DISCUSSION

B. S. Bailey[1] (*written discussion*)—The work and analysis of results reported sheds considerable light on a subject which needs much illumination. For after all if one is to estimate how eye irritation, visibility reduction, and the other manifestations of air pollution are to change in the years ahead as the result of vehicle system and fuel changes one must first understand how the composition and amount of these emissions are to change as a result of these vehicle system and gasoline changes. The present work which is concerned with the composition of the exhaust hydrocarbon emissions adds considerably to our understanding of the source of important exhaust hydrocarbons. The authors are to be complimented on their insight and ingenuity at developing correlations which indicate the probable source of various important exhaust hydrocarbons.

In the calculated photochemical reactivity data presented on page 86 and Fig. 9, it is obvious that the factor exerting the greatest effect on calculated reactivity is emission level. While the reduction of emission level is the singly most important means of combating automotive air pollution and must continue to be vigorously emphasized, emission reactivity probably will remain a problem area even in vehicles which emit low levels of emissions. The reason for this is that even at the low levels of atmospheric inputs projected for future cars there will remain the question as to whether further improvement in air quality can be made by control of emission composition. Thus, it appears that the emission composition-reactivity problem will remain with us well into the future.

In order to get at the emission reactivity problem in emission inventory and air quality studies there is need for a type of correlation not specifically considered by the authors. Here the need is for correlations which can be used to predict the concentration of various important categories of exhaust hydrocarbons from gasoline composition data for the vehicle systems of interest. In the past these correlations have been restricted to uncontrolled and first generation emission control vehicle systems and leaded gasoline compositions. Also they generally have not attempted to subdivide the exhaust hydrocarbon variables beyond the major categories of total aromatics, total olefins, and total saturates. In spite of these limitations, these correlations have been extremely useful in emission

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CARBON NUMBER	SATURATE	OLEFIN	AROMATIC
1 - 3	C13S	C23ϕ	
4 - 5	C45S	C45ϕ	
6+	C6+S	C6+ϕ	
6			C6A
7+			C7+A
ACETYLENES		CAϕ	
DIENES		CDϕ	
TOTAL	CTS	CTϕ	CTA

FIG. 10—*Exhaust hydrocarbon composition variables, percent PPMC basis.*

studies. Now the data provided by the authors offer an excellent opportunity to investigate possible extension and improvements to this type of correlation. In order to investigate this possibility, the duPont data were examined to determine whether correlations containing both vehicle system parameters and gasoline composition parameters could correlate the exhaust hydrocarbon data. Exhaust emission level as indicated by total parts per million carbon from the gas liquid chromatography (GLC) analysis was used to characterize vehicle system severity, and gasoline aromatic and olefin concentration as indicated by the fluorescent indicator adsorption (FIA) analysis was used to characterize gasoline compositions. The exhaust hydrocarbon GLC data were processed to develop the 13 compositional variables shown on Fig. 10. These compositional variables were selected for illustrative purposes and while useful for indicating various reactivity vectors are not intended necessarily to represent the optimum selection of exhaust composition variables.

Before presenting the results of the regression work, it is interesting to see how the emission level variable correlates these data.

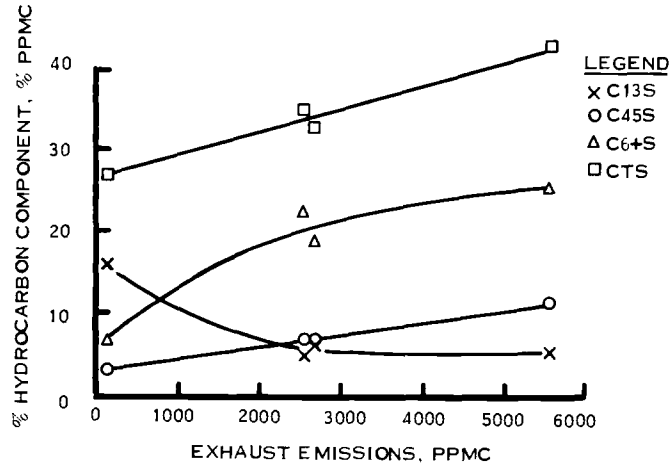

FIG. 11—*Percent exhaust saturates versus emission level, duPont data.*

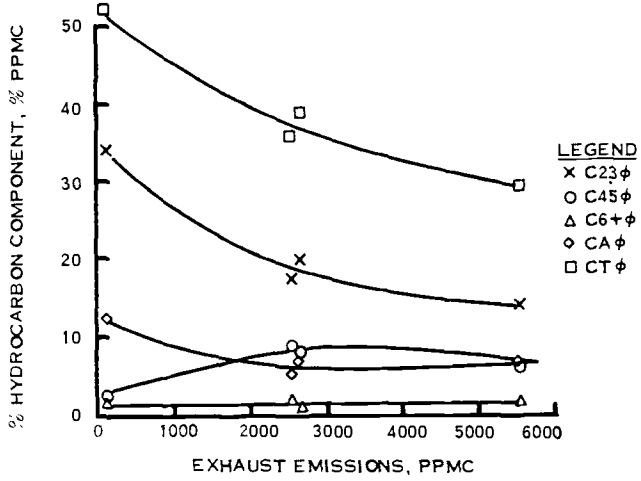

FIG. 12—*Percent exhaust olefins versus emission level, duPont data.*

Figure 11—Shows how the average values for the saturate concentration variables for the 15 fuels vary as exhaust emission level varies. The figure indicates that the concentration of light saturates increases, and the concentrations of C_4 and C_5 saturates, C_6+ saturates and total saturates decrease as emission level is reduced. Also note that some concentration relationships are linear while others are curvealinear.

Figure 12—Shows how average values for olefin concentration variables for 15 fuels vary as function of emission level. As expected the concentrations of light olefins and acetylenes increase as emission level is reduced; other olefins decrease.

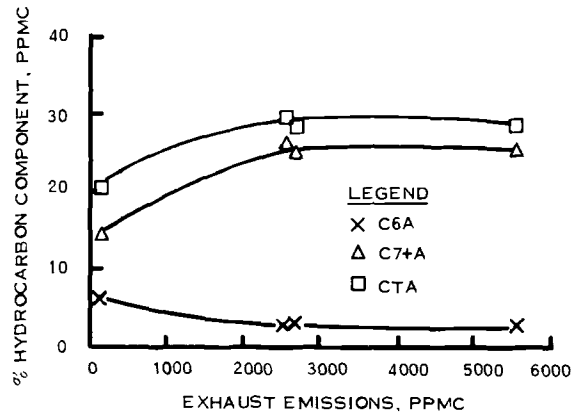

FIG. 13—*Percent exhaust aromatics versus emission level, duPont data.*

$$\text{MODEL: CXXHC} = a_0 + a_1 A(\text{FIA}) + a_2 \phi\,(\text{FIA}) + a_3 \frac{\text{PPMC}}{100} + a_4 \frac{10{,}000}{\text{PPMC}}$$

HYDROCARBON	a_0	$a_1 A$	$a_2 \phi$	$a_3 \frac{\text{PPMC}}{100}$	$a_4 \frac{10{,}000}{\text{PPMC}}$	SD	R
C13S	6.56	-.07	.02	.008	.078	1.4	.96
C45S	5.52	-.02	-.05	.109	-.007	1.5	.87
C6+S	24.50	-.28	-.12	.174	-.070	3.1	.94
CTS	36.55	-.37	-.15	.291	.001	3.2	.92
C23ϕ	28.81	-.24	-.03	-.167	.079	2.9	.95
C45ϕ	11.40	-.10	.09	-.065	-.053	1.3	.91
C6+ϕ	27.44	.01	.06	.012	.005	.6	.68
CAϕ	5.40	.01	.05	-.002	.045	1.6	.88
CTϕ	49.34	-.34	.20	-.270	.058	3.3	.95
C6A	1.44	.11	-.03	-.015	.019	.7	.94
C7+A	12.63	.59	-.02	-.006	-.078	3.7	.92
CTA	14.09	.71	-.05	-.021	-.059	3.4	.94

FIG. 14—*Gasoline exhaust hydrocarbon correlations, duPont data.*

Figure 13—Shows how average values for aromatic concentration variables vary as emission level changes. The concentration of benzene increases as emission level is reduced, while concentrations of other aromatics show a modest reduction.

Figure 14—Shows results of regression work using the model shown on the figure. Several points should be made about these results:

1. The standard deviations are low, and multiple correlation coefficients are high for most of the exhaust compositional variables where concentrations were high enough to be significant. This indicates strong correlations; however, one must keep in mind that these results are based entirely on data obtained from these fuels and cars, and their applicability to other fuels and vehicle systems have not been established. Further work in this area is indicated.

2. The exhaust compositional trends indicated by the gasoline composition and emission level coefficients generally agree with those pointed out earlier by Bill Morris and in my previous figures. However the correlations are particularly interesting for the quantitative information which they indicate concerning these trends. For example, the regression results indicate that the concentration of light C_{23} olefins in the exhaust is nearly independent of the olefin content of the fuel and is dependent upon the emission level. Heavy C_7+ aromatics and total *CT* aromatics are indicated to increase as gasoline aromatics are increased and decrease moderately as emission level is reduced. Other interesting trends are also apparent from the regression results.

3. The correlation model used in this analysis probably will need considerable modification to correlate data from other advanced control system vehicles; if in fact it will be possible to correlate data for all vehicle systems

with one model. Even if this is not possible and several models are required to correlate the data from all vehicle systems of interest, the successful development of such a system of equations will provide an important improvement in our capability of estimating the effect of future vehicle systems and gasoline modifications on emission composition and air quality.

In conclusion, I would like to reiterate my compliments to the authors for an interesting and informative paper. As indicated by my comments, I think that this is an important area in the fight to reduce pollution effects and further work and effort are required.

R. J. Campion[2] *and E. E. Wigg*[2] *(written discussion)*—At the outset, we would like to echo the comments of Mr. Bailey relative to the quality of the work presented by Messrs. Morris and Dishart. This study is a highly significant contribution to the developing literature of fuel composition-exhaust composition relationships. In the recent past, a comprehensive study of various aspects of this question was reported on by the U.S. Bureau of Mines[3] in work supported by the American Petroleum Institute. These two studies, taken together, form a basis for making realistic judgments relative to future emission control regulations. Indeed, these data have been used already, with the generous cooperation of the duPont Company and the Bureau of Mines (BOM), in a recent survey of emission inventories and projected atmospheric benefits as reported by the Los Angeles Joint Volatility Project.[4]

Major Conclusions

In our view, the major conclusions to be drawn from the duPont work are twofold:

(*a*) that fuel composition effects are generally small, within the scope of current commercial blends, and

(*b*) that emission control systems of the future will make fuel composition effects even more insignificant. (In the latter point, we disagree somewhat with the views of the previous commentator on the significance of emission levels from the thermal reactor car).

Areas Needing Some Qualification

While the overall conclusions of this research are quite valid and appropriate, there are several points which should be made in the way of qualifications.

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[3] Eccleston, B. H., Noble, B. F., and Hurn, R. W., "Influence of Volatile Fuel Components on Vehicle Emissions," Report of Investigations No. 7291, U.S. Department of the Interior, Bureau of Mines.

[4] "Gasoline Modification: Its Potential as an Air Pollution Control Measure in Los Angeles County, Nov. 1969.

The initial conclusion reached by the authors indicates that ethylene, propylene, and toluene contribute more than half the reactivity of the hydrocarbon emissions from all of the vehicles tested. We feel that this statement is somewhat misleading with respect to toluene.

Throughout the history of the development of the reactivity concept, much discussion has centered on the particular reactivity index or scale which was chosen to describe a particular hydrocarbon mixture. To meet the objections which always seemed to develop, a composite reactivity scale was generated by A. P. Altshuller of the U.S. Public Health Service (USPHS). This so-called USPHS scale, which has received general acceptance in the field, averages the various responses of individual hydrocarbons to the many smog manifestations usually cited, that is, eye irritation, aerosol formation, oxidant formation, etc. Other scales have been postulated which concentrate on only one of the manifestations; the General Motors Eye Irritation (GM-EIR) scale is one such ranking. While this recent GM work is deserving of close scrutiny, it is fair to say that the overall significance of this rather unusual set of reactivity indexes has yet to be determined. Thus, we feel that the PHS scale, which has an eye-irritation component, is a far more realistic rating scale than the GM-EIR. Using the duPont data, we have shown, in Table 4, an abbreviated Table 2, using the top four contributors to the overall reactivity. As is evident, toluene is either third or fourth by this procedure, but quite far removed in importance from ethylene and propylene. Therefore, we believe it is somewhat misleading to state that "ethylene, propylene, and toluene contribute more than half the calculated photochemical reactivity of hydrocarbon emissions . . ."

The second point we would like to comment upon is the question of the effect of higher aromatics on exhaust toluene concentration. In one part of the paper, no significant effect on toluene is noted as a function of the C_8 aromatic concentration except with the reactor vehicle (which has extremely low individual hydrocarbon emissions). Later, the suggestion is made that the total aromatic content may have an effect on toluene survival through all four emission control systems. Since the regression coefficients in Appendix Table A-3 for the effect of C_8+aromatics on exhaust gas toluene are not significant for three of the four vehicle systems, the reasoning for this stated effect of total aromatic content being related to toluene survival is not clear. We have some conceptual difficulty in visualizing a selective dealkylation of higher aromatics to toluene as opposed to complete dealkylation to benzene, side chain oxidation to acids and aldehydes, or ring opening.

Finally, addressing our comments to the points made by the previous commentor, the relationships derived from these data are to be viewed as specific rather than general. Mr. Bailey's regression expressions using the raw duPont data result in some very interesting predictions; however, the

TABLE 4—*Principle contributors to photochemical reactivity.*

USPHS scale
(% contributed by individual hydrocarbons)

	Uncontrolled Car	Modified Car	Air Injection Car	Reactor Car
Ethylene	27	32	28	68
Propylene	20	21	20	10
Isobutylene/1 butene	7	9	9	1
Toluene	8	6	6	4

use of these equations with the aforementioned BOM fuel and exhaust gas data result in poor correlations. Thus, the particular relationships emphasized in these types of studies are, as of now, a function of the experimental design chosen, in terms of vehicles, fuels, driving cycles, and perhaps sampling techniques.

While these latter comments are somewhat critical, we would like to re-emphasize the high technical quality of this research study and the fact that it is a quite significant contribution to a topical and increasingly important body of information. Again, our congratulations are extended to Messrs. Morris, Dishart, and the duPont Company.

W. E. Morris and K. T. Dishart (authors' closure)—In response to the comments by Mr. Bailey and by Mr. Campion and Mr. Wigg, we wish to expand on three points made in the paper.

1. The effects of fuel composition on composition of exhaust emissions from the thermal reactor car were statistically significant, but we do not consider these effects to be of practical importance because of the extremely low level of emissions from this control system.

2. We chose to analyze data in terms of two photochemical reactivity scales rather than any individual one. The USPHS scale is used widely and referred to and, as Mr. Campion already indicated, incorporates a number of different smog manifestations into the rankings, including eye irritation aerosol formation, plant damage, etc. The GM-EIR scale relates to only one such smog manifestation—but an important one—*eye irritation*. This scale, which is a relatively new one, was developed at General Motors using human subjects who exposed their eyes to smog chamber reaction atmospheres and indicated the severity of irritation. Aromatic hydrocarbons generally were found to produce significantly greater eye irritation than other hydrocarbon types and accordingly are weighted more heavily in this scale than in previous scales.

3. We were searching for the explanation for the positive intercept for the relation of exhaust toluene versus fuel toluene and theorized that total aromatic content may have influenced combustion temperature or some

aspect of combustion such that high aromatic content suppressed the survival of individual toluene molecules that were present in the fuel. If this were happening, the percentage survival of toluene would have been less for the high toluene (and high aromatic) fuels and more for the low toluene (and low aromatic) fuels, resulting in a positive intercept. All this is, of course, pure speculation. We did not mean to imply that the higher aromatics were breaking down to form toluene, except for the thermal reactor car.