2 would look like Figure 1. The only way that QSS can result in enhancement is by switching between multiple steady states as shown, for example, by Lynch (1983).

Equation 11 in our paper can be obtained from Figure 1 by inspection, but Figure 1 was in turn obtained by integration of eq 5a and 5b for boundary conditions given by eq 6 and 7. On the other hand, eq 11 does not apply to Figure 2 nor to the results shown in Figures 3 and 4.

The reaction sequence chosen in the paper is phenomenological as stated and consequently is not intended to necessarily represent a sequence at the molecular level. Often times it is legitimate and convenient to represent an elementary reaction sequence by lumping adsorption/desorption steps and separately lumping reaction steps as illustrated by our two-step phenomenological model in which AS* is the dominant reactive intermediate. The kinetic constants mentioned by Silveston and Hudgins are results of equation nondimensionalization, and their magnitudes are consistent with the scaling of the equations (dimensionless length to reactor length, dimensionless time to holding time).

Silveston and Hudgins claim "that the formulation used by Thullie et al. (eq 1) is actually a steady-state one." Obviously, the entire paper is devoted to showing that this is not the case. If their incorrect claim were true, then Figure 2 would be identical with Figure 1. Also Figure 3 would be a single horizontal line through unity ($R/R_0 = 1$, regardless of amplitude or frequency) as would Figure 4.

Silveston and Hudgins allude to what they call "catalytic storage" of species, based on their work with ammonia synthesis on iron catalysts. We assume that they mean species storage in the "bulk" of the solid catalyst resulting from the solubility of that species in the catalytic material. However, this phenomenon is irrelevant to our paper since we can arbitrarily neglect it for species A, B, and C. Even in real systems, bulk storage of many species does not occur.

Simply stated, there are many examples in the literature where steady-state kinetics are used in modeling the dynamic behavior of catalytic reactors and often times quite successfully. In our short paper, we wanted to show in a simple way why such an approach, if applied indiscriminantly, can lead to misleading results when one is modeling concentration forcing in regions of parameter space where improvements in production rate over the optimal steady state are expected.

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Comments on "Prediction of Cetane Number by Group Additivity and Carbon-13 Nuclear Magnetic Resonance"

Sir: A recent paper by DeFries et al. (1987), on the prediction of cetane number by a group additivity method using ^{13}C NMR spectroscopy, seems to present a novel approach to understanding the effect of hydrocarbon molecular structure on diesel fuel ignition quality. It is encouraging to see efforts to base the prediction of ignition quality of middle distillates on sound physical and chemical models rather than blind correlations. However, we have doubts related to some important steps in building up the proposed cetane number prediction technique. Also, there exists incomplete and misleading information related to the description of cetane number and a few dubious points that need clarification.

1. Contrary to the authors' claim, cetane number is not a kinetic property, but a *lumped* quantity which includes the total effects of spray formation, heating, vaporization, turbulent mixing, and the chemical induction time under specified conditions of the standard test engine. For more details on cetane number, the authors refer to a paper by Indritz (1985). Although this publication gives some useful information related to the measurement of cetane number, it contains fundamental errors related to autoignition and combustion phenomena in reciprocating internal combustion engines. Also, this paper (Indritz, 1985) does not discuss the physical effects on cetane number, which are functions of engine thermofluidmechanics, combustion chamber design, and thermophyiscal properties of the fuel.

2. DeFries et al. (1987) state that they collected "measured cetane numbers" for 142 pure compounds from two papers reported by Puckett and Caudle (1948) and by Olson et al. (1960). The paper by Olson et al. (1960) does not report any pure compound cetane numbers, but they do tabulate the cetane numbers for blends of a base fuel (a mixture of 75% isooctane and 25% *n*-hexadecane by

liquid volume) and pure compounds (5–20% in the base fuel). Puckett and Caudle (1948) list the cetane numbers of 22 pure hydrocarbons, and *cetene* numbers of 87 compounds. Although there exists an approximate relationship between cetane and cetene numbers, most of the cetene values quoted were obtained in a static bomb, not on a CFR engine. Also, Puckett and Caudle (1948) themselves point to the significant disagreements between the two ignition scales, and they conclude that available ignition quality data are not strictly comparable and predicting ignition qualities from scanty information will be fallacious. A good example is the cetane numbers reported by Gavrilov (1984); the cetane number of *n*-dodecylbenzene is given as 58 by Gavrilov, whereas it is 68 in Puckett and Caudle (1948). Also, cetane numbers of pure compounds predicted from the cetane numbers of blends of Olson et al. (1960) are not in agreement with the corresponding values given in Puckett and Caudle (1948). For example, if one estimates the cetane number of *n*-hexylbenzene from the cetane number measured as 39.8 for a blend of 80% base fuel (CN = 38.3) and 20% *n*-hexylbenzene by volume, the result is 46. The value given by Puckett and Caudle (1948) for *n*-hexylbenzene is 26 (32 for the blend cetane number). The data for *n*-alkylbenzenes and *n*-paraffins are reproduced from Puckett and Claudle (1948) and Olson et al. (1960) in Table I along with the cetane number values used by DeFries et al. (1987) to show the inconsistency in data selection. The authors' selection of cetane numbers from the quoted values is not justifiable. In light of these concerns, it is not clear how the authors collected "measured cetane number" data for 142 pure compounds from these two publications.

3. Determination of the group additivity value of the *phenyl* group seems to be quite arbitrary. The authors

Table I. Cetane Number Values Given by Puckett and Caudle (1948), Values Calculated from the Resulting Cetane Number of a Base Fuel Containing 5–20% Pure Compound Reported by Olson et al. (1960) for n-Alkylbenzenes and n-Paraffins, and Values Used by DeFries et al. (1987)

hydrocarbon	cetane number				
	Puckett and Caudle (1948)		Olson et al. (1960)		values used by DeFries et al.[c]
	pure[a]	blending[a]	blending[b]	mean[b]	
benzene	−10	0	32/23/15	24	0
toluene[d]		−5, −21	14/11/3	10	−5
ethylbenzene			12/8/4	8	5
n-propylbenzene			10/9/9	10	10
n-butylbenzene			34/25/17	26	16
n-amylbenzene	8	18	36/39/30	35	18
n-hexylbenzene	26	32	46/47/46	47	32
n-heptylbenzene	35	39			39
n-octylbenzene	32				32
n-nonylbenzene	50				50
n-decylbenzene[e]					56
n-dodecylbenzene	68				68
n-tetradecylbenzene	72				72
n-pentane			40/31/30	34	30
n-hexane			40/36/42	40	42
n-heptane	57	56	48/53/53	52	56
n-nonane			104/89/74	89	80
n-decane			86/88/81	85	81
n-undecane			100/89/79	90	78
n-dodecane	80	82			85
n-tetradecane			130/115/96	114	96
n-hexadecane	100		126/107/92	109	100

[a] Puckett and Caudle list two cetane values for some hydrocarbons, one is the cetane number of the pure compound and the other is the value that it would contribute when blended with other compounds. [b] Olson et al. give the resulting cetane numbers when the pure compound is added to base fuel, 5%, 10%, and 20% by volume. The column "blending" gives the respective three values of cetane number, calculated from the numbers given by Olson et al., for 5%, 10%, and 20% pure compound in base fuel, assuming that a linear mixing rule applies. The column titled "mean" gives the arithmetic mean of these three values. [c] These numbers are from a blown-up version of Figure 3 in DeFries et al. [d] Puckett and Caudle list two different blending cetane numbers for toluene. [e] No value is given either by Puckett and Caudle or by Olson et al.

used the cetane number of n-tetradecylbenzene (CN = 72) to determine the cetane value of the phenyl carbons as 0. If one tries the other pure compounds whose cetane or cetene numbers are listed in Puckett and Caudle (1948), the results are not all 0 for the value of phenyl carbons. For example, n-dodecylbenzene (CN = 68) yields 9, n-hexylbenzene (CN = 26) yields −9, n-octylbenzene (CN = 31.5) yields −14, 2-phenyltetradecane (CN = 49) yields −14, n-heptylbenzene (CN = 35) yields −3, and toluene (CN = −5) yields −3. If an averaging technique has been employed by the authors, it should have been explained by specifying the criterion used. Another point is the appropriateness of these alkylbenzenes for phenyl carbon additivity value determination. Middle distillate hydrocarbon mixtures, especially those from conventional crudes, contain mostly di- and trialkylbenzenes, rather than monoalkylbenzenes, with an approximate alkyl chain length of 2–4 carbons. Authors fail to specify group contribution cetane numbers for polysubstituted benzenes, which brings out some questions related to the validity of the proposed procedure for complex hydrocarbon mixtures. The ignorance of polysubstituted benzenes and polycyclic aromatics is not understandable.

4. The authors claim that their method "is the first effort to quantify the effect of branchiness" on cetane number. First, it is not clear from their paper what the molecular branching is or what are the factors determining the extent of branching. Although, the carbon counting scheme and ^{13}C NMR associate the number of branching vertices (atoms of degree of three or greater) and their mode of distribution, the dependence of cetane number on the extent of molecular branching is not very simple. An inspection of the data on pure compounds in Puckett and Caudle (1948) indicates that the cetane number does

not follow all the rules on branching. For example, for the isoalkanes 4-propyldecane, 5-butylnonane, and 2,5-dimethylundecane, with increasing degree of branching we observe an increase in the cetane number: 39.4, 53.4, and 57.8, respectively. The skeletal graph of 2,7-dimethyl-4,5-diethyloctane is even more branched and the molecule exhibits a cetane number of 39.4. Other examples can be shown, such as n-octylbenzene and 2-phenyloctane with the same cetane numbers, 32, or sec-butyltetralin and tert-butyltetralin with cetane numbers of 7 and 17, respectively. The inconsistent variations of the cetane number with the extent of molecular branching and the partial peak superimposition (overlapping) of CH$_n$ group types in the ^{13}C spectra of complex hydrocarbon mixtures prevent correct quantification of the effect of molecular branching extent on cetane number.

5. If the selected carbon counting technique is fundamental, one should be able to obtain the group additivity cetane number of naphthalene carbons. Using the carbon counting technique given by the authors, the cetane number for the group additivity of naphthalene carbons is −1 from α-methylnapthalene which has a cetane number of 0, by definition of the cetane scale, −6 from n-butyl-naphthalene (CN = 6 (Gavrilov, 1984)), −31 from n-octylnaphthalene (CN = 18 (Gavrilov, 1984)), and 1 from isobutylnaphthalene (CN = 3 (Gavrilov, 1984)). It should be clarified, as a result of these conflicting values of cetane numbers for naphthalene carbons, whether a different carbon counting method or different set of values for carbon groups must be generated for mixtures containing polyaromatic groups.

6. The authors state that, in order to get a more quantitative method than a gray scale, they regressed the cetane numbers of 93 streams against *the 18 regions* of the

spectrum. What are these 18 chemical shift regions? What are the regression coefficients of these groups in these 18 regions? If these are proprietary information and cannot be disclosed, what is the purpose of their paper? In an archival journal paper in the field of engineering chemistry, the author(s) should give sufficient details so that a competent worker could repeat the experiments. If the method is new and unpublished, all the needed details must be provided, but if the method has been previously published in a standard journal, then the literature reference should be given. Questions such as "how" and "how much" should be precisely answered by the author(s) and not left for the reader to puzzle over. Instead of giving details on the group additivity of density and its relationship to the molecular weight, which can be easily found in standard monographs (see, e.g., Van Nes and Van Westen, (1951) and Farkas (1953)), and trying to show an analogy between an intensive physical property like density and a lumped quantity (which is a function of multiple intensive and extensive properties and conditions) like cetane number, the space should have been devoted to illustration of the use of the method presented for complex hydrocarbon mixtures.

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