ethanol blends *are* acceptable for blending with present-day gasoline, even as low as −25°C, and in any conceivable mixture which might occur in the fuel tank of an FFV.

In the practical application of hydrous FFV blends, several factors could change the miscibility characteristics, however. Deposits and residue from the fuel system could contaminate the fuel blend, possibly changing its miscibility characteristics, and ethanol's hygroscopic nature could lead to additional water absorption in cases where the fuel surface is open to the atmosphere.

Consequently, the experimental results at hand should serve as a reference point for specifying relevant ethanol/gasoline/water fuel blends for full engine tests, in order to explore the practical feasibility of FFV blends with ethanol purities at or below the azeotropic level.

5. Conclusion

The miscibility of gasoline and hydrous ethanol has been investigated experimentally, mapping the phase separation curves at −2°C and −25°C.

The obtained results showed that the ethanol/water azeotrope (95.6% ethanol by mass) is miscible with present-day Euro95 gasoline, up to a gasoline concentration of at least 95% in the blend, and as low as −25°C. At gasoline concentrations of less than 95% in the ternary blend, hydrous ethanol with a higher water content than the ethanol/water azeotrope can be used.

Furthermore, the minimum ethanol purity was found for ethanol flex fuels, which must be miscible with a specified gasoline-rich flex fuel.

It was found that an ethanol fuel blend *can* use ethanol with a purity in the 94–95% purity range and still be acceptable as a flex fuel together with pure gasoline, even as low as −25°C, and in any conceivable mixture which could occur in the fuel tank of a flex fuel vehicle, without phase separation occurring. Furthermore, it was demonstrated that the higher the ethanol content of the gasoline-rich flex fuel blend, the less restrictive the purity demand of the ethanol-rich flex fuel blend will be.

In conclusion, the present experimental results give a great incentive for further research into the practical feasibility of fuel blends of gasoline and hydrous ethanol.

Acknowledgments

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Appendix I: Algorithm for Calculation of Ethanol Purity Requirement

The algorithm calculates the ethanol purity requirement of ethanol-rich FFV blends when coupled with different gasoline-rich flex fuel blends (FFB)—based on experimental data and the geometrical relationships of ternary phase diagrams, as shown in Figure 7. (The immiscible zone is shown much smaller than it really is for the blend—the proportions have been chosen mainly to illustrate the algorithm for calculating flex fuel water tolerances.)

In the figure, point E is a water-free gasoline-rich fuel blend, which may or may not contain ethanol—if that is not the case, point E will coincide with H, the gasoline corner.

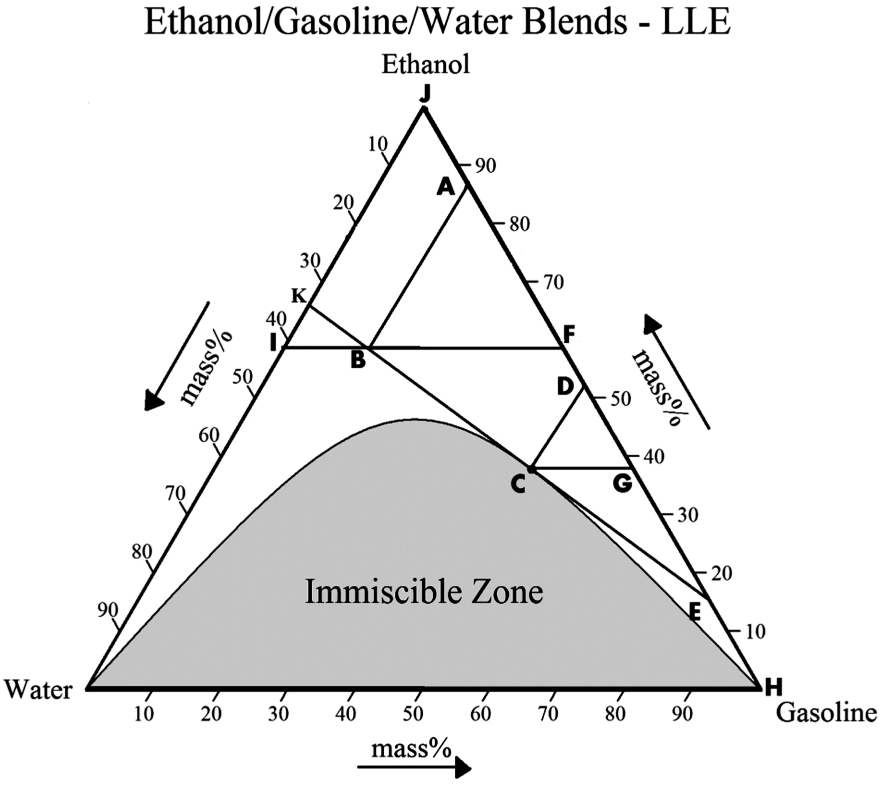

Figure 7. Illustration of flex fuel miscibility algorithm.

Point C is an experimental data point on the phase separation curve, chosen such that a line through E and C will be an approximate tangent to the phase separation curve. B is an ethanol-rich flex fuel which is just acceptable for mixing in any proportions with the blend at point E—the tie line between the two is tangent to the phase curve but does not cross it.

At the start of the calculation, the ethanol content of the gasoline-rich flex fuel blend (FFBG) is chosen (marked by point E), whereupon the data point C on the experimental phase curve is chosen in such a way that the line EC is tangent to the phase separation curve. Using the points E and C along with the choice for the gasoline content of the ethanol-rich flex fuel blend (FFBE), the water content at point B can be calculated by using the geometrical relations of the ternary diagram.

Initially, the following values are known:

|CD| (Water content at C, the phase separation data point)
|GH| (Ethanol content at C, the phase separation data point)

The following values are the independent variables, which are decided initially:

|EH| (Ethanol content at E, the gasoline-rich FFV blend)
|IB| (Gasoline content of the ethanol-rich FFV blend)

Lastly, the following lengths need to be found, in order to know the composition of the acceptable ethanol-rich FFV blends:

|AB| (Water content of ethanol-rich FFB)
|FH| (Ethanol content of ethanol-rich FFB)

Because the triangles CDE and ABE are similar in a geometrical sense, the following relationship holds:

$$\frac{|AB|}{|AE|} = \frac{|CD|}{|DE|}$$

Because AB is parallel to IJ, and because IJF and ABF are equal-sided:

$$|IB| = |JA|$$

The following additional relations can then be deduced from the geometry and equations above:

$$|DE| = |GH| + |CD| - |EH|$$

$$|AH| = 100 - |IB|$$

$$|AE| = |AH| - |EH|$$

$$\Rightarrow |AE| = 100 - |IB| - |EH|$$

$$\Rightarrow$$

$$|AB| = \frac{(100 - |IB| - |EH|) \cdot |CD|}{|GH| + |CD| - |EH|}$$

$$\Leftrightarrow$$

$$H2O\%_{FFBE} = \frac{(100 - Gasoline\%_{FFBE} - EtOH\%_{FFBG}) \cdot H2O\%_{PSP}}{EtOH\%_{PSP} + H2O\%_{PSP} - EtOH\%_{FFBG}}^{5}$$

And because the content percentages EtOH%, H2O%, and Gasoline% add up to 100:

$$|FH| = 100 - |IB| - |AB|$$

$$\Leftrightarrow$$

$$EtOH\%_{FFBE} = 100 - Gasoline\%_{FFBE} - H2O\%_{FFBE}$$

In this way, the required values EtOH%$_{\mathrm{FFBE}}$ and H2O%$_{\mathrm{FFBE}}$ have been found from the known data points.

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[5] Meaning of subscripts: FFBE is mass percentage relates to the ethanol-rich FFB; FFBG is mass percentage relates to the gasoline-rich FFB; PSP is mass percentage relates to the blend at the phase separation point.

Appendix II: Experimental Data

Table II-1
Phase separation points at −2°C

EtOH%, % by mass	Gasoline%, % by mass	Water%, % by mass	Ethanol purity, % by mass
69.65	7.34	23.01	75.16
68.55	16.25	15.20	81.85
63.90	25.96	10.14	86.30
56.75	35.86	7.40	88.47
48.58	46.05	5.38	90.03
39.62	56.34	4.40	90.75
30.27	66.96	2.77	91.62
20.53	77.83	1.64	92.61
10.40	88.74	0.86	92.34
5.22	94.05	0.73	87.74

Phase separation theory would predict a continuously rising ethanol purity requirement with gasoline content. In the experiments at −2°C, it can be seen that this does not hold for the test samples with gasoline contents at or above ~90%. In all probability, this result is due to experimental inaccuracies.

Table II-2
Phase separation points at −25°C

EtOH%, % by mass	Gasoline%, % by mass	Water%, % by mass	Ethanol purity, % by mass
72.85	7.67	19.48	78.91
71.17	16.87	11.97	85.60
65.21	26.49	8.29	88.72
57.71	36.47	5.82	90.84
49.09	46.53	4.38	91.80
40.10	57.02	2.89	93.29
30.43	67.30	2.27	93.06
20.59	78.09	1.32	93.98
10.43	88.97	0.60	94.54
5.25	94.48	0.27	95.11