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IDENTIFICATION OF ADDITIVES TO RENDER MIXTURES OF GASOLINE AND THE ETHANOL-WATER AZEOTROPE MISCIBLE

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SUMMARY

The economical production of gasohol, in terms of both energy and dollars, is dependent upon the use of pure, water-free ethanol. Since a small amount of water will cause phase separation in the gasohol, the ethanol must be completely water free. Rather than using pure ethanol, it was proposed to use the ethanol-water azeotrope and some kind of modifier to remove the phase splitting that would occur from using the azeotrope, thus removing the burden of producing water-free ethanol.

A thermodynamic analysis of a set of mixtures containing the gasoline, ethanol azeotrope, and an additive was performed. Each system was evaluated using a computer algorithm which interfaced liquid-liquid equilibrium calculations with the UNIFAC activity coefficient prediction model. The amount of each additive necessary to produce a single phase in the mixture was then determined.

Thirty six compounds were evaluated as possible additives and, of these, six were found to require less than 10% by volume added in order to produce complete miscibility in the gasoline-ethanol azeotrope mixture. All six of these additives were alcohols. Another six components were also found for which 10 to 20% by volume added was required to produce single phase behavior.

INTRODUCTION

Due to recent economic considerations, the use of a fuel "extender" as a means of curtailing expenses has received attention.[1] Alcohols, mainly methanol and ethanol, which are used as fuels themselves,[2] are used as extenders of gasoline. This gasohol mixture incorporates the combustion properties of the alcohols so as to be used with no loss of efficiency relative to straight gasoline. In this study, gasohol will refer to a mixture of ethanol and gasoline.

Gasohol is 90% by volume unleaded gasoline and 10% pure ethanol.[3] At this composition, no adjustments are necessary on the fuel systems of conventional internal combustion engines. However, a mixture that contains more than approximately 20% ethanol by volume would require engine adjustments to compensate for the significantly increased vapor pressure of the mixture.

One of the key points in the production of gasohol is the use of pure ethanol. Any water left over from the production of the ethanol would most likely be enough to cause phase separation to occur when the ethanol is mixed with the gasoline. In a 90/10 mixture of gasohol at 30°C, the water tolerance is 0.50% by volume.[4] If a greater amount of water is present, two distinct phases, one consisting mainly of gasoline and the other alcohol and water, are formed. This alcohol and water phase would cause difficulties with the fuel systems of conventional engines.

Another consideration in the use of gasohol is the comparison of the amount of energy needed to produce the gasohol and the energy obtained from burning the gasohol. This net amount of energy currently depends on the method of purification of the ethanol, and could be rather costly in economical terms.[5,6]

The use of an additive is proposed to eliminate the phase separation. This additive would have to be used in small enough quantities in order to make the idea economically attractive, yet still be able to cause the two liquid phases to form a single phase. This additive would have to be a compound that is combustible, and would not significantly change the combustion properties of the gasohol mixture.

The additive would have to be a compound containing some kind of polar functional group, or groups, in order to associate with the water and ethanol by hydrogen bonding. In order to be soluble in gasoline, the additive molecule must also have a hydrocarbon part. Thus, additives to be considered would have to have hydrogen bonding polar groups along with a major hydrocarbon portion.

The objective of this study then is to find a number of additives which can be added to a gasoline-ethanol azeotrope mixture to produce total miscibility. These additives must be common materials in liquid form that will not drastically affect the combustion properties of the gasoline and ethanol.

ANALYSIS

The actual liquid-liquid equilibrium calculations were based on the condition that the fugacity of the i-th component is the same in each of the two phases. The rigorous thermodynamic condition of minimum Gibbs free energy at equilibrium is not used in this study, due to the complexity of the mathematics. The derivatives used in determining the point of equilibrium are extremely complicated for any number of components greater than three. With certain simplifying assumptions (explained below) though, the fugacity condition at equilibrium can be reduced to a relatively simple set of equations.

The equilibrium calculations were performed using the computer program of Prausnitz, et al.[7], with a number of modifications implemented to take advantage of the advanced FORTRAN V compiler. In addition, the method of calculation of the activity coefficients in the program by Prausnitz is replaced with the UNIFAC model.

Activity coefficients can be determined from experimental data. However, a very large set of data, which preferably would include data for binary, ternary, and higher mixtures, is required to get an accurate calculation of the activity coefficients. In this study, the number of components is such that the required set of data would be practically impossible to obtain and correlate. Therefore, the UNIFAC method[8], a prediction model based on group contribution theory, is used. A computer program by Fredenslund, et al.[9] is used to calculate the activity coefficients using UNIFAC. Rather than using parameters obtained from vapor-liquid equilibrium data, updated parameters obtained from liquid-liquid equilibrium data[10] are used in order to provide a better representation of the behavior of the two liquid phases. Several minor changes are implemented in the program to facilitate its use in this study.

In an attempt to maintain the accuracy of the calculations, gasoline would have to be modeled as a mixture of a large number of components. A sample of a typical unleaded gasoline marketed in the Atlanta area contains over 140 identifiable compounds; the gasoline components and their respective compositions are listed in the Appendix. However, the gasoline used in this study is represented by a 38-component mixture. All components within a group of compounds (e.g., aromatics, normal paraffins, etc.) that consist of identical functional groups as defined by UNIFAC are combined; components with relatively small mole fractions in the overall mixture are also combined. This updated gasoline composition is also given in the Appendix. Also shown in the Appendix are 89- and 5-component representations, which are discussed later.

The idea of determining the amount of an additive needed to produce total miscibility can be thought of as determining the location of the two liquid phase envelope. The implemented procedure begins with no additive for the fixed gasoline-azeotrope composition (two phases present), and adds an incremental amount until a single phase is encountered or convergence is not obtained. Once this point is located, calculations continue with a large amount of additive present (single phase behavior). An incremental amount of additive is removed until two phases are encountered, or, again, convergence is not obtained. The region bracketed by these calculations is assumed to be the area through which the two-phase envelope passes.

A wide variety of additives was considered using the above mentioned procedure. The ranges of amounts were divided into four categories: 1) promising - less than 10% by volume of additive in addition to the gasoline-ethanol azeotrope mixture, 2) possible - 10 to 20% of additive, 3) poor - greater than 20% of additive needed, and 4) indeterminate - the range between single-phase and two-phase behavior is too broad to make an evaluation.

CALCULATION OF LIQUID-LIQUID EQUILIBRIUM

The evaluation of the equilibrium conditions for a given mixture can be broken down into three areas: 1) the thermodynamic evaluation at equilibrium, 2) the calculation of the separation of the mixture at equilibrium, and 3) the prediction of activity coefficients. A brief description of each of these tasks follows. More detailed descriptions are given by Georgeton.[11]

Thermodynamics of Liquid-Liquid Equilibrium

The thermodynamic treatment of the equilibrium condition in this study is based on the component fugacities. For two liquid phases at equilibrium, the condition of equilibrium for the i-th component in terms of its fugacities (f_i) is:

$$f_i' = f_i'' , \tag{1}$$

where the superscripts ' and " refer to the two liquid phases. In order for the above equation to have any practical use, the component fugacities are expressed in terms of composition and quantities which involve composition and temperature in the calculations. Since the systems under consideration in this work are at atmospheric pressure and at ambient temperature, both the Poynting Correction Factor and the fugacity coefficient of pure saturated vapor for component i may be assumed to be equal to unity. Thus:

$$\gamma_i' \, x_i' \, (P_i^o)' = \gamma_i'' \, x_i'' \, (P_i^o)'' , \tag{2}$$

where, for each phase and component i, γ_i is the liquid-phase activity coefficient, x_i is the mole fraction, and P_i^o is the vapor pressure of the pure liquid component at the temperature of interest. Equation (2) can be further simplified by using the same standard state for both phases, such that the vapor pressures are equal. The resulting relation (Equation (3)) is the key equation in the calculation of liquid-liquid equilibria:

$$\gamma_i' \, x_i' = \gamma_i'' \, x_i'' \tag{3}$$

Calculation of Mixture Separation

In a liquid mixture which separates into two liquid phases, the determination of the relative amounts of the phases is analogous to determining the fraction vaporized in an isothermal flash in vapor-liquid equilibria. However, the strong composition dependence of the equilibrium ratios make this system more difficult to solve than its vapor-liquid counterpart. Again, details of these material balance calculations are given by Georgeton.[11]

Calculation of Activity Coefficients

Activity coefficients were calculated in this study with the UNIFAC group contribution method. This model is very adaptable to this study due to the relatively small number of functional groups used to represent a fairly large number of components. A more thorough development of this model can be found in the literature.[8,9]

The binary group interaction parameters used in this study were those determined from known liquid-liquid equilibria data.[10]

ALGORITHM

All calculations were made using either a CDC Cyber 170/730 or 170/760 computer, with single precision 14-place accuracy. Plotter routines from the system library were used, and all programs were compiled on the system's FORTRAN V compiler.

Before any actual calculations were done, a solvent component for each phase was determined. The two solvent components of the mixture are defined as the two components 1) which are present in an appreciable amount in the overall mixture, and 2) that have the lowest binary solubility between them. Initial guesses for the two phase compositions were then made, assuming that only the two solvent components were initially present. The mole fractions of all of the other components were initially set equal to zero. The solvent component in its corresponding phase was assigned a mole fraction of 0.98, and the other solvent component, 0.02. This choice of initial estimates is suggested by Prausnitz, et al.[7] in order to avoid divergence or spurious convergence in the highly nonlinear equilbrium functions.

Using these estimates of composition, initial values of the activity coefficients were calculated and used to find K-values. An initial estimate for the fraction of azeotrope phase present was determined, and an overall loop set up for calculating phase compositions. On every other iteration beginning with the third, the phase compositions were accelerated using a bounded Wegstein method as employed by Prausnitz, et al.[7] With the new phase compositions, updated values of activity coefficients and K-values were calculated. A check to determine the proximity of the plait point was made, and if the mixture was too close, the calculations were stopped. Once the calculations had converged, and if the mixture was in the two-phase region, the phase compositions were then prepared for plotting on an equilateral triangular diagram.

Whenever it had been determined that a mixture was indeed in the two-phase region, more additive was then added, the system normalized, and the equilibrium calculations repeated until the system reached the single phase region or failed to converge due to the proximity of the plait point. Once out of the two phase region, control was transferred back to the last mixture having converged in the two-phase region. At this point, additive was added in smaller increments, and the calculations continued until the mixture reached the single-phase region or did not converge. The last amount of additive used, in which the system was in the two-phase region, was set as the lower limit on the range of amount of additive needed to produce total miscibility.

Once the minimum amount of additive was established, a relatively large amount of additive was used as the new starting point, and the two-phase envelope was approached from the single-phase region. Calculations were performed similarly to the two-phase procedure. If the mixture was determined to be in the single phase-region, the point was prepared for plotting, and then calculations resumed with a smaller amount of additive.

If the mixture was in the two-phase region, or if there was no convergence due to the proximity of the plait point, calculations were resumed with the last amount of additive giving single-phase behavior. A smaller decrease in the amount of additive was then used until the two-phase envelope was encountered. The last amount of additive was set as the upper limit on the amount of additive needed to make the gasoline-azeotrope system form a single, miscible phase.

It should be noted that liquid-liquid separation processes operate at conditions away from the plait point. The results of the algorithm reflect this, and will be more accurate at conditions removed from the plait point than at conditions close to it.[7]

CALCULATION PRELIMINARIES

Representation of Gasoline

As mentioned previously, the gasoline used in this study was represented as a 38-component mixture. The gasoline analysis obtained actually had over 140 compounds. The combining of components having identical functional groups reduced the number of separate components to 89, which are listed in the Appendix. This 89-component representation of gasoline was evaluated with 10% by volume azeotrope using the liquid-liquid equilibrium algorithm, and was found to exist as a single miscible phase. This result, which is assumed to be incorrect, was not considered further to determine where the algorithm failed. However, it is possible that, with such a large number of components, the water was being "lost" in the mixture, and the small compositions would produce large activity coefficients.

The next step was to further reduce the number of components in the gasoline model. This was done by combining a number of similar, related compounds, which had relatively small mole fractions in the mixture. This new representation, which had 38 components (see the Appendix), was tested in the equilibrium algorithm, and the results indicated the presence of two phases (gasoline plus ethanol-water azeotrope).

Preliminary Check of the Equilibrium Algorithm

The liquid-liquid equilibrium algorithm described earlier was used to predict the equilibrium curves and tie lines for several known systems. Some modification of the computer program performing the calculations was necessary in order to predict these curves, but the equilibirum and activity coefficient routines were not altered.

The 2,2,4-trimethylpentane - 2-butanone - water system was used in the algorithm to compare against the experimental data of Moulton and Walkey.[12] The predicted equilibrium curve (in mass fractions) in Figure 1 agrees well with the experimental equilibrium data points, as do the tie lines at conditions away from the top of the curve near the plait point. Yet even at the top of the two-phase envelope, the predicted results give a fair qualitative representation.

Another ternary system used in determing the reliability of the algorithm was the acetone - methylisobutylketone-water system. Again, the calculated results agreed well with the experimental data of Othmer, et al.[13] at conditions removed from the plait point.

The next step was to use a multicomponent mixture, i.e., gasoline, in the algorithm. The experimental data of Tedder[14] were compared with both the 5-component and 38-component gasoline-ethanol-water systems. In both cases, the predictions agreed reasonably well with the experimental data. The results obtained when using the 38-component gasoline mixture agreed more closely with the experimental data than did the results from using the 5-component gasoline representation. This was contrary to expectations, since prediction methods of activity coefficients tend to become poor as the number of components increases. Both systems, however, agreed with experimental data at points well removed from the plait point. These results (see Figure 2 for the 38-component representation, again in mass fractions) along with the results of the two ternary systems, indicate that the algorithm can predict liquid-liquid equilibria with reasonable accuracy.

Additives Studied

The compounds examined as additives in this study consisted of a hydrocarbon part and at least one polar functional group. The behavior of the additives was to be analogous to that of soaps in

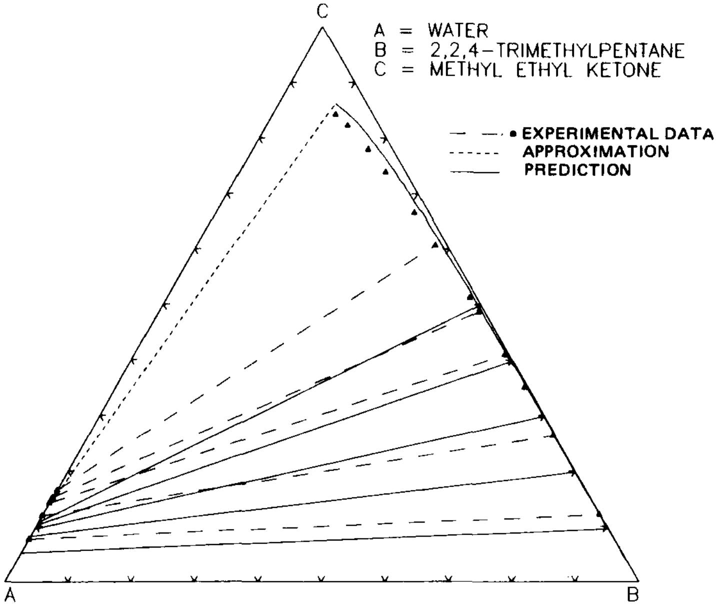

FIGURE 1

Comparison of calculated liquid-liquid equilibrium diagram with experimental data[12] for the ternary system 2,2,4-trimethylpentane-2-butanone - water at 298^0 K.

an "oily" environment where water was also present. The polar groups were included so as to hold the water and ethanol by hydrogen bonding, and the hydrocarbon part was intended to increase the solubility of this complex in the organic (gasoline) part of the mixture.

A total of 36 compounds were considered as potential additives to the gasoline-ethanol azeotrope system. The particular kinds of additives considered were classified, in general, as alcohols, ethers, esters, or ketones. Several "miscellaneous" additives that contained more than one of the polar functional groups implied above were also used.

Certain compounds were not examined due to their physical properties. The corrosive nature of carboxylic acids prohibit

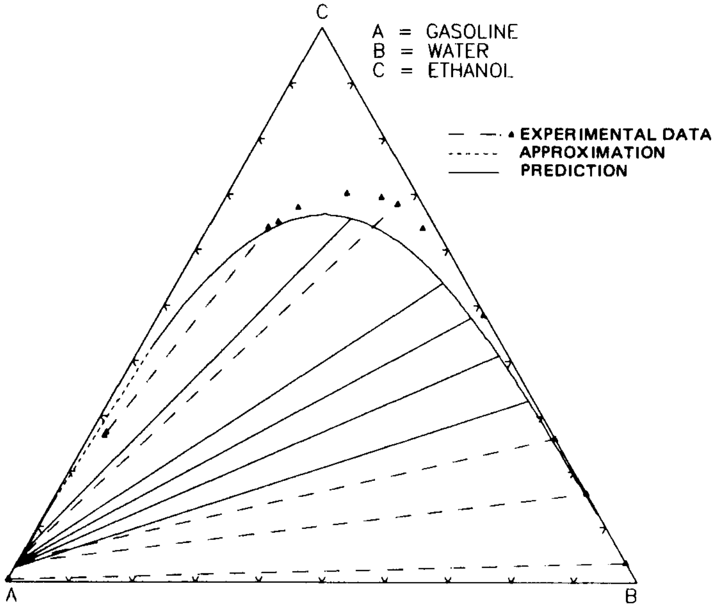

FIGURE 2

Comparison of calculated liquid-liquid equilibrium diagram with experimental data[14] for the pseudo-ternary system gasoline (38 components) - ethanol-water at 298° K.

their practical use in conventional metal engines. Aldehydes undergo autooxidation producing carboxylic acids, and were therefore not considered. Even though compounds containing nitrogen (e.g., amides, nitriles) have very strong hydrogen bonding characteristics, they can be causes of NO_x emissions in conventional combustion engines, and were also dropped from consideration. Anhydrides were not considered due to their reaction with water to produce carboxylic acids.

RESULTS AND DISCUSSION

Presentation of Results

The results of the calculations are shown on ternary, mass fraction diagrams with the corners of the equilateral triangle representing gasoline, azeotrope, and additive. The overall mixture composition is not shown in the two-phase region, but tie lines are drawn to connect the two sides of the equilibrium curve. In all cases the top part of the equilibrium curve was not closed by approximation. The approach towards the equilibrium curve from the single-phase region is shown by a line passing through squares, which represents overall mixture composition. If extended completely, this line would intersect the base of the diagram at a specific point, corresponding to a fixed ratio of azeotrope to gasoline. The single-phase approach line is the same for each additive, thus maintaining a constant ratio of azeotrope to gasoline (10 to 90 on a volumetric basis). All of the evaluations in this study were performed isothermally at 298^{O}K.

If similar calculations were performed with a different ratio of azeotrope to gasoline in order to obtain more points on the equilibrium curve, this would probably produce different tie lines with different equilibrium points. In a true ternary mixture, movement along a tie line does not affect the end points. In this study, however, such movement might produce a different set of end points, and thus a different equilibrium curve. This is due to the very real possibility that some or all components of the gasoline would split differently between the azeotrope and gasoline phases if the azeotrope - gasoline ratio changed. This is evident on a ternary diagram where at least two of the corners represent a group of components rather than a single component.

Each additive was classified according to the range of amount of additive by volume necessary to produce total miscibility in the system. The four categories were defined as 1) promising - less than 10 volume % added, 2) possible - 10-20%, 3) poor - greater than 20%, and 4) indeterminate - the end points of the range are separated by more than 20%. These ranges represent the per cent by volume of additive needed in the gasoline-ethanol azeotrope mixture. These categories were not always strictly adhered to, as in the possibility when the two end points of a range fell into two or more different categories. In this case, the additive was classified by using the upper limit of the range. In case the lower value of the range was in the poor category, the upper value was ignored in classifying the additive. Due to density and molecular weight differences between the gasoline mixture and the additive, the volumetric range may have been quite large and could actually have been considered indeterminate, even though the difference in the range in terms of mole percent was small. This led to the method described for categorizing the additives.

Class One Additives

Six of the 36 compounds evaluated as potential additives fell into the category of Class One. Each of these additives and the amount needed to produce total miscibility is shown in Table I. All six of these additives are alcohols, and all of these systems can be classified as liquid-liquid equilibria Type I. All of these calculations were performed using the 38-component gasoline representation.

Figure 3 is the equilibrium diagram obtained when n-butanol was used as the additive. This diagram is typical of the diagrams obtained for the other additives that are considered promising. The equilibrium diagrams of 2-methyl-1-propanol and 2-methyl-2-propanol are almost identical to that of n-butanol. This implies that a mixture of these isomers could be used as an additive, without the added difficulty of separating the isomers.

In the Class One category of additives, the compound requiring the least addition is phenol. The small two-phase region, evident in Figure 4, makes the use of phenol attractive, but an additional desired characteristic is the benzene ring in phenol. The presence of the benzene ring in gasoline is beneficial in that it increases the octane rating of the gasoline. Benzene is quite insoluble in water, thus posing problems with phase separation. The use of phenol would remove the problem of phase splitting and would also be helpful in maintaining the gasoline's combustion qualities. At room temperature phenol is a solid; however it is very soluble in ethanol, and also reasonably

Table I. Class One Additives

Additive	Vol. % Added	Mass % Added
n-Butanol	4.24 - 9.55	4.51 - 5.41
2-Methyl-1-propanol	4.29 - 9.64	4.51 - 5.41
2-Methyl-2-propanol	4.37 - 9.63	4.51 - 5.41
Cyclopental	4.21 - 9.47	5.24 - 6.28
Cyclohexanol	3.90 - 9.13	4.87 - 6.09
Phenol	1.58 - 5.99	2.29 - 4.58

All calculations performed using 38-component gasoline.

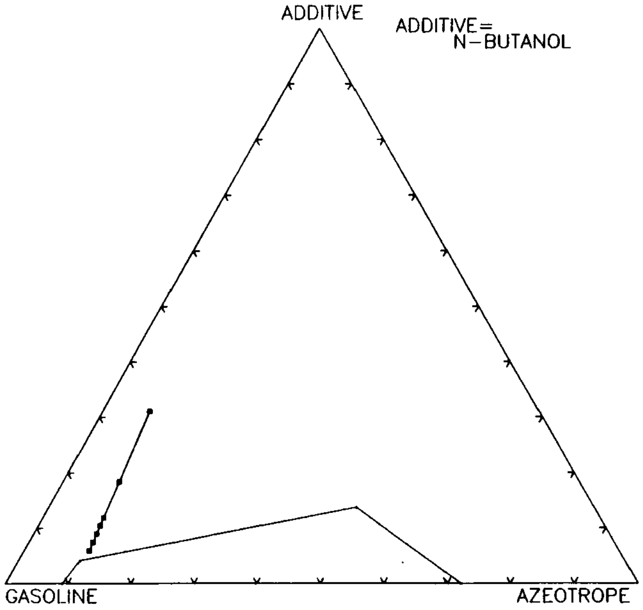

FIGURE 3

Calculated liquid-liquid equilibrium diagram for the pseudo-ternary system gasoline (38 components) - azeotrope (ethanol-water) - n-butanol at 298^{0} K.

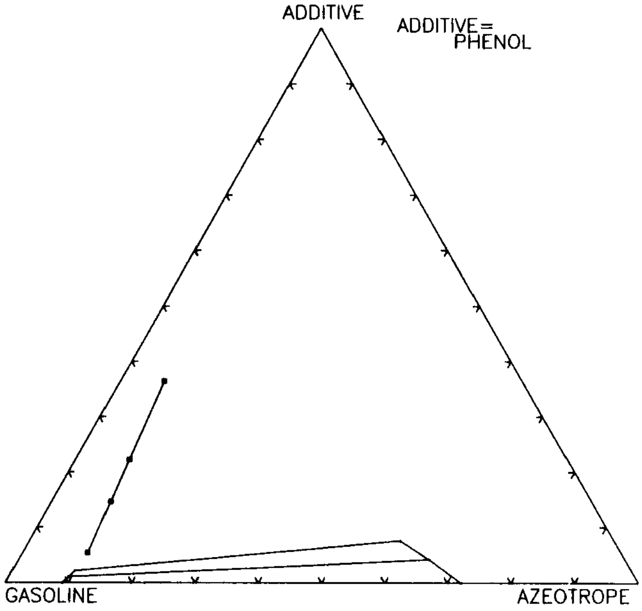

FIGURE 4

Calculated liquid-liquid equilibrium diagram for the pseudo-ternary system gasoline (38 components) - azeotrope (ethanol-water) - phenol at 298^0 K.

soluble in water. Therefore a quantitative amount could be added that would make a "solution" of the alcohol and water in the gasoline. The corrosive nature of phenol, though, would have to be considered before a further evaluation of this additive be undertaken.

Cyclopentanol (Figure 5) and cyclohexanol (Figure 6) exhibited phase behavior similar to the above four alcohols. Somewhat smaller amounts by volume of these cyclic alcohol were required than for the straight chain alcohols, but a larger amount was needed in terms of moles.

Class Two Additives

Table II shows the six compounds which fall into the Class Two category and the respective amounts used. Of these six components,

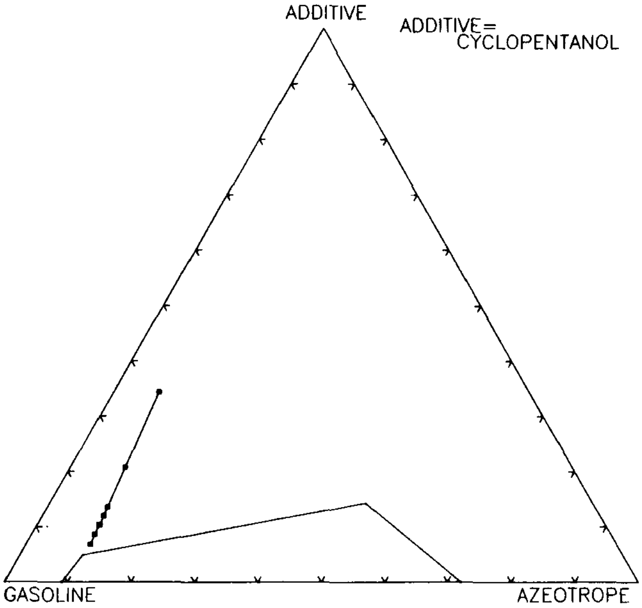

FIGURE 5

Calculated liquid-liquid equilibrium diagram for the pseudo-ternary system gasoline (38 components) - azeotrope (ethanol-water) - cyclopentanol at 298^0 K.

five are alcohols, and one is an ether. All calculations for these additives were performed using the 38-component gasoline representation. All the additives with the exception of 1-octanol result in liquid-liquid equilibria Type I phase diagrams.

The results obtained from using isopropyl alcohol as an additive are shown in Figure 7. Even though this compound is classified as a Class Two additive, it could still be useful as an additive since the upper end point of the range is close to the upper limit of the Class One category. The real benefit of using isopropyl alcohol would be an economical one, since this compound is very common and inexpensive.

Benzyl alcohol was evaluated as an additive with the intent of finding another compound with the same characteristics, but not

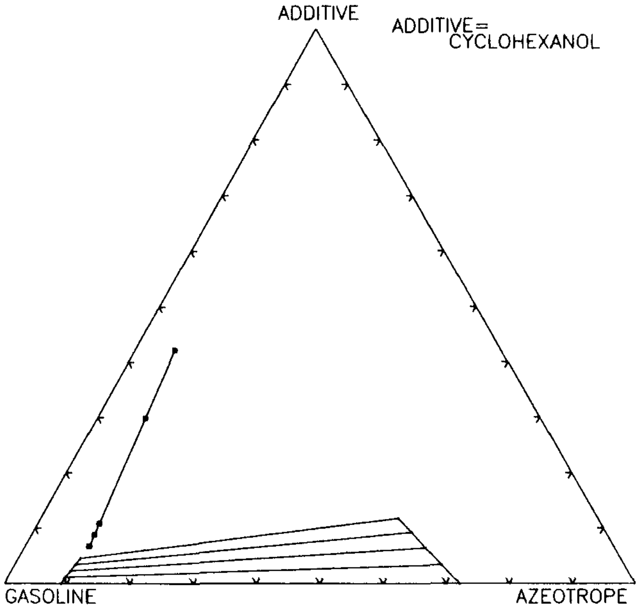

FIGURE 6

Calculated liquid-liquid equilibrium diagram for the pseudo-ternary system gasoline (38 components) - azeotrope (ethanol-water) - cyclohexanol at 298^0 K.

Table II. Class Two Additives

Additive	Vol. % Added	Mass % Added
Isopropyl alcohol	5.84 - 12.30	5.84 - 6.58
Dimethyl ether	6.71 - 19.55	5.60 - 8.40
1-Hexanol	0.0+ - 10.82	0.0+ - 6.21
2-Hexanol	5.85 - 13.16	6.21 - 7.45
Benzyl alcohol	6.87 - 18.73	9.20 - 13.15
1-Octanol	5.79 - 13.56	6.33 - 7.92

All calculations performed using 38-component gasoline.

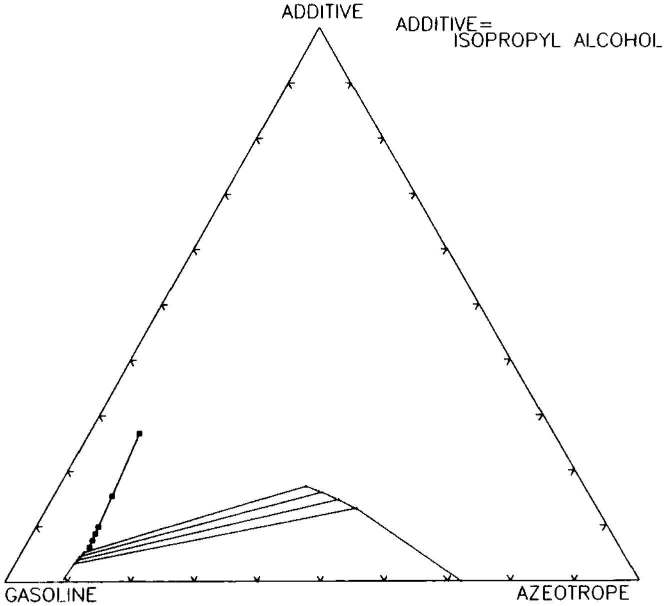

FIGURE 7

Calculated liquid-liquid equilibrium diagram for the pseudo-ternary system gasoline (38 components) - azeotrope (ethanol-water) - isopropyl alcohol at 298^0 K.

as corrosive, as phenol. Figure 8 shows that a considerable amount of benzyl alcohol is needed to produce total miscibility. This amount is greater than that required of phenol, but since it falls in Class Two, may still be considered as a possible additive.

The equilibrium diagram of 1-octanol (Figure 9) indicates a liquid-liquid equilbria Type II system; 1-octanol is the only alcohol evaluated in this study to exhibit this kind of behavior. If the two-phase area were completed in Figure 9, the segment along the additive - azeotrope side might be attributed to the immiscibility of the longer chain alcohol in water, and thus in the azeotrope. A fairly large volume of 1-octanol is needed in this system, but this is due to the large molecular weight of the

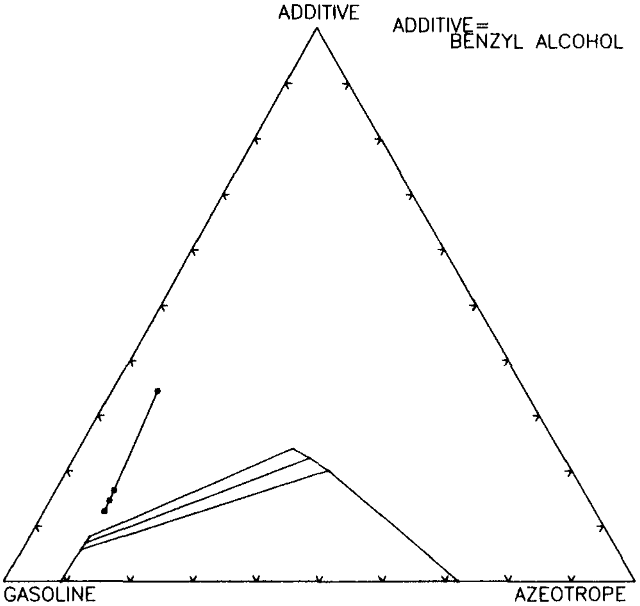

FIGURE 8

Calculated liquid-liquid equilibrium diagram for the pseudo-ternary system gasoline (38 components) - azeotrope (ethanol-water) - benzyl alcohol at 298^0 K.

additive; only a small number of moles is necessary to produce miscibility in the system under consideration.

Class Three Additives

Seventeen of the compounds evaluated as additives fell into the Class Three classification. The components falling into this range consisted of esters, ethers, ketones, and bifunctional alcohols. Table III shows these additives, the respective amounts, and the gasoline representation used in the calculations. Bifunctional alcohols (diols) were evaluated as additives with the idea that two OH groups would be considerably better than one. However, this was not the case, as all of the components fell into the poor

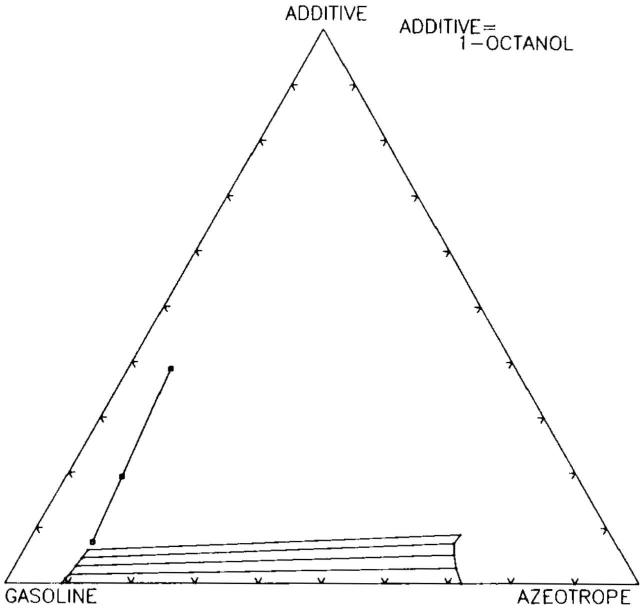

FIGURE 9

Calculated liquid-liquid equilibrium diagram for the pseudo-ternary system gasoline (38 components) - azeotrope (ethanol-water) - 1-octanol at 298^{0} K.

category of additives. The results improved as the chain length increased, as long as the OH groups were very close to each other.

The diols resulted in Type II systems, but the two-phase area was positioned opposite from the Type II system (with 1-octanol) mentioned before. The binary immiscibility that occurred was between the additive and the gasoline, and not between the additive and the azeotrope, as in the earlier system.

Four of the five ketones evaluated in this study fell into the Class Three category. Acetone and 2-butanone resulted in Type I diagrams, while the others resulted in Type II diagrams. Again, as the length of the carbon chain increased, the immiscibility with water came into effect. All of the ethers evaluated resulted

Table III. Class Three Additives

Additive	Vol. % Added	Mass % Added	Gasoline Model (No. of Components)
Ethylene glycol	493.39*	188.63*	5
Diethylene glycol	835.32*	322.50*	5
1,4-Butanediol	599.73 - 1210.72	234.44 - 235.54	5
2,3-Butanediol	617.89 - 1247.39	234.44 - 235.54	5
1,2-Pentanediol	261.16 - 530.17	144.33 - 145.60	5
2,3-Hexanediol	126.21 - 258.32	91.94 - 93.38	5
3-Methyl -2,4-heptanediol	35.89 - 76.31	33.77 - 35.55	5
Acetone	13.79 - 27.27	12.71 - 13.42	38
2-Butanone	12.62 - 25.34	12.27 - 13.15	38
3-Pentanone	12.57 - 25.51	12.57 - 13.61	38
2-Heptanone	12.15 - 25.05	12.18 - 13.39	38
Diethyl ether	7.84 - 25.61	6.31 - 9.91	5
Methyl isopropyl ether	13.29 - 26.82	11.71 - 12.61	38
Methyl n-propyl ether	13.03 - 26.30	11.71 - 12.61	38
Methyl isobutyl ether	15.65 - 31.57	13.93 - 15.00	38
Diisopropyl ether	26.38 - 56.63	19.87 - 21.12	5
n-Butyl propionate	9.53 - 22.48	9.50 - 11.08	5

*Calculations stopped while in two-phase region.

in Type II equilibrium diagrams. The projected segment of immiscibility along the additive - azeotrope side was expected since some shorter chain ethers, being immiscible with water, are used as extractants of compounds in water. An evaluation of longer chain ethers was performed to determine if there was any trend suggesting

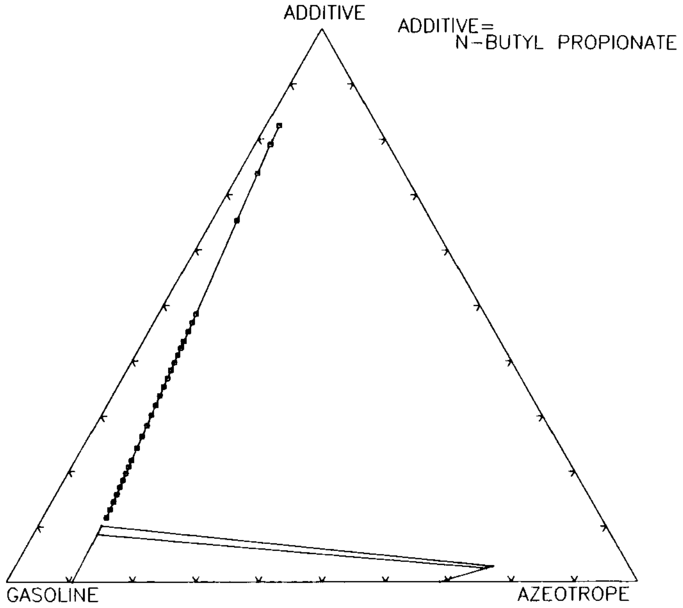

FIGURE 10

Calculated liquid-liquid equilibrium diagram for the pseudo-ternary system gasoline (5 components) - azeotrope (ethanol-water) - n-butyl propionate at 298^{0} K.

a smaller quantity of ether necessary to produce miscibility. However, this was not the trend observed, as the amount necessary for total miscibility of the system actually increased.

The only ester for which evaluation was possible was n-butyl propionate, shown in Figure 10. The polar nature of the COOR group proved to be inadequate in producing miscibility, as is evidenced by the Type II system suggested by Figure 10.

Class Four Additives

Seven components fell into the category containing systems for which classification was not possible due to the range of amount of additive required being too broad. Table IV shows these additives

Table IV. Class Four Additives

Additive	Vol. % Added	Mass % Added
Methyl acetate	4.46 - 620.34*	5.40 - 157.59*
Ethyl acetate	5.50 - 311.57	6.43 - 104.98
n-Propyl acetate	4.82 - 52.48	4.87 - 23.59
n-Propyl propionate	15.66 - 202.94*	16.94 - 84.72*
Isopropyl acetate	11.49 - 763.87	11.52 - 172.78
Methyl ethyl ether	11.68 - 382.37	10.23 - 91.32

All calculations performed using 38-component gasoline.

*Calculations stopped while in two-phase region.

and the corresponding amounts necessary. All systems were evaluated using the 38-component representation of gasoline. Five of the six esters evaluated in this study fell into this indeterminate category. The COOR functional group most likely causes the activity coefficient for the additive to be relatively large; coupling of this possibility with the inaccuracies of the algorithm around the plait point probably results in the inability to evaluate these systems.

CONCLUSIONS AND RECOMMENDATIONS

The following conclusions were drawn from the results of this study:

1. The use of azeotropic ethanol and an additive in the production of gasohol is a very promising alternative to using pure ethanol, which is costly in terms of both energy and dollars.
2. The UNIFAC method of prediction of activity coefficients, while tested against only two known multicomponent mixtures, can be used with a fair amount of confidence for prediction of liquid-liquid equilibria in large multicomponent systems. However, there seems to be some

number of components beyond which results from the UNIFAC model cannot be taken as reasonable, though this point is not specifically examined in this work.

Several questions have arisen during the course of this study, the answers to which would aid in the understanding of liquid-liquid equilibria. During this study, the equilibrium calculations were performed assuming that only two liquid phases were present. Several of the equilibrium diagrams show peculiar behavior that could possibly be interpreted as the existence of a third liquid phase. One area of future interest would be the thermodynamic evaluation of a system to determine the actual number of liquid phases present.

Another point, mentioned in the second conclusion above, that needs investigation is finding the number of components beyond which UNIFAC cannot predict activity coefficients with any assurance of accuracy. This point would be of interest in both liquid-liquid and vapor-liquid equilibrium calculations.

A final recommendation for future work would be to perform experimental equilibrium determinations on the most promising additives in order to verify the results from this study. The evaluation of the additives could also be carried one step further by actual testing of the modified gasohol mixture in an internal combustion engine to determine the benefits or detriments of the particular additive.

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APPENDIX

ACTUAL GASOLINE COMPOSITION

COMPONENT	MOLE FRACTION	COMPONENT	MOLE FRACTION
Normal Paraffins		3-Methylpentane	0.0174
Propane	0.0005	2,4-Dimethylpentane	0.0133
n-Butane	0.1111	3,3-Dimethylpentane	0.0007
n-Pentane	0.0434	2,3-Dimethylpentane	0.0268
n-Hexane	0.0128	2-Methylhexane	0.0122
n-Heptane	0.0075	3-Methylhexane	0.0115
n-Octane	0.0026	2,2,4-Trimethylpentane	0.0575
n-Nonane	0.0015	2,5-Dimethylhexane	0.0053
n-Decane	0.0019	2,4-Dimethylhexane	0.0065
n-Undecane	0.0014	2,2,3-Trimethylpentane	0.0012
n-Dodecane	0.0006	3,3-Dimethylhexane	0.0011
		2,3,4-Trimethylpentane	0.0182
Isoparaffins			
Isobutane	0.0141	2,3,3-Trimethylpentane	0.0160
Neopentane	0.0007	2,3-Dimethylhexane	0.0017
Isopentane	0.1082	3-Ethyl-2-methylpentane	0.0014
2,2-Dimethylbutane	0.0017	2-Methylheptane	0.0046
2,3-Dimethylbutane	0.0100	4-Methylheptane	0.0019
2-Methylpentane	0.0271	3,4-Dimethylhexane	0.0010

COMPONENT	MOLE FRACTION	COMPONENT	MOLE FRACTION
3-Methylheptane	0.0054	Cyclohexane	0.0024
2,2,5-Trimethylhexane	0.0047	1c3-Dimethylcyclopentane	0.0043
2,3,5-Trimethylhexane	0.0007	1t3-Dimethylcyclopentane	0.0042
2,2-Dimethylheptane	0.0002	1t2-Dimethylcyclopentane	0.0029
2,4-Dimethylheptane	0.0005	1c2-Dimethylcyclopentane	0.0021
3,5-Dimethylheptane	0.0007	Methylcyclohexane	0.0045
2,6-Dimethylheptane	0.0004	Ethylcyclopentane	0.0018
2,5-Dimethylheptane	0.0015	1,1,3-Trimethylcyclopentane	0.0005
3,3-Diethylpentane	0.0006	1t2c4-Trimethylcyclopentane	0.0014
4-Methyloctane	0.0011	1t2c3-Trimethylcyclopentane	0.0008
3-Ethylheptane	0.0002	1c3-Dimethylcyclohexane	0.0011
2-Methyloctane	0.0013	1-Ethyl-c3-methylcyclopentane	0.0016
3-Methyloctane	0.0024	1-Ethyl-t3-methylcyclopentane	0.0015
3,3,5-Trimethylheptane	0.0014	1,1,2-Trimethylcyclopentane	0.0038
5-Methylnonane	0.0003	1-Ethyl-1-methylcyclopentane	0.0004
5-Methyldecane	0.0006	1t2-Dimethylcyclohexane	0.0006
4-Methyldecane	0.0003	1t3-Dimethylcyclohexane	0.0012
2-Methyldecane	0.0008	Isopropylcyclopentane	0.0001
Naphthenes		1,1-Diethylcyclopentane	0.0001
Cyclopentane	0.0050	Olefins	
Methylcyclopentane	0.0143	Propylene	0.0001

COMPONENT	MOLE FRACTION	COMPONENT	MOLE FRACTION
Isobutene	0.0033	t3-Methyl-2-pentene	0.0044
t2-Butene	0.0053	1-Methylcyclopentadiene	0.0003
c2-Butene	0.0045	1-Methylcyclopentene	0.0055
3-Methyl-1-butene	0.0012	2,3-Dimethyl-1-pentene	0.0005
1-Pentene	0.0048	2-Methyl-t3-hexene	0.0005
2-Methyl-1-butene	0.0086	4-Methyl-c2-hexene	0.0003
2-Methyl-1,3-butadiene	0.0003	4-Methyl-1-hexene	0.0009
c2-Pentene	0.0076	2-Methyl-1-hexene	0.0013
2-Methyl-2-butene	0.0190	c3-Heptene	0.0058
Cyclopentadiene	0.0003	3-Ethyl-2-pentene	0.0004
c1,3-Pentadiene	0.0002	t2-Heptene	0.0013
Cyclopentene	0.0034	c2-Heptene	0.0022
4-Methyl-1-pentene	0.0008	t2-Octene	0.0005
3-Methyl-1-pentene	0.0010	c2-Octene	0.0004
2,3-Dimethyl-1-butene	0.0010	Aromatics	
2-Methyl-1-pentene	0.0029	Benzene	0.0110
1-Hexene	0.0016	Toluene	0.0433
c3-Hexene	0.0039	Ethylbenzene	0.0117
2-Methyl-2-pentene	0.0056	p-Xylene	0.0096
c3-Methyl-2-pentene	0.0030	m-Xylene	0.0264
t2-Hexene	0.0038	o-Xylene	0.0157
c2-Hexene	0.0035		

COMPONENT	MOLE FRACTION	COMPONENT	MOLE FRACTION
Isopropylbenzene	0.0011	1,2-Dimethyl-4-ethylbenzene	0.0046
n-Propylbenzene	0.0045	1,2-Dimethyl-3-ethylbenzene	0.0008
1-Ethyl-3-methylbenzene	0.0138	1,2,4,5-Tetramethylbenzene	0.0026
1-Ethyl-4-methylbenzene	0.0063	1,2,3,5-Tetramethylbenzene	0.0035
1,3,5-Trimethylbenzene	0.0085	1,2,3,4-Tetramethylbenzene	0.0014
1-Ethyl-2-methylbenzene	0.0057	Naphthalene	0.0038
1,2,4-Trimethylbenzene	0.0238	1,3-Diethyl-5-methylbenzene	0.0006
1,2,3-Trimethylbenzene	0.0057	1-Ethyl-4-propylbenzene	0.0161
2,3-Dihydroindine	0.0045	2-Methylnaphthalene	0.0027
Isobutylbenzene	0.0008	1-Methylnaphthalene	0.0010
sec-Butylbenzene	0.0007		
1-Isopropyl-3-methylbenzene	0.0011		
1-Isopropyl-2-methylbenzene	0.0005		
1,3-Diethylbenzene	0.0018		
1-Methyl-3-propylbenzene	0.0040		
n-Butylbenzene	0.0017		
1-Methyl-4-propylbenzene	0.0026		
1,3-Dimethyl-5-ethylbenzene	0.0039		
1-Methyl-2-propylbenzene	0.0012		
1,4-Dimethyl-2-ethylbenzene	0.0033		
1,3-Dimethyl-4-ethylbenzene	0.0043		

89-COMPONENT GASOLINE REPRESENTATION

COMPONENT	MOLE FRACTION	COMPONENT	MOLE FRACTION
Propane	0.0005	2,5-Dimethylhexane	0.0161
n-Butane	0.1127	3,3-Dimethylhexane	0.0011
n-Pentane	0.0440	2,3,4-Trimethylpentane	0.0185
n-Hexane	0.0130	2-Methylheptane	0.0121
n-Heptane	0.0076	2,2,5-Trimethylhexane	0.0048
n-Octane	0.0026	2,3,5-Trimethylhexane	0.0007
n-Nonane	0.0015	2,2-Dimethylheptane	0.0008
n-Decane	0.0019	2,4-Dimethylheptane	0.0031
n-Undecane	0.0014	4-Methyloctane	0.0051
n-Dodecane	0.0006	5-Methylnonane	0.0017
Isobutane	0.0143	5-Methyldecane	0.0017
Neopentane	0.0007	Cyclopentane	0.0051
Isopentane	0.1098	Methylcyclopentane	0.0145
2,2-Dimethylbutane	0.0017	Cyclohexane	0.0024
2,3-Dimethylbutane	0.0101	1c3-Dimethylcyclopentane	0.0137
2-Methylpentane	0.0451	Methylcyclohexane	0.0064
2,4-Dimethylpentane	0.0407	1,1,3-Trimethylcyclopentane	0.0044
3,3-Dimethylpentane	0.0007	1t2c4-Trimethylcyclopentane	0.0022
2-Methylhexane	0.0240	1c3-Dimethylcyclohexane	0.0062
2,2,4-Trimethylpentane	0.0758	1-Ethyl-1-methylcyclopentane	0.0004

COMPONENT	MOLE FRACTION	COMPONENT	MOLE FRACTION
1,1-Diethylcyclopentane	0.0001	2-Methyl-t3-hexene	0.0008
Propylene	0.0001	4-Methyl-1-hexene	0.0009
Isobutene	0.0034	2-Methyl-1-hexene	0.0013
t2-Butene	0.0099	c3-Heptene	0.0094
3-Methyl-1-butene	0.0012	3-Ethyl-2-pentene	0.0004
1-Pentene	0.0049	t2-Octene	0.0009
2-Methyl-1-butene	0.0087	1-Octene	0.0001
2-Methyl-1,3-butadiene	0.0003	Benzene	0.0112
c2-Pentene	0.0077	Toluene	0.0439
2-Methyl-2-butene	0.0193	Ethylbenzene	0.0119
Cyclopentadiene	0.0003	p-Xylene	0.0524
c1,3-Pentadiene	0.0002	Isopropylbenzene	0.0011
Cyclopentene	0.0034	n-Propylbenzene	0.0046
4-Methyl-1-pentene	0.0018	1-Ethyl-3-methylbenzene	0.0262
2,3-Dimethyl-1-butene	0.0010	1,3,5-Trimethylbenzene	0.0386
2-Methyl-1-pentene	0.0029	2,3-Dihydroindene	0.0046
1-Hexene	0.0016	Isobutylbenzene	0.0008
c3-Hexene	0.0114	sec-Butylbenzene	0.0007
2-Methyl-2-pentene	0.0132	1-Isopropyl-3-methylbenzene	0.0016
1-Methylcyclopentadiene	0.0003	1,3-Diethylbenzene	0.0018
1-Methylcyclopentene	0.0056	1-Methyl-3-propylbenzene	0.0079
2,3-Dimethyl-1-pentene	0.0005	n-Butylbenzene	0.0017

COMPONENT	MOLE FRACTION
1,3-Dimethyl-5-ethylbenzene	0.0171
1,2,4,5-Tetramethylbenzene	0.0076
Naphthalene	0.0038
1,3-Diethyl-5-methylbenzene	0.0169
2-Methylnaphthalene	0.0038

38-COMPONENT GASOLINE REPRESENTATION

COMPONENT	MOLE FRACTION
n-Butane	0.1127
n-Pentane	0.0440
n-Hexane	0.0292
Isopentane	0.1248
2,3-Dimethylbutane	0.0119
2-Methylpentane	0.0451
2,3-Dimethylpentane	0.0414
2-Methylhexane	0.0240
2,2,4-Trimethylpentane	0.0956
2,4-Dimethylhexane	0.0158
3-Methylheptane	0.0121
2,2,5-Trimethylhexane	0.0055
2,5-Dimethylheptane	0.0033
3-Methyloctane	0.0057
5-Methylnonane	0.0017
2-Methyldecane	0.0019
Cyclopentane	0.0051
Methylcyclopentane	0.0169
1-cis-3-Dimethyl cyclopentane	0.0137
Methylcyclohexane	0.0064
1-trans-2-cis-4-Trimethyl cyclopentane	0.0027
1-trans-3-dimethyl cyclohexane	0.0029

COMPONENT	MOLE FRACTION
1-Ethyl-cis-3-methyl cyclopentane	0.0076
t-2-Butene	0.0133
2-Methyl-1-butene	0.0460
2-Methyl-2-pentene	0.0320
1-Methylcyclopentene	0.0059
c-3-Heptene	0.0134
1-Octene	0.0010
Benzene	0.0112
Toluene	0.0439
m-Xylene	0.0543
1,2,4-Trimethylbenzene	0.0750
1,2-Dimethyl-4-ethylbenzene	0.0317
1,2,3,5-Tetramethylbenzene	0.0076
Naphthalene	0.0039
2-Methylnaphthalene	0.0038
1,3-Diethyl-5-methylbenzene	0.0169

5-COMPONENT GASOLINE REPRESENTATION

COMPONENT	MOLE FRACTION
n-Butane	0.1859
Isopentane	0.3888
Methylcyclopentane	0.0553
2-Methyl-2-butene	0.1116
Toluene	0.2583