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Subject: Butane Blending Technical Analysis

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To: Docket

EPA is considering a modification to its regulations which would allow blending of butane into reformulated gasoline (RFG) outside of the high ozone season, with relaxed sampling and testing requirements. This modification would make butane blending into finished RFG at terminals a more feasible option. This memorandum examines the potential effects of blending butane into RFG. The analysis contained in this memorandum supports the following conclusions:

> When butane is blended into RFG, the resultant blend is likely to conform to the toxics and NOx performance standards applicable to non-VOC- controlled RFG. Performance, as measured by the applicable compliance model, the winter complex model, may actually improve after butane blending.
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> Blending butane into RFG is likely to substantially increase the Reid Vapor Pressure (RVP) of the gasoline, particularly when the "before blending" gasoline has an RVP characteristic of VOC-controlled gasoline.
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> The winter complex model does not consider the effects of RVP on emissions performance. Increases in RVP, in addition to causing increases in non-exhaust VOC and non-exhaust toxics emissions, may also cause increases in exhaust emissions, including NOx. Therefore, the winter model may not fully characterize the adverse emissions impacts of butane blending.
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> Although the potential for adverse environmental impacts resulting from such emissions increases is small, the potential can be further reduced if butane is not blended into RFG at terminals during the shoulder seasons.

Analysis

RFG performance is evaluated by computing emission reductions relative to a baseline gasoline, using a specified compliance model. The Phase II complex model, the applicable compliance model for Phase II RFG is described in 40 CFR 80.45. There are two versions of this model; a summer model used to determine the compliance of VOC-controlled gasoline required during the summer high ozone season, and a winter model used for non-VOC-controlled gasoline. Certain fuel properties are input parameters for the complex model. The parameter values for the summer and winter baseline gasolines are also specified in the regulation.

Non-VOC-controlled Phase II RFG per-gallon performance standards for toxics and NOx respectively, are 20% and 0.0% reductions. The averaged standards for toxics and NOx are 21.5% and 1.5%. In order to demonstrate that RFG will continue to comply with these standards after butane blending, sets of properties representative of RFG before blending were selected, property changes from butane blending were estimated, and the winter complex model was used to confirm that the resultant blends still comply with these standards. Both “winter gasoline” and “summer gasoline” before-blending properties were selected. Although the relaxed sampling and testing will apply to blending of butane into RFG only outside of the VOC season, these summer properties may be representative of gasoline at terminals at the close of the VOC season.

Calendar year 2000 RFG Survey data were used to determine representative sets of RFG properties. Property averages for Sussex County Delaware were selected as parameters for this analysis. Although Sussex County’s average RFG performance was substantially better than performance standards, the area ranked at or near the bottom of areas surveyed in year 2000 for both winter and summer toxics and NOx performance. Parameter values are shown in table 1, below:

Table 1-Sussex County, DE Average Property Values-Year 2000 RFG Surveys

	Summer 2000	Winter 2000
Total oxygen (wt%)	2.01	2.00
MTBE (wt% oxygen)	1.65	1.47
ETBE (wt% oxygen)		
Ethanol (wt% oxygen)		
TAME (wt% oxygen)	0.33	0.50
SULFUR (ppm)	134	225
RVP (psi)	6.43	
E200 (%)	45.5	53.5
E300 (%)	81.6	82.8
AROMATICS (vol%)	24.87	20.33
OLEFINS (vol%)	11.04	12.03
BENZENE (vol%)	0.730	0.652

Although TAME contributed a substantial portion of total oxygen and small quantities of oxygenates other than MTBE and TAME were present, it was assumed for this analysis that all oxygen was from MTBE (i.e. total oxygen weight was assigned to MTBE for complex model calculatios.) This has some effect on complex model toxics, but none on NOx. The winter RFG surveys do not measure RVP, since, for compliance determinations, RVP is set to a value of 8.7 psi in the winter complex model. Data from the Alliance of Automobile Manufacturers (AAM) winter surveys for year 2000 were used to select an RVP value for the winter gasoline. Since Philadelphia, PA is an RFG area geographically close to Sussex County, DE, 13.3 psi, the average RVP value for regular grade gasoline from the AAM Philadelphia survey, was selected.

It was assumed that RVP would blend linearly on mole-fraction basis when butane was blended with gasoline. A relative density of 0.73 and a molecular weight of 105 were assumed for the gasoline before blending. Based on a table of physical constants of paraffins 51.7 psi was used as the butane RVP, since this was the listed vapor pressure at 100 F for n-butane. With these assumptions, if butane is blended at 3 volume percent with 13.3 psi gasoline, the resultant blend RVP is around 14.9 psi. According to ASTM Standard D-4814, the highest winter gasoline vapor pressure/distillation class for Delaware is E, with a maximum RVP of 15.0 psi. Therefore, blending butane at 3 volume percent into this winter gasoline should be a representative blending case. The highest ASTM volatility class standard for Delaware during the latter part of September is C, with a maximum RVP of 11.5 psi. With the above blending assumptions, if butane is blended at 8 volume percent with 6.43 psi RVP gasoline, the resultant blend RVP is around 11.5 psi, consequently blending butane at 8 v% into this summer gasoline should also be a representative blending case.[1] Other properties of the blend were calculated assuming linear volumetric blending for aromatics, olefins, benzene, E200 and E300, and gravimetric blending for sulfur and oxygen. It was also assumed that the butane used for blending had some olefin, aromatic and sulfur content. The values for these parameters are the maximums for non-commercial grade butane, applicable after January 1, 2004.[2] Tables 2 and 3 show the before and after blending property values for these two cases.

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[1] Sussex County had the lowest average RVP of areas surveyed, so 8 v% butane blending is about the maximum amount of butane that could be blended to meet the 11.5 psi class C limit. See http://www.epa.gov/otaq/regs/fuels/rfg/properf/rfgperf.htm for a survey data summary.

[2] The potential effect of butane blending on the emissions performance of gasoline is largely due to the impurities that may be present in the butane. For example, if butane with high sulfur and olefin content were blended with gasoline with lower sulfur and olefin content, the resultant blend could have poorer NOx emission performance than the before-blending gasoline. Consequently, the non-commercial olefin maximum was used in this analysis, to represent a "worst case" condition. The olefin maximum does not change after January 1, 2004, however the sulfur maximum decreases from 140 ppm to 30 ppm. Since this rule is unlikely to become final in time to have any substantial impact prior to 2004, the 30 ppm value was used.

Table 2-Properties Before and After Butane Blending at 3 v%

Winter gas			
	Gasoline	Butane	After blending 3v%
MTBE (wt% oxygen)	2.00	0	1.95
ETBE (wt% oxygen)		0	
Ethanol (wt% oxygen)		0	
TAME (wt% oxygen)		0	
SULFUR (ppm)	225	30	220
RVP (psi)	13.3	51.7	14.9
E200 (%)	53.5	100	54.9
E300 (%)	82.8	100	83.3
AROMATICS (vol%)	20.33	2	19.78
OLEFINS (vol%)	12.03	10	11.97
BENZENE (vol%)	0.652	0.03	0.633
relative density	0.73	0.584	
molecular weight	105	58	

Table 3-Properties Before and After Butane Blending at 8 v%

Summer gas			
	Gasoline	Butane	after blending 8 v%
MTBE (wt% oxygen)	2.01	0	1.88
ETBE (wt% oxygen)		0	
Ethanol (wt% oxygen)		0	
TAME (wt% oxygen)		0	
SULFUR (ppm)	134	30	127
RVP (psi)	6.43	51.7	11.5
E200 (%)	45.5	100	49.9
E300 (%)	81.6	100	83.1
AROMATICS (vol%)	24.87	2	23.04
OLEFINS (vol%)	11.04	10	10.96
BENZENE (vol%)	0.730	0.03	0.674
relative density	0.73	0.584	
molecular weight	105	58	

The winter complex model, used for compliance calculations outside of the high ozone-season, is used with a default RVP value of 8.7 psi for both the winter baseline fuel and the fuel being compared to the baseline. Use of the same RVP for both fuels, rather than the actual RVP, zeros out the effects of RVP change on exhaust emissions.[3] The winter model ignores non-exhaust benzene emissions, which are a component of total toxics in the summer model.[4] Using the winter complex model to evaluate the performance of the before and after-blending formulations shows that these after-blending formulations not only still comply with the toxics and NOx performance standards, but that the performance for both toxics and NOx improves.[5] This is shown in table 4, below. (Reductions from baseline fuel emissions are shown as negative numbers, so larger negative numbers denote better performance.)

Table 4-Winter Complex Model Performance (Both cases)

Winter Complex Model Performance (% change from baseline) Using 8.7 psi RVP				
		Before blending	Blending @ 3v%	Blending @ 8 v%
winter gas	Toxics (exhaust)	-24.81	-25.58	not calculated
	NOx	-4.86	-5.15	not calculated
summer gas	Toxics (exhaust)	-22.15	not calculated	-24.60
	NOx	-8.13	not calculated	-8.60

[3] The RVP levels of the fuels in the database used to develop the complex model ranged from 6.5 to 10 psi, lower than the typical range for winter fuels. Since data on the exhaust emission effects of fuels with winter RVP levels under winter conditions were very limited, EPA could not model the effects of winter RVP levels on exhaust emissions. Consequently, although RVP is likely to have some effect on wintertime exhaust emissions, EPA opted to assume no effect in the winter complex model.

[4] The winter model also assumes that non-exhaust VOC emissions differences, which would be affected by RVP differences as well as ambient temperatures, are zero.

[5] As noted, Sussex County Delaware RFG ranked near the bottom in average NOx and toxics emissions performance in year 2000. Both the sulfur and olefin content of the RFG in this analysis exceeded the levels in the butane, so blending reduced these parameters, with a beneficial effect on NOx. If this impure butane were blended into RFG with lower sulfur and/or olefin content than the butane, these parameter values in the blend could be higher than the before-blending gasoline values. This may result in an increase, rather than a decrease in NOx after blending. However, gasoline with low sulfur and olefin content would be expected to have superior NOx performance. Thus, blending-related increases in NOx emissions, as measured by the winter complex model, would be expected only where there is extreme overcompliance in the before-blending RFG.

This shows that butane blending at the terminal is unlikely to result in non-VOC controlled RFG which fails to comply with toxics or NOx performance standards.[6] However, the above analysis ignores any effect that the increase in RVP may have on emissions Therefore, one cannot unequivocally conclude that toxics and NOx emissions will not increase as a result of butane blending into RFG. To further investigate if any adverse emission effect (even one that would not affect compliance) is likely as a result of butane blending, the summer complex model, which considers RVP effects, was used to evaluate the "summer gas" case. Results are shown in table 5, below:

Table 5-Summer Complex Model Performance (8v% case)

Summer Complex Model Performance (% change from Baseline)			
		Before blending	Blending @ 8v%
Summer gas	exhaust VOC	-16.37	-2.17
	non-exhaust VOC	-49.86	139.46
	total VOC	-28.15	47.65
	exhaust toxics	-26.95	-28.03
	total toxics	-29.87	-28.53
	NOx	-7.62	-6.66

The summer complex model predicts that exhaust toxics performance will improve after blending, but that NOx performance will get worse. The model predicts that non-exhaust VOCs, which are a function of RVP, will increase substantially, and that total toxics will increase slightly (Non-exhaust benzene emissions increase because of the RVP increase.) Exhaust VOC emissions increase as well.

Alternative NOx models, which EPA developed to evaluate California's RFG oxygenate waiver request, confirm that NOx emissions could increase after butane blending. These results are shown in table 6, below:

Table 6-Alternative NOx Model Emission Estimates Before and after Blending (8v% case)

	Alternative NOx Model Results-Before and After Blending						
	Model 2	**Model 3**	**EPA-3**	**Model 5**	**Model 6**	**Model 7**	**average**
Summer gas before blending (gm/mile)	0.75892	0.75201	0.75364	0.75828	0.75973	0.75674	
After blending 8v% butane (gm/.mile)	0.79797	0.80409	0.79496	0.79049	0.79468	0.78184	
% change before to after	5.15%	6.93%	5.48%	4.25%	4.60%	3.32%	4.95%

[6] Although this analysis addressed butane blending into RFG, the same general conclusion holds for blending into conventional gasoline; i.e. butane blending is likely to reduce winter complex model exhaust toxics and NOx emissions.

However, in general, these models also indicate that the NOx emissions of the after-blending formulations are lower than the emissions of the 1990 winter baseline fuel as measured by the same models. Consequently, these models indicate that the NOx performance after blending, even considering the effect of RVP increase, is likely to be as good as or better than 1990 winter baseline gasoline, consistent with the intent of the RFG regulations [7]:

Table 7-Alternative Model Comparisons to Winter Baseline Emissions (both cases)

	Alternative NOx Model-Comparison of After-Blending and 90 Baseline						
	Model 2	**Model 3**	**EPA-3**	**Model 5**	**Model 6**	**Model 7**	**average**
90 winter bl gasoline	0.85733	0.85246	0.85396	0.84416	0.84878	0.85196	
Blending at 3% into winter gas	0.84920	0.87024	0.85078	0.83688	0.84370	0.82471	
% change from winter baseline	-0.95%	2.09%	-0.37%	-0.86%	-0.60%	-3.20%	-0.65%
Blending at 8% into summer gas	0.79797	0.80409	0.79496	0.79049	0.79468	0.78184	
% change from winter baseline	-6.92%	-5.67%	-6.91%	-6.36%	-6.37%	-8.23%	-6.74%

These results should be viewed with some caution. It is uncertain that either the complex model or any of these alternative NOx models accurately predicts the effect of RVP's in this range on NOx emissions. The upper limit of the acceptable RVP range for the complex model is 10.0 psi for RFG and 11.0 for conventional gasoline. Observations with RVP>10 were excluded from the data used to develop these alternative NOx models.

Butane blending downstream of oxygenate blending will dilute the oxygen content. Thus, there could be an increased probability of oxygen survey series failures. There is also the possibility that some RFG would fall below the per gallon minimum for oxygen. Neither situation is likely to have any significant adverse environmental effect.

In summary, butane blending will have no compliance consequences for non-VOC - controlled RFG, other than its effect on oxygen content. However, blending butane into gasoline, could degrade its emissions performance in ways not considered in the winter complex model. Butane blending could significantly increase the RVP of gasoline at terminals at the close of the ozone season. Consequently, the exhaust and non-exhaust VOC emissions performance of the

[7] The actual RVP for winter baseline gasoline (11.5 psi) was used in these calculations. These alternative models use T50 and T90 distillation parameters. T50 and T90 values were 200F and 333F for the winter baseline, 189.8F and 328.0F for the 3% blend, and 200.1F and 329.1F for the 8% blend.

after-blending gasoline would be substantially worse than before blending. NOx emissions performance is likely to be adversely affected, as well. Toxics emissions may also be adversely affected, because of non-exhaust benzene increases not included in the winter model, but butane blending also benefits exhaust toxics emission performance (e.g. through dilution of benzene and aromatics content) offsetting any “uncounted” non-exhaust increase.

Since butane blending will not contribute to noncompliance with performance standards outside of the VOC control season, and since there is already substantial overcompliance with both toxics and NOx performance standards, it is unlikely that any uncounted NOx or toxics increases would have a substantial adverse environmental effect during this time period.[8] VOC performance is controlled and a stricter standard applies to NOx during the VOC control season because these pollutants, in summertime atmospheric conditions, are involved in the photochemical reactions that form ozone. Additionally, for a given fuel composition, summertime ambient temperature profiles are likely to result in greater non-exhaust benzene emissions than wintertime profiles.

However, summertime conditions can exist outside of the VOC control season. Consequently, the presence of VOC-controlled RFG, which may be in the distribution system, could potentially provide additional benefit relative to non-VOC-controlled RFG. This benefit may be reduced if butane blending into this RFG occurs at terminals. Both the likelihood of VOC-controlled RFG in the distribution system and the likelihood of any additional benefit from this RFG would be greatest in the shoulder seasons.

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[8] The Mobile Source Air Toxics rule will help maintain RFG’s toxics overcompliance and the Tier 2 sulfur requirements should maintain or increase NOx overcompliance.