Approaches to Automotive Emissions Control

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FOREWORD

The ACS Symposium Series was founded in 1974 to provide a medium for publishing symposia quickly in book form. The format of the Series parallels that of its predecessor, Advances in Chemistry Series, except that in order to save time the papers are not typeset but are reproduced as they are submitted by the authors in camera-ready form. As a further means of saving time, the papers are not edited or reviewed except by the symposium chairman, who becomes editor of the book. Papers published in the ACS Symposium Series are original contributions not published elsewhere in whole or major part and include reports of research as well as reviews since symposia may embrace both types of presentation.

PREFACE

The course of automotive emissions control has profound influence both on attaining improved environmental quality and on meeting the energy needs of the transport sector. Thus this symposium, "Approaches to Automotive Emissions Control," simultaneously addresses two issues that will dominate the national research and development effort for a long time.

The symposium was conceived as a vehicle to foster recognition and critical examination of the interaction between auto emissions control and energy requirements. Taken together, the papers provide excellent background for insight into the interplay of automotive emissions control, fuel economy, and overall energy requirement. These elements of transportation technology have been considered independently for too long. Now, because of the potentially critical problems in meeting fuel demand, a reasonable balance must be drawn between control requirements and the preservation of potential for improved fuel economy.

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The Influence of Fuel Composition on Total Energy Resources

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A meaningful discussion of the subject of this paper is only possible within predefined limits. If all energy used is in the form of electricity generated by solar power or nuclear fusion, fuel composition is of no significance. However, since chemical fuels, particularly liquid chemical fuels, represent a convenient and inexpensive way of storing large amounts of energy in a small, light container, it is probable that they will be used for self-propelled vehicles at least for many years to come. The air pollution problems associated with their use are well on the way to being solved. The chemical fuels can be easily distributed and handled and they can be synthesized from available raw materials. This discussion will be limited to chemical fuels.

Since the combustion products of fuels for oxidation processes must be capable of being handled by the biosphere without damaging it, the useful elemental compositions are limited. Elements whose oxidation products are irritating or toxic (for example sulfur) cannot be considered nor can those whose scarcity precludes their general use. Thus chemical fuels must probably be compounds of carbon, hydrogen, oxygen, and perhaps nitrogen, although inclusion of nitrogen compounds under some circumstances creates problems.

Obviously, during the twentieth century the most widely used liquid fuels have been hydrocarbons, and these compounds have many advantages as chemical fuels. Their physical properties vary widely, making possible the tailoring of fuels to meet varying combustion requirements. Since they have been manufactured in quantity, the technology for their efficient distribution and use has been developed. Most importantly, their energy content per unit mass is higher than that of other eligible compounds. Figure 1 shows the net heat of combustion in Btu/# as a function of molecular weight for hydrocarbons, and some oxygen, nitrogen and sulfur compounds. As would be expected, as the oxygen content of a molecule increases the heat of combustion decreases.

For hydrocarbons, the net heat of combustion is essentially a function of hydrogen content, Figure 2. The curve of Figure 2 is defined by the equation:

$$H_c = 14,100 + 402.5 \times \%w\ H - 4.26\ (\%w\ H)^2 \qquad (1)$$

This equation can be generalized to give an approximation of the heat of combustion of other organic compounds of interest. The generalized equation is:

$$\text{Net } H_c = \left(1 - \frac{\%\ S}{100} - 1.126\ \frac{\%\ O}{100} - \frac{\%\ N}{100}\right)\left[14,100 + 402.5\right.$$
$$\left.\left(\frac{(\%\ H - \frac{\%\ O}{8})\ 100}{\%\ C + \%\ H - \frac{\%\ O}{8}}\right) - 4.26\left(\frac{(\%\ H - \frac{\%\ O}{8})\ 100}{\%\ C + \%\ H - \frac{\%\ O}{8}}\right)^2\right] + 82 \times \%\ S \quad (2)$$

Although the equation is based on compounds containing only one kind of hetero atom, it can be used to estimate the heat of combustion of kerogen, shale oils, coal, etc., from the elemental composition. Figure 3 illustrates the agreement between measured and calculated heats of combustion for some hydrocarbons and non-hydrocarbon compounds. Points representing two coals are also shown.

As has been pointed out previously (1), many other properties of hydrocarbons, specific gravity, refractive index, smoke point, etc., can be related to the hydrogen content. Even a property as sensitive to molecular structure as viscosity correlates in a general way with this parameter - consider the difference between graphite and methane. This trend can be illustrated qualitively by the viscosity on the C_{26} saturated hydrocarbons synthesized by API Research Project 42 at Pennsylvania State University (2) - Figure 4. Here the absolute viscosity in centipoise at 210° F is plotted against the number of rings in the molecule. The average value and range of data are indicated. Essentially the same curve can be drawn for aromatic rings, so that hydrogen content alone does not determine viscosity, but the trend of increasing viscosity with decreasing hydrogen content is obvious. (Also certain specific highly sterically hindered structures have been synthesized. The inclusion of data on these structures increases the scatter of the points, but does not affect the general conclusion.)

The manufacture of chemical fuels from crude oil, i.e., petroleum refining, can be considered as the process of adjusting the molecular weight and hydrogen content of the hydrocarbons present to meet product specifications, and the amount of high valued products which can be manufactured from a given crude is limited by the amount of hydrogen available. Nearly all crude oils contain less hydrogen than the most desirable product mix. Typical data for crudes and currently acceptable fuels are shown in Table 1. Only residual fuel oil and asphalt contain less
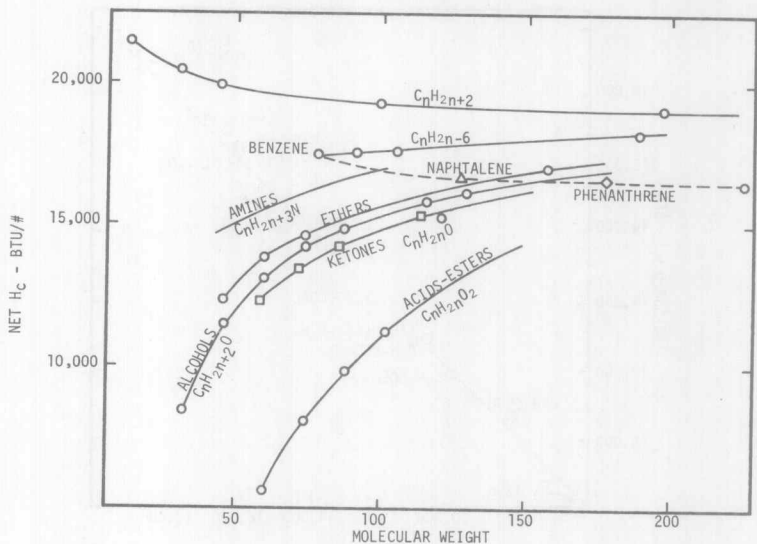
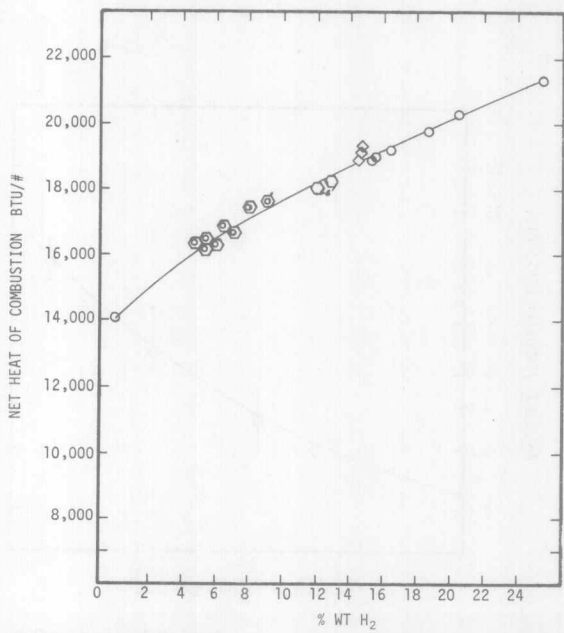*Figure 1.   Heat of combustion as a function of molecular weight*

Figure 2.   Heat of combustion as a function of hydrogen content
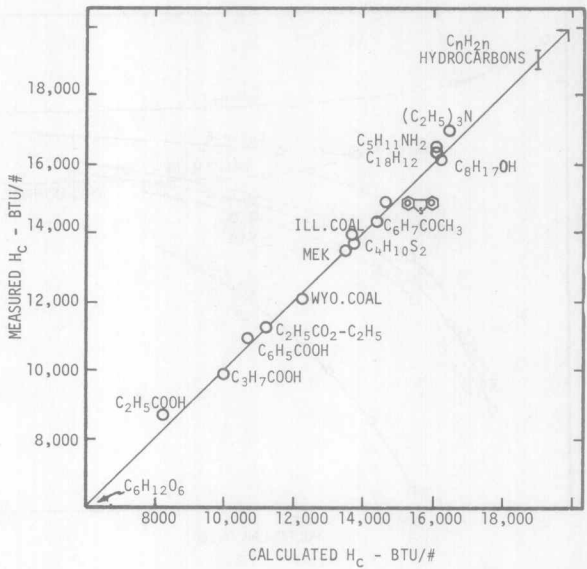
Figure 3. *Calculated and measured heats of combustion*
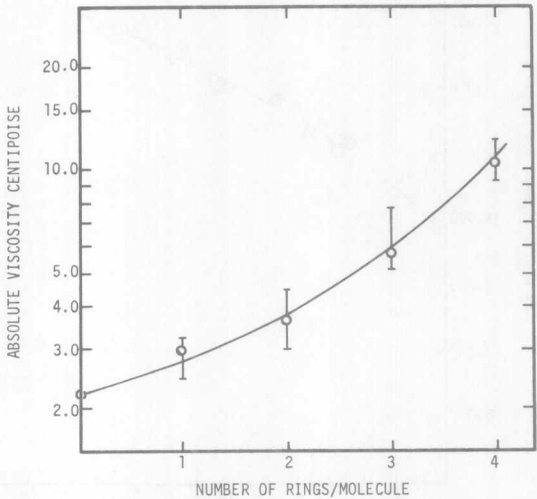
Figure 4. *Viscosity of saturated pure hydrocarbons with 26 carbon atoms/molecule*

Table 1

Hydrogen Contents of Fossil Fuels and Some

Current Specification Products

	%w H	
	Typical	(Range)
Crude Oils	12.3	(10-14)
Residues from Crudes	11.8	(9.5-12.5)
Natural Gas	22.5	
Liquified Petroleum Gases	17.5	
"Regular" Gasoline	14.3	
"Premium" Gasoline	13.7	
Aircraft Turbine Fuel	13.8	
Diesel Fuel - No. 2 Furnace Oil	12.3	
Residual Fuel - No. 6 Fuel	10.0	
Asphalt	11.2	

hydrogen than the residue from which many products must be made.
When fuels are derived from other sources, shale, tar sands, or
coal, the problem is aggravated. Not only are these materials
poorer in hydrogen than most crude oils, but they also contain
higher concentrations of sulfur and nitrogen. Compounds of
these elements must be removed to comply with air pollution
regulations, and at the present state of knowledge, their removal
can be accomplished practically only by hydrogenation. Unless
the chemical fuels of the future can be of high molecular weight,
high viscosity, and of poor burning quality, it seems probable
that their production will require the generation of hydrogen.

The usable hydrogen content of the raw material from which
a fuel is to be made has a significant effect on the energy
required to produce it. The energy required to deliver by
pipeline to a Gulf Coast refinery a pound of hydrogen combined
with carbon in crude oil is approximately 300–400 Btu. To
generate the same pound of hydrogen by steam-methane reforming
would require 85,000 Btu. When the starting material contains
sufficient hydrogen so that auxiliary generation is not needed,
the efficiency of energy resource use can be high. The impor-
tance to current refining practice of efficient use of hydrogen
is obvious.

When fuels are to be manufactured from raw materials of
lower hydrogen content than that desired in the finished prod-
uct, additional hydrogen must be generated, probably from water
and excess carbonaceous material. The production of pure hydro-
gen from coke is a commercially practical, if expensive, process.
Such a process might achieve a thermal efficiency, defined as
the net heat of combustion of the hydrogen produced divided by
the net heating value of the coke needed for the reaction and
to provide the power required for the oxygen plant, separation
equipment, etc., of about 55%. (Current efficiencies are in
the range of 46–47%.) This would be equivalent to the con-
sumption of 6.7 pounds of coke for each pound of hydrogen pro-
duced. Using this efficiency, the weight of fuel of a given
hydrogen content which can be produced from a unit weight of
coke can be calculated by simple stoichiometry. (The heat of
formation of hydrocarbons is sufficiently small so that it can
be neglected in this context.) Figure 5 shows this relationship.
The assumptions used in this and subsequent calculations are
summarized in Table 2. By combining this curve with that
relating heat of combustion to hydrogen content, Figure 2, a
curve relating fuel hydrogen content to the fractional reduction
in total available energy can be constructed for the synthesis
of hydrocarbon fuels from coke, air and water, Figure 6. From
this curve it is obvious that unaltered carbon should be used
as a source of energy whenever this is feasible without serious
efficiency penalty. The generation of methane from coke carries
with it a penalty of about 38% of the energy reserves.

The preceding picture is greatly oversimplified. Coals, not
coke, are usually available, and these contain sulfur, which must

Table 2

Assumptions Used in Energy Calculations

Thermal Efficiency of Hydrogen Generation:

        Gasification of coal or coke to – 55%
        hydrogen only

        Steam–Hydrocarbon Reforming   62%

To Remove S, N, or O by Hydrogenation

        Hydrogen required for S – 4 moles H_2/mole S –
        Thiophene desulfurization

        Hydrogen required for N – 4 1/2 moles H_2/mole N – N
        removal – from Pyridine and Pyrrole

        Hydrogen required for O – 2 1/2 moles H_2/mole O – O
        removal – from Esters, Furans, Phenols

The additional H not associated with H_2S, NH_3 and H_2O is
incorporated in the fuel.

Hydrogen in coal or shale oil available to react with impurities.

All char-carbon gasified before additional coal used.

Net Heat of Combustion of fuels:

$$H_c = \left(\frac{\% \ C}{100} + \frac{\% \ H}{100} - \frac{\% \ O}{800} \right) \left[14{,}100 + 402.5 \times \left(\frac{(\% \ H - \frac{\% \ O}{8}) \ 100}{\% \ C + \% \ H - \frac{\% \ O}{8}} \right) \right.$$

$$\left. - \ 4.26 \times \left(\frac{(\% \ H - \frac{\% \ O}{8}) \ 100}{\% \ C + \% \ H - \frac{\% \ O}{8}} \right)^2 \right] + 82 \times \% \ S$$
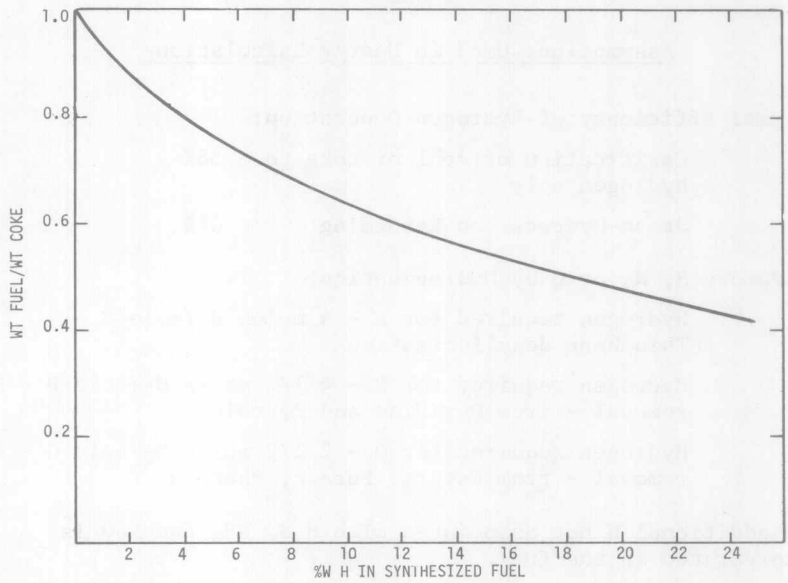
All % are weight

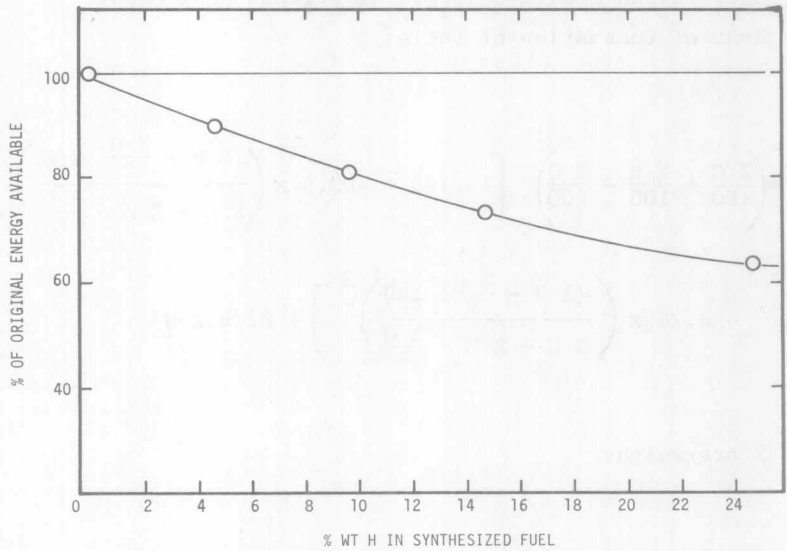Figure 5.   Weight recovery of hydrocarbons produced from coke

Figure 6.   Energy recovery in hydrocarbons produced from coke

be removed before or after combustion, as well as oxygen and
nitrogen. Shale oil contains more hydrogen than coal, but is
also rich in sulfur and nitrogen compounds which require hydro-
gen for their elimination. Practical conversion processes
produce a range of compounds of varying hydrogen contents rather
than a single, most desirable one. Literature data on coal hydro-
genation in pilot plant equipment show products ranging from
H_2S, NH_3 and CH_4, to residual fuel (3). The presence of impur-
ities, and the limitations of reaction mechanisms, qualitatively
increase the hydrogen requirements to produce fuels of given
properties, and thus reduce the fraction of energy recoverable.

Analyses of the organic material in oil shale (4) and of
the oil derived therefrom by retorting (5), have been published,
as have elemental compositions of several coals (3). Table 3
shows typical data. In the case of shale, it is not unreasonable
to assume that the heat needed for retorting can be supplied by
combustion of the unrecovered fraction of the kerogen, and thus
that the initial raw material is the retorted oil. By making
the assumptions shown in Table 2, it is possible to calculate
the fuel yield and the fraction of the original energy recovered
from shale oil as a function of hydrogen content of the final
fuel. Figures 7 and 8 show these relations.

Similar calculations can be made for coals of varying compo-
sition, and curves for an Illinois No. 6 bituminous and a Wyoming
subbituminous are included in Figures 7 and 8. The curves are
based on dry, ash-free coals, and represent an idealized situa-
tion. It has been assumed that the oxygen, sulfur and nitrogen
in the coal can be removed by reaction with a portion of the
hydrogen present, and that the remaining hydrogen can be included
in the hydrocarbon fuel manufactured. Only excess carbon is
gasified (with a thermal efficiency of 55%) to produce hydrogen.
The curves in Figures 7 and 8 extend between a point equivalent
to the hydrogen content of the oxygen, sulfur and nitrogen-free
raw material, and the composition of methane. The actual raw
material points (at 100% recovery) are also shown. Obviously,
the higher the usable hydrogen content of the starting material,
the higher will be the percent of the original energy recovered.

Because of the relatively high costs associated with the
processing schemes discussed, it is logical to assume that only
fuels of high value, synthetic natural gas, LPG, gasoline, and
light fuel oils should be produced by these costly synthetic
routes. Since these fuels are the most probable ones for small
self-propelled vehicles, the remainder of this discussion will
consider only the manufacture of them.

Several studies have been made over the years which have
attempted to evaluate octane number of gasoline which minimizes
the cost of transportation to the motorist. In each case the
approach has been similar. First it is necessary to establish
a relationship between compression ratio and mileage at a
constant level of performance; second, to relate octane number

Table 3

Elemental Composition	%w C	%w H	%w N	%w S	%w O
Kerogen – Mahogany Zone Green River Formation	80.5	10.3	2.4	1.0	5.8
Shale Oil – NTU Retort	84.25	11.41	2.02	0.72	1.61
Illinois No. 6 Coal – Dry (ash free basis)	79.50	5.53	1.02	3.54	10.41
Wyoming Subbituminous Coal – Dry (ash free basis)	75.46	4.71	1.10	0.66	18.07