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Carbon dioxide emissions from fossil fuels: a procedure for estimation and results for 1950–1982

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ABSTRACT

With growing concern about climatic changes that could result from increased atmospheric carbon dioxide, it is appropriate to use the improved statistics on the production and use of fossil fuels which are now available and to review the CO_2 discharges to the atmosphere from fossil fuel burning. Data on global fuel production and the chemical composition of these fuels have been re-examined and an attempt has been made to estimate the fraction of fuel which is used in the petrochemicals industry or otherwise not soon oxidized. Available statistics now permit more systematic treatment of natural gas liquids than in earlier calculations. Values used for combustion efficiency and non-fuel use on a global scale still require some estimation and extrapolation from United States data but can be bounded with sufficient precision that they add little uncertainty to the calculation of global CO_2 emissions. Data now available permit the computation to be made with confidence that there are no major oversights. The differences from earlier calculations of CO_2 emissions are minor, well within the uncertainty limits in the data available. The fundamental problems of assembling a data set on global fuel production limit the utility of striving for too much precision at other steps in the calculation. Annual CO_2 emissions retain an uncertainty of 6–10%.

Results of the calculations for 1980 through 1982 show decreases from 1979 CO_2 emissions. This is the first time since the end of World War II that the emissions have decreased 3 years in succession. During the period following the 1973 escalation of fuel prices, the growth rate of emissions has been less than half what it was during the 1950s and 1960s (1.5%/year since 1973 as opposed to 4.5%/year through the 1950s and 1960s). Most of the change is a result of decreased growth in the use of oil.

1. The problem

In attempting to identify the possible causes and consequences of the observed increasing atmospheric CO_2 concentration, the source of the CO_2 is a major concern. Through the past several decades, the combustion of fossil fuels has grown immensely and it is clearly an important source of CO_2.

The intent of this study was two-fold: (1) to provide detailed documentation for a procedure to estimate CO_2 emissions from fossil fuels, and (2) to make independent and updated estimates of the rate at which fossil fuel combustion has released carbon dioxide to the atmosphere. The CO_2 issue has achieved such significance that it is appropriate to review the analysis of Keeling (1973) and affirm that the much used data sets of CO_2 emissions from Rotty (1979, 1981), using Keeling's procedure, do not contain significant oversights. This work is intended to provide independent and updated estimates of CO_2 emissions and undue significance should not be attached to minor differences from peviously published values.

The result of the calculations described here will be a table which displays, for the period 1950 through 1982, the amount of fossil fuel produced and the amount of CO_2 discharged to the atmosphere as a consequence. A final graph will display, for each fuel and for the global total, how CO_2 emissions have varied as a function of time.

2. Rationale

The calculation of CO_2 emissions from fossil fuels is conceptually very simple. For each type of fuel, the annual CO_2 emissions are the product of three terms: the amount of fuel produced, the fraction of the fuel that becomes oxidized, and a factor for the carbon content of the fuel. For CO_2 calculations, fossil fuels can conveniently be divided into the usual groups of gases, liquids, and solids. For each fuel goup, we start with annual fuel production data (P). Multiplying P by the fraction of each year's fuel production that is oxidized (FO) and by the average carbon content of each fuel group (C) will give the CO_2 emissions for that fuel group. That is,

$$CO_{2_i} = (P_i)(FO_i)(C_i) \quad (1)$$

where subscript i indicates a particular fuel group and CO_{2_i} is expressed in mass of carbon.

The data for annual fuel production must recognize that all coal (or natural gas or crude oil) is not of the same composition, and thus may have varying energy content and CO_2 potential. It is easiest to accomplish this by using fuel production data in either energy or energy equivalent units (for example, tons of coal equivalent).

The second factor in eq. (1), the fraction becoming oxidized, requires examining the use of fuels. For coal, nearly all the production at present is for combustion, and the effectiveness of the combustion process determines the fraction of the carbon that is oxidized. For liquids and gases we must account not only for inefficient combustion but also for non-fuel uses. Derivation of this factor for each fuel group is based on data for the products of petroleum refineries and natural gas processing plants.

There is no systematic tabulation of data on the carbon content of fuel produced all over the world. For liquid fuels and for natural gas, the hydrogen–carbon ratio largely determines the heating value and for solid fuels most of the combustion energy is from oxidation of carbon. Thus, for each fuel the heating value is closely correlated to the carbon content and the energy equivalence concept used in the tabulation of production data makes it possible to deduce fuel composition quite accurately. The final term in eq. (1) is a factor which relates carbon content to energy content for each fuel group.

The complete combustion of a fossil fuel can be represented by

$$C_xH_y + (x + \tfrac{1}{4}y)O_2 \rightarrow x CO_2 + \tfrac{1}{2}y H_2O(\text{gas}) + \Delta H_L \quad (2a)$$

or

$$C_xH_y + (x + \tfrac{1}{4}y)O_2 \rightarrow x CO_2 + \tfrac{1}{2}y H_2O(\text{liquid}) + \Delta H_H \quad (2b)$$

where ΔH is the heat of reaction and C_xH_y denotes generalized fuel. For combustion of hydrocarbons, the heat of reaction is negative in the thermodynamic sense, meaning that heat is given off. When all the water in the products of combustion is liquid (for combustion at relatively low temperature) the higher (or gross) heating value, ΔH_H, is appropriate. ΔH_H is always greater than the lower (or net) heating value ΔH_L because of the energy required in the vaporization of water. Real fuels vary considerably in composition—both in time and place—hence x and y are different not only for average natural gas and petroleum, and for different petroleum products (gasoline versus fuel oil), but also for crude oil from different fields. This makes development and use of global averages very important and is accomplished by using the energy equivalence basis, i.e. the implicit relations between ΔH and x and y.

In the past, CO_2 emissions have often been based on United Nations fuel production data using similar procedures (described by Keeling (1973) and Rotty (1973)). During the past decade, the UN statistical office has modified its reporting toward a more consistent fuel equivalence basis. This has necessitated modifications in the procedures for calculating CO_2 emissions to assure consistency. Most recently, Rotty (1983) calculated the global emissions from fossil fuel for the years 1950–79 and estimated 1980 emissions from incomplete data. The final section of this report contains an updated version of these emissions computations with values for 1981 and 1982.

3. Fuel production data

In approaching calculations of CO_2 emissions, it is useful to begin by examining the first term on the right in eq. (1). A consistent set of global fuel data is clearly required and the form of the other two

factors will be dictated by the definitions and accounting units used in the fuel production data.

Most investigators calculating the production of CO_2 from fossil fuels have relied on data published by the United Nations. The US Bureau of Mines, the Energy Information Administration of the US Department of Energy, the World Bank, the Organization for Economic Cooperation and Development, and numerous other national and international organizations also maintain data on fuel use and energy activities. The UN Statistical Office energy unit offers the most complete and consistent time series for global fossil fuel production and consumption, partly because information from the other sources is used in the development of the UN data, but most importantly because the UN data set is continually modified and updated. The reliability of the data (and the suitability of its use in CO_2 calculations) has consistently improved through the years as more information has become available to the UN staff and as energy information has become more important in world activities.

Although the UN data are now in relatively consistent energy or energy-equivalent units, the nature of our computations and common usage in the various disciplines insure that a mixture of units of measure are encountered. Despite the potential for confusion with mixed units, we believe it important to distinguish between data taken from other sources and data which have been manipulated by us. Although our computations are in SI units we have tried to consistently indicate the primary units from our sources of data and any manipulations requiring, for example, mass to volume or mass to energy-content conversions are carefully documented. Throughout this document "tons" should be understood to be metric tons.

3.1. *Production of natural gas*

Although we are interested in global data, the pattern for gas production and distribution in the US is useful in helping to understand terms and processes. Fig. 1 has been prepared from data published by the Energy Information Agency of the US DOE and shows the 1980 flows of natural gas in the United States. In calculating the CO_2 emissions, we must account for all the gas that is withdrawn from wells and becomes oxidized. Gas reinjected into the earth to repressure oil wells should not be counted and we will account separately for gas vented and flared. Hence "marketed production" is our starting point. The tabulations illustrated in Fig. 1 permit accounting for the loss of gas volume during processing for recovery of liquids ("extraction loss"). The systematic approach of combining liquids extracted from natural gas with other liquid fuels has been adopted here. To avoid counting this quantity twice, the basic number we must consider in our analysis of CO_2

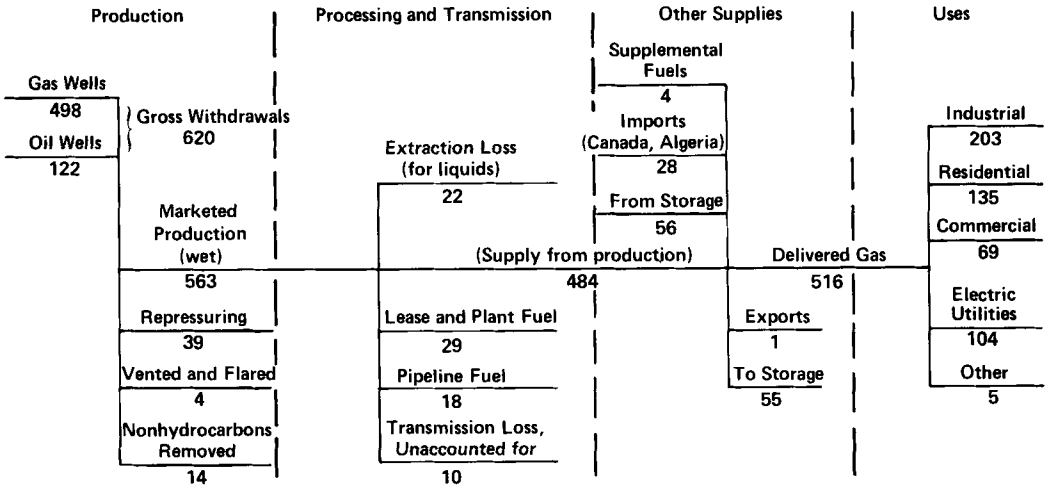

Fig. 1. US flows of natural gas, 1980 (in 10^9 m^3; converted from cubic feet at 1 ft^3 = 0.0283 m^3). Data from US DOE (1982a).

emissions from gas is the marketed production minus the extraction loss. In fact, this is the number now recorded by the UN Statistical Office as natural gas production. The UN reports this natural gas production for all the producing countries.

Of course, all of the gas produced in a given year is not necessarily consumed in the same year. One reason for this is net changes in storage, but the numbers shown as "to storage" and "from storage" in Fig. 1 show that for 1980, the error on this account is less than 1% in the US. Over periods of very few years, the changes in storage will tend to balance and global totals of imports and exports should also balance. Fig. 1 suggests another issue which cannot be neglected by balancing over a few years or integrating over the whole globe. Some fraction of the industrial-use gas is for non-fuel uses and will be oxidized over time periods ranging from essentially immediate to decades. These uses include, for example, ammonia and methyl alcohol production and a variety of other petrochemical feedstock requirements. In the following section we will make allowance for the fraction of fuels produced but not oxidized.

In their early fuel data the UN tabulated natural gas production in cubic meters, counting gases with widely varying compositions on the same basis. Natural gas data were later changed to reflect the energy content of the gas and were tabulated in teracalories. Beginning with the publication of the *1979 Yearbook of World Energy Statistics* (UN, 1981) the data are given in terajoules. The UN has now converted all the published gas data (i.e., back to 1950) to the TJ basis. Because the carbon content is closely correlated with the heating value of the gas, we believe that this has improved the estimates of CO_2 emissions from natural gases.

Many of the UN data sets for natural gas are received in the statistical office in energy units. That is, in response to the UN questionnaires, the individual countries (or organizations acting on behalf of individual countries) submit natural gas data in terms of the energy content of the gas. The UN maintains a reference table of heating values for gas from each country, but it must be pointed out that the published values are not usually used in making volume to energy conversions in the UN office. Although it is not always clear, most of the published values are as reported by the individual countries, and most appear to be based on higher heating values of the fuel. We will use these conversion factors to characterize the carbon content of natural gas. The most recently revised UN data for natural gas production during the period 1950–82, are given in our summary, Table 14, column 1. Because the gas industry has been so tightly regulated, recent gas production numbers for the US are likely to be correct within ±5%. Non-US production numbers are less accurate, but we suggest that the figures for annual global totals are within ±10%. Our confidence in the global figures is enhanced by recognition that the quality of the data should be improving with time, and that the historic data are heavily dominated by US production. It was in 1974 that US production first dropped below 50% of the world total and as recently as 1960, US production of natural gas exceeded 75% of the world total.

3.2. *Production of liquid fuels*

As in the case of natural gas, the global production and use of liquid fuels can be viewed through the analog of the detailed flow of liquid fuels for the United States. Based on data from the US DOE, the 1981 mix and flow of liquid fuels in the US can be depicted as in Fig. 2. Note that liquids derived from natural gas are treated here as a separate production source.

Just as with natural gas, imports and exports do not have to be considered if CO_2 emissions are based on global fuel production. However, if interest is on the distribution of CO_2 emissions among countries (or parts of the world), different procedures must be considered. The distribution based on consumption is drastically different from the distribution based on production because such a large fraction of the crude petroleum produced is involved in international trade. On the other hand, because the net change in stocks is a small number, using total production numbers to indicate total consumption and CO_2 emissions introduces negligible error.

As indicated in Fig. 2, most of the liquids are used as fuels and hence oxidized within a relatively short time of production. However, the use of production data for liquid fuels in computing CO_2 requires a correction for the liquids that are not oxidized in their use. Non-fuel uses of petroleum liquids come primarily under the "other" category in the last column of Fig. 2 and it is here that major adjustments will be made.

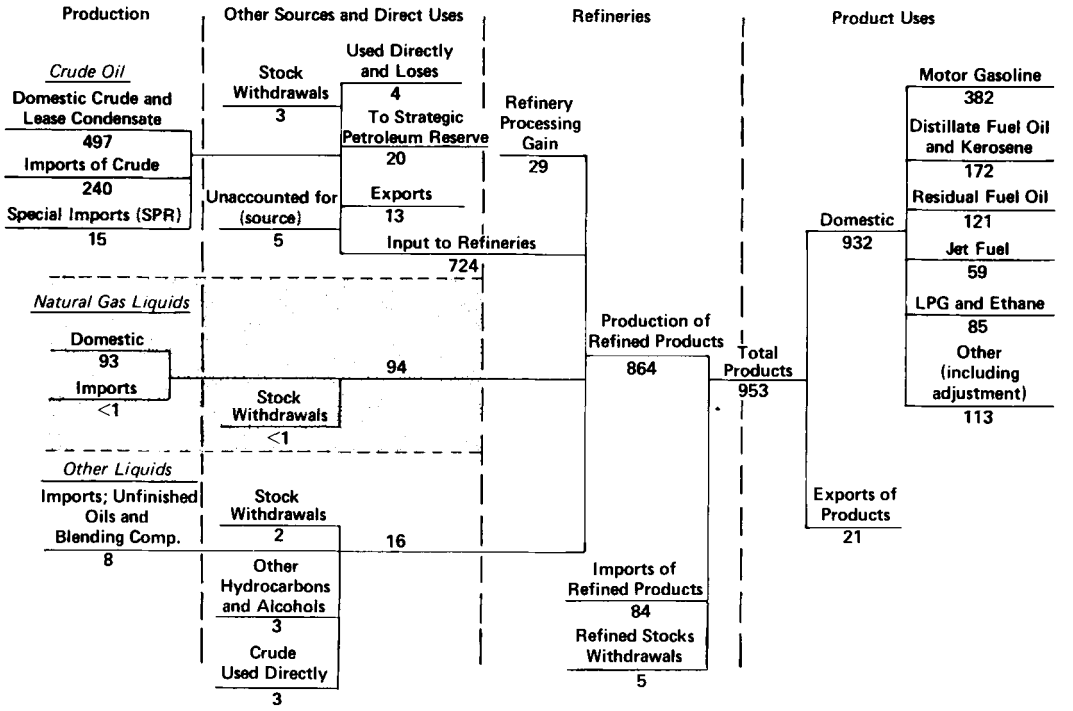

Fig. 2. US flows of liquid fuels, 1981 (in 10^6 m^3; converted at 1 barrel = 0.159 m^3). Data from US DOE (1982b). (In keeping with the US DOE data source, units in this figure are measures of volume whereas later calculations are based on UN values in mass units.)

The United Nations combines US DOE statistics with official or unofficial tabulations from other nations to arrive at world production statistics for crude petroleum and for natural gas liquids. As in the case of natural gas, the UN data are taken to be the best available for our purposes because of their completeness, historical consistency, and clear conformity with other available data. The UN production data for liquids, like those for other fuel types, are widely quoted by others and are essentially identical to "independent" values published elsewhere (see, for example, Table 1). The agreement of the UN data with data published by other organizations does not imply that the data are accurate to a limit described by these variances. Frequently, the primary sources are identical, and some of the differences are due to interpretations and assumptions about standards.

In considering sources of error in the data on liquid fuels, an area of concern is the handling of natural gas liquids. These liquids comprise a mixture of compounds, some of which are used directly

Table 1. *World crude oil production as reported by different sources** (10^6 *tons oil equivalent*)

	UN (1982)**	Enright et al. (1981)	US CIA (1981)	API (1981)
1980	2986	2974	2974	
1979	3127	3122	3134	
1978	3012	3011	3011	3033
1977	2985	2982	2987	2998
1976	2870	2872		2901
1975	2644	2651		2669
1974	2789	2795		2811
1973	2780	2793		2788
1972	2548	2514		2546
1971	2413	2394		2418
1970	2275	2266		2288

* All data (except UN) were reported in barrels or barrels per day and were converted to tons oil equivalent by assuming a mean gravity of 32.5° API.

** UN (1982) and Data Tape of UN Energy Statistics.

as fuel or chemical feedstocks and some of which are combined with crude petroleum or its intermediate products in refineries. On the average, natural gas liquids (NGLs) have a lower carbon-to-hydrogen ratio than crude petroleum, and thus, on a per unit mass basis, a higher energy content. Because the UN data on liquid fuels are designed to be representative of the energy content of the fuel, their liquid fuel data set (on an energy equivalent basis) is compiled by multiplying NGLs by 1.06052 and then adding this figure to the crude petroleum production. The factor 1.06052 is the UN correction factor to reflect that the NGLs have a 6.052% greater heating value per unit of mass than average crude petroleum.

For the purpose of calculating CO_2 emissions, we do not wish to employ this weighting factor introduced to account for more hydrogen in the fuel, so have adopted the procedure of simply adding the mass of natural gas liquids to the mass of crude petroleum. On the assumption that crude petroleum contains 85% carbon (see discussion below regarding carbon content of crude petroleum) and that NGLs contain between 80 and 84% carbon (C_2H_6 is 80% carbon, C_7H_{16} is 84% carbon), the error in considering the combination as all crude is very small. For the world as a whole, the mass of NGLs is about 3% of the mass of crude petroleum production. The carbon fraction for the mixture should be about

$$(0.97)(0.85) + (0.03)(0.82) = 0.8491,$$

which is so close to the carbon fraction of crude petroleum as to make any error from the combination procedure negligible. However, in the future, as more liquids are captured from natural gas and as the mixture of natural gas liquids shifts toward lighter compounds, consideration might be given to revising the procedure of simply adding data for NGLs to data for crude production. At present, the most appropriate liquid fuel data for our purpose are obtained by adding the UN data for mass of crude petroleum to the UN data for mass of natural gas liquids. The result for world liquid fuel production is given in column 3 of the summary table (Table 14).

The global accounts for world production of liquid fuels consist of data for many parts of the world. In some cases these data appear to be highly reliable, e.g. OECD nations, but in others where smaller resources are committed to documentation, the data are less reliable. The UN staff has attempted to evaluate the reports and make appropriate adjustments when evidence warrants, but quantifying the reliability is impossible. Because most of the crude oil is produced in relatively few countries and because the value of each unit of oil has become so high, we believe that since 1974 the world oil accounts involve uncertainty that does not exceed some ±8%, and would be better if data from Iran and Iraq were more reliable. Before the higher prices and more careful accounting resulting from the 1973–74 embargo, the uncertainty could have been more, but at that time the data from Iran were much better than now, and the data from the US, USSR, and Saudi Arabia have probably been consistently reliable. Information now available is inadequate to allow formal calculations of uncertainties for global petroleum production. We estimate the data for the period before 1974 to contain an uncertainty of ±10%.

3.3. *Production of solid fuels*

Coal is an immensely variable commodity; both its heating value and carbon content vary over wide ranges. The American Society for Testing and Materials (ASTM) scheme for classification of coals by rank (Table 2) makes it clear that tons of "coal" is not a fully adequate value for establishing how much carbon is likely to be released during burning. We need, in addition, some indication of the quality of the coal and this is basically what the UN Statistical Office has tried to achieve in reporting tons of coal equivalent. The UN basis for coal equivalency comprises 29.31×10^9 J/t (7000 cal/g).

Adopting United Nations data for coal production subsumes most of the questions about coal quality in the coal production numbers. When the UN reports coal production in units of tons of coal equivalent, they have already made the conversion, in energy-equivalent units, from a ton of, say New Zealand brown coal, to tons of coal equivalent. We consider how well the UN standard of 29.31×10^9 J/t represents average coal.

That 29.31×10^9 J/t is an appropriate base for coal equivalents is supported by the compilation of Zubovic et al. (1979), who summarized analytical data on 617 bituminous coal samples from the eastern US. The arithmetic mean heating value came out to be 29.45×10^9 J/t (12,670 Btu/lb), the

Table 2. *Classification of US coals by rank*

Class	Group	Fixed carbon limits (%) (dry, mineral-matter-free basis)		Volatile matter limits (%) (dry, mineral-matter-free basis)		Calorific value limits (Btu/lb)* (moist, mineral-matter-free basis)		Agglomerating character
		⩾	<	>	⩽	⩾	<	
(I) Anthracitic	1. Meta-anthracite	98	—	—	2	—	—	non-agglomerating
	2. Anthracite	92	98	2	8	—	—	
	3. Semianthracite	86	92	8	14	—	—	
(II) Bituminous	1. Low volatile bituminous coal	78	86	14	22	—	—	commonly agglomerating
	2. Medium volatile bituminous coal	69	78	22	31	—	—	
	3. High volatile A bituminous coal	—	69	31	—	14,000	—	
	4. High volatile B bituminous coal	—	—	—	—	13,000	14,000	
	5. High volatile C bituminous coal	—	—	—	—	11,500	13,000	
						10,500	11,500	agglomerating
(III) Subbituminous	1. Subbituminous A coal	—	—	—	—	10,500	11,500	non-agglomerating
	2. Subbituminous B coal	—	—	—	—	9,500	10,500	
	3. Subbituminous C coal	—	—	—	—	8,300	9,500	
(IV) Lignitic	1. Lignite A	—	—	—	—	6,300	8,300	
	2. Lignite B	—	—	—	—	—	6,300	

From: ASTM (1974), reproduced with original units for heating value.
* 12,600 Btu/lb = 29.31×10^9 J/t.

geometric mean heating value 29.26 × 10^9 J/t (12,590 Btu/lb). An earlier study by Swanson et al. (1976) led to a mean heating value at 28.50 × 10^9 J/t (12,260 Btu/lb) for 277 bituminous coal samples. The US Bureau of Mines has consistently used a heating value of 29.52 × 10^9 J/t (12,700 Btu/lb) for anthracite.

US BOM and US DOE data show the decreasing higher heating value of bituminous coal and lignite produced in the US (Table 3). The US value has been below 29.31 × 10^9 J/t since 1967 as the electric utility industry has increased use of western coals with reduced heating values. Coal used at large US electric power plants (>25 MW) had an average heating value of only 25.23 × 10^9 J/t (10,850 Btu/lb) in 1976 and 25.63 × 10^9 J/t (11,030 Btu/lb) in 1977 (National Coal Association, 1978). To have the reported amount of coal truly reflect the annual energy use (and carbon content), the UN has countered the decreasing heating values by applying correction factors to lower grade fuels and reporting coal equivalent tons.

Table 3. *Decreasing heating value of produced US coal*

	Higher (gross) heating value[a] (× 10^9 J/t)		Lower (net) heating value[b] (× 10^9 J/t)	
1980		(26.34)[c]	25.03	(25.03)[c]
1979	26.10	(26.31)[c]	24.99	(24.99)[c]
1978	26.10	(26.77)[c]	25.43	(25.43)[c]
1977	26.41		25.54	
1976	26.91		25.58	
1975	26.96		25.63	
1974	27.58		25.21	
1973	27.90		26.55	
1972	27.95		26.59	
1971	28.17		26.80	
1970	28.57		27.17	
1969	28.94		27.51	
1968	29.12		27.68	
1967	29.24		27.80	
1966	29.40		27.97	
1965	29.54		28.10	
1964	29.64		28.18	
1963	29.66		28.22	
1962	29.73		28.26	
1961	29.73		28.26	
1960	29.82		28.35	
1959	29.85		28.39	
1958	30.19		28.72	
1957	30.19		28.72	
1956	30.19		28.72	
1955	30.22		28.72	
1954	30.45		28.93	
1953	30.45		28.93	
1952	30.45		28.93	
1951	30.45		28.93	
1950	30.45		28.93	

[a] 1973–79 data from US DOE (1980a); 1972 and prior from US BOM (1976).

[b] UN (1983).

[c] 1978–80 data in parentheses are from UN (1981a).

Beginning with the publication of *World Energy Supplies 1973–78*, (UN, 1979) the UN staff has made efforts to insure that all coal is adjusted to coal equivalents. Between 1973 and 1979 there were adjustments for low grade hard coals in Norway, United Kingdom, Czechoslovakia, New Zealand, USSR, India, Pakistan, German Democratic Republic, and Hungary (UN, 1979). Prior to 1973, there was adjustment only for USSR and Pakistan. Table 4 shows the progressive changes in world coal production reported by successive UN annual volumes. *The World Energy Supplies* series published prior to 1979, indicate the changes made as a result of additional information or revisions of individual country data. Beginning with UN (1979), changes in the data are larger and consistently downward, reflecting the adjustments for reduced heating value of coals from more and more countries.

The changes between times of publication of UN (1979) and UN (1981b) included not only downward adjustment made for lower grade coals, but also a beginning of a change from a higher heating value to a lower heating value basis ("gross heat value" to "net heat value," in UN terms). Thus, for example, the reduction in the value reported for 1975 between UN (1979) and UN (1982) is 246 × 10^6 t of coal equivalent (9.5%) and is the result of a combination of further adjustments for coal quality plus adjustment to "net heat value." The UN has now completed the shift to a "net heat value" basis for at least 60% of the world coal production. It appears that the coefficient to convert Chinese coal to coal equivalents is also on a "net heat value" basis and this would raise the percentage to 77% of the total world production. Table 3, column 2, gives the heating values used by the UN (1982) when converting tons of US coal to tons of coal equivalent.

Table 4. *World coal production as reported by the UN statistical office in successive annual reports (in 10^6 tons of coal equivalent)*

	World Energy Supplies (annual volumes)				*Yearbook of World Energy Statistics*	
Year	UN (1976)	UN (1977)	UN (1978)	UN (1979)	UN (1981b)	UN (1982)
1979					2737	2614
1978				2784	2608	2476
1977			2775	2763	2570	2447
1976		2714	2702	2650	2482	2393
1975	2634	2640	2633	2577	2427	2331
1974	2513	2517	2503	2457	2325	2234
1973	2481	2483	2470	2426	2308	2220
1972	2439	2438	2426	2384	2275	2191
1971	2398	2397	2395	2362	2256	2173
1970	2420	2397	2399	2356	2260	2179

The UN decision to tabulate coal production on a "net heat value" basis complicates the computation of CO_2 emissions because most coal analytical data provide chemical composition and higher heating value. However, because the UN publications provide the most reliable and consistent set of global data for coal, we will continue to rely on them and make an adjustment to the factor for the carbon content to accommodate the UN use of "net heat values." Thus the UN data for solid fuel production form the base used in calculating CO_2 emissions. These production data for solid fuels are given in column 5 of the summary table (Table 14).

The estimation of uncertainty in the solid fuel data, already difficult, is made even more so because the process of revising the coefficients for coal equivalents is still in progress at the UN (but appears to be nearing completion). With some uncertainty still associated with the change to net heat value, we judge these data to include an uncertainty of around 11%. This is based on an uncertainty of $\pm 5\%$ for the production data in mass units and $\pm 10\%$ for the conversion to a coal equivalence basis. Collecting these as $\sqrt{\sum E_i^2}$, where the E_i's are the individual uncertainty estimates, we have $\sqrt{100 + 25} = 11.2\%$.

3.4. *Flaring of natural gas*

The lack of markets and infrastructure for using natural gas as a fuel leads to massive flaring at oil fields in some remote locations. The UN makes no attempt to tabulate the amounts of natural gas flared from any nation. Data for non-US levels of natural gas flaring prior to 1971 are nonexistent. To develop a usable data set, Rotty (1974) used unpublished gas flaring data for 1968–71 (included on questionnaires returned to the US BOM) with published oil production data from many countries to estimate a time series for gas flaring. Rotty assumed that essentially all gas flared is "associated gas" from oil fields where facilities for the recovery of the gas are not present, and used the ratio of gas flaring to oil production for separate areas of the world. Although Rotty's numbers are somewhat speculative, they contribute a small fraction of the total emissions and are used here for the period 1950–70 without change.

Beginning about the time of Rotty's estimates, the US DOI, and more recently the US DOE, have published annual values for the global flaring of natural gas. We use these data for the years 1971 through 1978 (US DOI, 1974; US DOE, 1979; US DOE, 1980b) but note that the published values are labeled "partly estimated." This data set appears fully compatible with the estimates of Rotty (1974) and this combination provides the best available consistent data sequence for global gas flaring (see Table 14).

Although there is no strong incentive to account for gas flaring, the recent data represent an attempt to account for this loss. Formal calculation of the

uncertainty involved in these data would require more information than is available. The flaring of gas associated with oil production is at best as uncertain as the oil production, but the approximate agreement of the estimates of Rotty (1974) with attempts by the US DOE to tabulate a time sequence of recent global flaring suggests the uncertainty is not unbounded. We lack great confidence in all flaring data (earlier values in particular) and believe an uncertainty of ±20% is appropriate here.

3.5. *Production data versus consumption data*

Carbon dioxide is emitted when fossil fuel is oxidized, i.e., consumed. Global fuel accounts are published as both fuel production and fuel consumption. The difference is not simply an increase or decrease in storage, but includes adjustments for various amounts of the fuel produced that are employed in many different end uses. In addition to use as common fuels and in processing fuels, some is used as special fuel, some as "non-fuel" in which the carbon is quickly oxidized, and some as "non-fuel" in which the carbon remains unoxidized for very long times.

Keeling (1973) elected to use production data and make estimates of the fraction of the fuel that was ultimately oxidized. At that time, fuel accounting for many parts of the world was not sufficiently advanced to provide suitable data sets to account for all the end uses all over the world. Production data have been and are more reliable and consistent from year to year. Using the fuel production numbers to calculate CO_2 emissions can be thought of as metering the man-induced carbon flow from the earth's crust to the atmosphere at the boundary where the carbon crosses the earth's surface.

Use of fuel consumption data might be intellectually more satisfying because it is in the consumption that the CO_2 is produced. However, the consumption data available cover what the UN calls "apparent consumption." The UN obtains "apparent consumption" by adding a country's excess of imports over exports to its production, and subtracting the amount used in bunkers and for increases in stocks. The amounts of consumption as tabulated by the UN have been consistently less than the aggregated amounts of production—even when changes in stocks are considered. Much of the difference appears to be in the use of fuel to produce fuel, particularly the use of oil in refineries to produce those products that make up the consumption numbers.

Coal and gas consumption data can easily give a reasonably accurate picture because very little transformation takes place between the raw (mined) fuel and the fuel used by the consumer. The calculation of emissions from inland consumption data for coal and gas is straightforward and gives results that are consistent and nearly identical with those determined from fuel production data. The fact that global imports of each fuel for a given year almost always exceed global exports indicates that "apparent consumption" data include some accounting difficulty, but the difference is generally about 0.1% of production.

Crude petroleum presents a different problem in that almost none of the fuel is consumed as crude. Rotty (1983) attempted to reconcile the world production of crude petroleum and natural gas liquids with the consumption of liquid fuels and other petroleum products as tabulated by the UN Statistical Office. The balance he achieved for the liquid fuels account for 1979 is indicated in Table 5. In the same paper, Rotty (1983) calculated the 1979 CO_2 emissions from all of the fossil fuels on both production and consumption bases. When all of the fuel consumption data were considered along with properly corrected CO_2-factors, the calculations for 1979 showed a total of 5191×10^6 t of carbon as CO_2. For comparative purposes, the calculations based on production data showed a total of 5224×10^6 t—a difference of 0.6%. (Later in this report 5254×10^6 t C is given as the result for 1979, the difference being a combination of using recently revised UN fuel data and new estimates for (FO) and (C) developed in the following sections.) Clearly, the difference between the result based on fuel consumption data and that based on fuel production data is small in comparison to the probable error in fuel statistics.

Because fuel production and consumption data are so closely linked and because the production data are easier to use and are more reliable as an historic data set, our computations will continue to rely on the fuel production data.

4. Fuel fraction not oxidized

As acknowledged in eq. (1), a fraction of the fossil fuel produced each year is not oxidized

Table 5. *1979 world liquid fuels balance sheet*

Production	Amount (10^6 t)	Consumption	Amount (10^6 t)
Crude petroleum production	3123	Loss of mass in refineries (used as fuel?)	113 (3.5%)
Gain in commerce of crude (imports–exports–increased stocks)	23	Energy products (2817): inland consumption by nations	2605 (80.3%)
		bunkers (international)	152 (4.7%)
Natural gas liquids to refineries	38	increase in stocks	16 (0.5%)
Subtotal, input to refineries	(3184)	loss in commerce of products (exports–imports)	44 (1.4%)
LPG from natural gas	60	Non-energy products (314):	
		rapid oxidation	118 (3.6%)
		slow or non-oxidation	196 (6.0%)
Total	3244	Total	3244

From: Rotty (1983) based on data from UN (1981b).

during time frames of interest here. Part of the unoxidized carbon results from incomplete combustion in burners (resulting in soot and unburned hydrocarbons) and part of it results from diversion of some of the produced "fuel" to non-fuel uses (e.g., use as raw materials for the chemical industries). In this section, we derive values for FO_f in eq. (1), the effective fraction of each year's production which is soon oxidized. In both the fuel and the non-fuel cases, the hydrocarbons not burned are oxidized in the environment with times varying from very short (weeks or months) to many years. In the aggregate, this slow (non-combustion) oxidation could be approximated by an exponential decay law. In such a situation, over long-time scales, the amount oxidized each year will equal the amount produced each year as long as the amount produced each year is nearly constant. When the average lifetime of the unoxidized materials is very long or when the amount produced each year is growing, there is a net amount that remains unoxidized. We suggest that when the mean life of a species exceeds some 6 to 10 years and the production rate is growing, the total amount not oxidized in a given year can be approximated as a fraction of that year's production, and this is what is implied in speaking of "long-lifetime products." Attempting to estimate production growth rates and decay rates for each unburned or incompletely oxidized hydrocarbon species would become extremely involved. Instead we have aggregated for all liquid fuels and have made subjective estimates of the extent to which production and net oxidation are likely to differ during a given year. Although this is never fully satisfying, it is important to recognize that most of the hydrocarbons are oxidized as fuels and that the data cited do provide close bounds for the fractions which are likely not to be oxidized. The probable error introduced through this aggregation and estimation procedure is small in comparison to uncertainties in the fuel production data, and more rigorous examination of the non-combustion oxidation rates does not seem justified for the calculation of CO_2 emissions.

4.1. *Natural gas produced but not oxidized*

As illustrated in Fig. 1, most of the natural gas produced in the United States is used for fuel. Data required to obtain the non-fuel use of natural gas globally are not available in formal references, so we have based our estimates on what data are available for the US. Non-fuel gas use in the United States is no longer being published by the US DOE, but we note the mean value for 1970–76 is 3.16% of production (Table 6). The lack of markets and infrastructure for using natural gas as a fuel leads to massive flaring at oil fields in some parts of the world and also leads us to expect that the fraction of marketed gas that ends up in non-fuel uses may be significantly larger in those areas than in the US. On the other hand, the total world production is still dominated by countries like the US, the UK, Canada, and the Netherlands where gas is largely used as a fuel. Based on the data for the US given in Table 6, we estimate that global non-fuel use of gas is about 3% of production. Because the non-fuel use is small, any error in

Table 6. *Non-fuel use of US natural gas (10^9 m^3)*

Year	Gas production	Non-fuel use	Non-fuel as a % of production
1976	540.6	17.4	3.22
1975	545.1	16.8	3.09
1974	580.8	20.1	3.46
1973	615.8	19.8	3.22
1972	618.8	18.5	2.99
1971	618.6	18.4	2.97
1970	601.3	18.9	3.14
1970–76 average			3.16

Gas production data from UN (1981b) (heating value of US natural gas taken to be 38,017 kJ/m³); non-fuel use is from API (1977).

basing the estimate on the biggest producers gives uncertainties that are small fractions of total marketed production. A large fraction of the non-fuel gas goes to ammonia production during which the carbon in the gas is mostly oxidized, the remainder to uses in which the carbon will be oxidized at varying rates over a period of years. The total quantity for non-fuel use has been increasing with time and, in accord with the principle that slowly oxidizing material decays exponentially with time, this suggests that a small amount of unoxidized gas accumulates each year. As a result of increasing non-fuel use and the production of long-lifetime products, we assume that over time, an amount of carbon equivalent to 2/3 of the carbon in each year's non-fuel-use gas is oxidized during that year. Because non-fuel use is 3% of production, this is the same as assuming that, on the average, 1% of each year's produced gas remains unoxidized for long periods as a result of non-fuel uses. Although not clearly related to fossil fuel production, recent measurements do show an increasing atmospheric concentration of methane (Rasmussen and Khalil, 1981).

Because of incomplete combustion, a small amount of the carbon in the gas used as a fuel will not be oxidized and will remain as soot either around the burner, in the stack, or in the environment. Although the amount of unoxidized carbon is impossible to determine on a global scale, it is extremely small in modern combustion systems and we use, as an upper limit, that 1% of the carbon in gas produced globally remains unoxidized during combustion processes.

For natural gas, the fraction of annual production remaining unoxidized each year is thus taken to be 0.02, i.e. 0.01 for unoxidized non-fuel uses and 0.01 for unoxidized carbon in combustion. The sequence of assumptions here imposes an uncertainty on the gas oxidized of about 1% of the gas produced. Thus the fraction of gas oxidized is $FO_g = 0.98 \pm 0.01$.

4.2. *Liquids produced but not oxidized*

A key question for CO_2 production from crude oil and natural gas liquids is the fraction of production which is burned or otherwise oxidized on a short time scale as opposed to that which ends up in e.g., fibers, lubricants, or paving materials, and is oxidized only over a longer interval.

The UN statistics separate refinery output into energy products (aviation gasoline, motor gasoline, jet fuel, kerosene, gas-diesel oil, residual fuel oil, LPG, and refinery gas) and non-energy products (naphthas, white spirits, lubricants, bitumen (asphalt), petroleum waxes, petroleum coke, and others) with the non-energy products comprising 10.2% of the total in 1979. UN data also distinguish the components of natural gas liquids (natural gasoline, condensate, LPG, and "other natural gas liquids"). With the exception of some of the LPG, most of the natural gas liquids are consumed as fuels.

Turning again to US data for guidance, we find in Fig. 2 that about 12% of US refinery output in 1981 is "other" products. Table 7 subdivides this "other" category and allows identification of petroleum fractions which are used in ways that do not lead to immediate oxidation. In addition, a major fraction of the liquified petroleum gases and ethane in Fig. 2 may not undergo prompt oxidation. The total remaining unoxidized depends to a large degree on both the amounts used in the petrochemical industry and the way in which those products are used. Without a belabored analysis of the world petrochemical industry, we use US data as an analog in making estimates of unoxidized carbon from UN data. Starting with the UN tabulations for refinery non-energy products and the LPG and ethane from gas liquids plants, we estimate the fraction that is likely to remain unoxidized for long periods of time.

Most of the LPG from refineries is probably consumed as fuel and the UN lists LPG as an energy product from refineries. Therefore, we

Table 7. *1981 US refinery output of "other" products (see Fig. 2) (10^6 t)*

Natural gasoline	4.2
Unfractionated stream	Neg.
Aviation gasoline	1.3
Petrochemical feedstocks	23.9
Special naphthas	3.1
Lubricants	8.0
Wax	0.9
Coke	16.7
Asphalt	20.5
Road oil	0.1
Still gas for fuel	23.6
Miscellaneous products	4.9
DOE reclassification (adjustment)	−13.3
	93.9

From: US DOE (1982b). (All products converted from barrels to tons using factors in UN (1982) except petrochemical feedstocks and still gas at 0.1144 t/bbl, wax and road oil at 0.1431 t/bbl and unfractionated, miscellaneous and reclassified at 0.1350 t/bbl.)

estimate the amount of LPG and ethane that is used in the petrochemical industry as a fraction of only the LPG and ethane produced in natural gas liquids plants. This does not imply that all the LPG used in the petrochemical industry comes from gas processing plants, but only that the global quantity can be estimated as a fraction of the LPG produced in gas processing plants. In the US, the LPG and ethane sold for chemical and industrial uses in 1981 represent 50.7% of that produced in gas processing plants. The industrial sales include use as a standby fuel, in space heating, flame cutting, metallurgical furnaces, and plumber's torches. They also include sales for use as refinery fuel. Chemical use includes those gases employed as raw materials, solvents, and in the production of synthetic rubber. Data for 1981 are not available, but in 1979 the split was 80% to chemical use and 20% to industrial fuel use. Thus, the equivalent of (0.8)(50.7) = 40.6% of the LPG and ethane produced in US natural gas liquids plants is used in applications in which oxidation occurs very slowly. Because the petrochemical industry outside the US depends more heavily on feedstocks from refineries, especially certain naphthas, we estimate that, on a worldwide basis, about 40% of the LPG and ethane produced from natural gas processing plants ends up in materials which are not soon oxidized. (That is, for a given year, oxidation of current year production plus the sum from continuing oxidation of previous year's production amounts to 60% of current year production.)

In the UN tabulation of non-energy refinery products, what is defined as naphthas is largely used as chemical feedstocks, and nearly half of the petrochemical feedstocks in Table 7 is naphtha. This is a major feedstock to the western Europe petrochemical industry and we estimate that about 80% of the naphthas produced globally remain unoxidized for long times in plastics, tires, and fabrics.

A substantial part of the non-energy refinery products is asphalt. Even when paved roads, parking areas, and roofs deteriorate or are removed, most of the asphalt remains in an unoxidized state. Thus, assuming that virtually all of the UN reported asphalt production from petroleum refineries remains unoxidized for long periods, introduces a small overestimation. Petroleum waxes are used in manufacture of candles, polishes and water-proofing of containers, wrappings, etc. White spirits are used as paint solvents and as dry cleaning materials. Petroleum coke is mostly used in metallurgical processes and the fraction of the carbon that remains unoxidized is probably small. We estimate that these non-energy products except asphalt are mostly oxidized rather promptly and that assuming full oxidation introduces small error of opposite sign from assuming that all asphalt is not oxidized.

The UN category of lubricants gives us a problem because a non-negligible part of lubricating oil is oxidized in use. Spillage and oil drained from engines are frequently flushed into other waste liquid streams or disposed of in absorbants or containers in land fills. We have used the estimate that approximately 50% of lubricants produced by petroleum refineries remain unoxidized for long periods of time.

Our assumption is that, allowing for errors of both inclusion and omission, the quantity of liquid fuels not oxidized each year is approximated by the sum of 40% of the LPG and ethane from gas liquid plants, 80% of the naphthas from petroleum refineries, all of the asphalt, and 50% of the lubricants. This is summarized in Table 8. The conclusion is that 6.5 to 6.9% of petroleum liquids is not soon oxidized and we adopt 6.7% for our computations. For comparison Hatch and Matar

(1977a) reported that in 1974, 6.5% of world crude went into petrochemicals. Also, Flavin (1980) estimated that 1979 production of synthetic materials amounted to 10×10^6 t of synthetic rubber, 10×10^6 t of synthetic fiber, and 60×10^6 t of plastic. The sum of the unoxidized LPG, ethane and naphthas in Table 8 is 93.5×10^6 t. Our analysis suggests it is unlikely that the true value of unoxidized liquids is greater than 8.7% or less than 4.7% of annual production.

Having based this analysis on data for the last decade, there remains the question of changes in the unoxidized fraction during earlier decades in the 1950–82 period. UN data on non-energy products from refineries for 1970–80 published in UN (1981b, 1982) differ markedly from those published in UN (1976), the most recent figures being, on average, a factor of 1.33 larger for the 5 years of overlap. Thus, we assume that data for non-energy products before 1970 are subject to sizable revision and a better estimate of non-oxidative uses can be obtained by applying a 1971–80 average to the crude production uniformly rather than trying to itemize non-energy uses. API (1975) data also suggest that the time-dependent bias implicit in carrying a constant fraction back to 1950 is small. Lacking better information, we shall use the 6.7% factor for the entire 1950–82 period.

The other situation for which we should make some adjustment in the CO_2 computation is the failure to achieve 100% combustion of fuels actually delivered to burners. Carbonaceous materials that are discharged not completely oxidized include those, like CO, which undergo complete oxidation fairly promptly in the environment; others, like soot, which do not oxidize to a significant degree on time scales of interest here; and others, like methane, which oxidize in the environment at a rate such that some finite fraction is oxidized in the first and each succeeding year of interest. For this third class of compounds, any difference between the total amount of carbon being oxidized in a given year and an estimate thereof based on full oxidization of current year discharge must be a consequence of an increase in production rate. The simple assumption of an equivalent fraction of material not oxidized during a current year will not introduce significant error so long as the total fraction of material in this class is small.

To estimate the fraction of liquid fuel which goes to burners but is not fully oxidized, we used US EPA estimates of nationwide pollutant emissions in the United States (US EPA, 1977). In 1976, US emissions of hydrocarbons to the atmosphere amounted to 27.9×10^6 t, of which 14.7×10^6 t were related to transportation and oil and gas refining, production, and marketing (Table 9). Another 1.4×10^6 t were from stationary fuel combustion sources. Of the 13.4×10^6 t of total suspended particulates discharged to the atmosphere, 1.3×10^6 t were from transportation and

Table 8. *Estimate of world petroleum liquids produced but not oxidized each year (10^6 tons)*

	40% of LPG and ethane from gas plants	80% of naphtha	Asphalt	50% of lubricants	Total	% of liquids produced
1980	25.8	58.5	97.9	19.6	201.9	6.53
1979	26.0	67.5	101.5	19.7	214.7	6.63
1978	23.4	66.0	97.8	18.4	205.6	6.62
1977	23.2	66.4	91.4	17.6	198.5	6.45
1976	22.2	65.9	85.9	16.5	190.5	6.44
1975	21.9	56.2	85.7	15.6	179.4	6.57
1974	21.8	70.9	88.1	17.2	198.0	6.88
1973	21.2	70.6	90.0	16.5	198.4	6.92
1972	20.2	60.7	83.6	15.2	179.7	6.83
1971	18.5	55.4	80.4	14.8	169.1	6.79
						av. 6.67

1976–80 data from UN (1982).
1971–75 data from UN (1981b).

Table 9. *1976 US emission of hydrocarbons and total suspended particulates** (10^6 *t/yr*)

Source category	TSP	HC
Transportation	1.2	10.8
highway vehicles	0.8	9.3
non-highway vehicles	0.4	1.5
Stationary fuel combustion	4.6	1.4
electric utilities	3.2	0.1
industrial	1.1	1.2
residential, commercial and institutional	0.3	0.1
Industrial processes	6.3	9.4
chemicals	0.3	1.6
petroleum refining	0.1	0.9
metals	1.3	0.2
mineral products	3.2	0
oil and gas production marketing	0	3.0
industrial organic solvent use	0	2.9
other processes	1.4	0.8
Solid waste	0.4	0.8
Miscellaneous	0.9	5.5
forest wildfires and managed burning	0.6	0.8
agricultural burning	0.1	0.1
coal refuse burning	0.1	0.1
structural fires	0.1	0
miscellaneous organic solvent use	0	4.5

* From: US EPA (1977).

petroleum refining with another 4.6×10^6 t from stationary fuel combustion sources. Table 9 lists emissions from many sources, but we are concerned here only with those associated with combustion of liquid fossil fuels, having already discounted quantities for non-fuel uses such as organic solvents.

In these calculations, we assume that 1/2 of the hydrocarbons and 1/4 of suspended solids from stationary fuel combustion represent carbonaceous materials attributable to burning liquid fuels, the remainder being from other fuels. Then, for the United States, 15.4×10^6 t of hydrocarbons and 2.5×10^6 t of suspended carbonaceous particulate material represent incompletely oxidized liquid fuels from combustion applications. If this material undergoes oxidation in the environment with time (some of it very slowly), we can consider that some fraction of 17.9×10^6 t represents the portion of the 1976 US liquid fuel consumption which should not be counted as CO_2 production.

Many of the hydrocarbons emitted, especially from engine exhausts, are partially oxidized and hence highly reactive (NRC, 1979). Data on selected urban aerosols suggest that the aerosols are of the order of 20% carbon and that 30–40% of this carbon is graphitic soot and the remainder primary and secondary organic material (NRC, 1979). The total, 17.9×10^6 tons, represents about 2.4% of the 751×10^6 tons of liquid fuels consumed in the US in 1976. Because a fraction of the 17.9×10^6 tons is oxidized in the environment in a relatively short time, something approximating $1.5 \pm 1\%$ of the liquid fuel that goes to burners each year remains in the environment unoxidized.

The US data can only provide a useful approximation of the extent of unburned material globally. The amount unburned is clearly a small fraction of the total and we note that US emissions of some materials have declined in recent years because of technological improvements. Our procedure probably gives low estimates of global emissions of unburned carbon (and hence high CO_2 estimates). In addition, the assumption of a constant 1.5% for the unburned fuel introduces some time-dependent bias in the estimate.

The total mass of liquid fuels lost directly to the environment is not large in comparison to the amount produced. Oil spills at sea amounted to 237,600 tons in 1978 (UN Environment Programme, 1979) and there are smaller but much more numerous losses throughout the processing/delivery system. Loss of organic compounds as liquid effluent at an oil-fired power plant is estimated to be of the order of 15% of the airborne hydrocarbons (UN Environment Programme, 1979). None of these is large enough to make a significant correction to the calculations already detailed.

In summary, about $6.7 \pm 2\%$ of the liquids produced end up in petrochemical applications where they are not soon oxidized and another equivalent fraction of $1.5 \pm 1\%$ passes through burners and is deposited in the environment without being oxidized. We believe the factor for oxidation of liquid fuel produced is $FO_l = (1 - 0.082) = 0.918 \pm 0.03$.

4.3. *Solid fuels produced but not oxidized*

Incomplete combustion results in the discharge from boilers of coal dust, gaseous hydrocarbons, and unburned char. The concentration of carbon monoxide (CO) in flue gas can be used as a first-order indicator of the completeness of the combustion process and data on CO emissions collected

by the US National Air Pollution Control Administration (1970) show that emission factors depend strongly on the type and size of the coal-burning unit. Carbon monoxide emissions per unit of energy can be two orders of magnitude larger from small and/or less efficient units than from large, modern pulverized-coal boilers. Any attempt at a general, time-independent factor to compensate for incomplete combustion must recognize that, e.g., 82% of the US coal consumed in 1981 was burned in utility boilers while only 17% was so burned in 1949 (Fig. 3). Transportation accounted for 15% of US consumption in 1949 and virtually none in 1981. Employing a constant for the unburned fuel fraction for both current US electric utility boilers and steam locomotives is, of course, only marginally justifiable, and then only because the total fuel used in locomotives (in 1949, for example) was of the order of 10% of present solid fuel use.

The UN Environment Programme (1979) has estimated that of 3×10^6 t of coal burned in a 1000 MW(e) power plant, 860 t of carbon end up in CO, 3000 t as particulates, and about 400 t in unburned hydrocarbons. If we assume, as a first approximation, that the CO and unburned hydrocarbons are soon fully oxidized in the environment (Chameides and Davis (1982) show the lifetimes of CO and methane in the atmosphere as about 65 days and 7 years, respectively) while the particulate matter remains largely unoxidized, the unoxidized fraction will amount to only 0.14% of the carbon. As an extreme example, Harding (1920) has written "probably the worst fuel loss that a locomotive fireman has to contend with is that which occurs through the escape of unburned fine coal. When the percentage of fine coal is very high, this loss may amount to one-quarter or even one-third of the coal fired," and "even at best there is considerable fuel loss through soot."

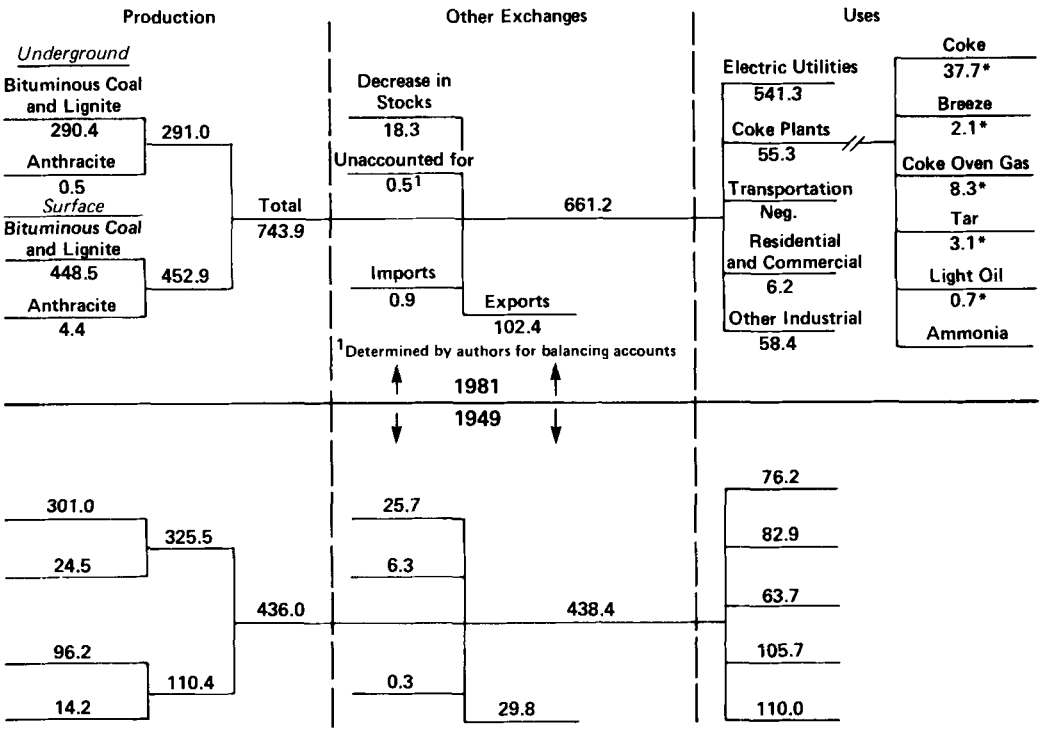

Fig. 3. US flows of coal in 1981 and 1949 (in 10^6 t). Data from US DOE (1982c, 1982d).
The most recent data available for coke plant products are for 1980 when 60.5×10^6 t of coal were consumed by coke plants. Data are in coal equivalents with both data and heating values taken from US DOE (1982d). Coke converted to coal equivalents at 0.9 from UN (1982).

Block and Dams (1976) compared the composition of fly ash from an industrial boiler (24-h capacity of 14 t of coal) with that of a small home furnace in Belgium (24-h capacity of 0.024 t of coal). The concentrations of inorganic components in fly ash from the home furnace were 2–10 times smaller than in the industrial boiler, apparently due to dilution with large emissions of unburned material. Unburned material comprised about 35% of the fly ash from the home furnace.

Another useful perspective can be obtained by examining data from current large coal consumers. Data on combustion efficiency at the Tennessee Valley Authority's Bull Run Steam Plant show that 1% of the stack ash is combustible matter; for the Shawnee Plant, 5% is more typical, and during a recent period of poor performance the Widows Creek Plant ran between 9 and 20% combustible matter in the fly ash (J. Lokey, 1981, personal communication). Because these plants operate on pulverized coal with about 80% of the ash being collected by the stack precipitators, this is probably representative of the average fraction of unburned coal. Taking a representative value of mean ash content for the coal of about 12%, between 0.14 and 2.7% of the combustible fraction of the coal remains unburned. Typical values are near 0.7% and the lower limit is similar to the UNEP number cited above. The Belgian home mentioned above was burning anthracite with 3.1% ash, implying that 1.1% of the coal was discharged unburned.

With this information, it seems reasonable to assume that above 1 ± 1% of the carbon in coal currently supplied to furnaces is discharged unoxidized. Using this fraction over the full 1950–present interval probably introduces a time-dependent bias because the number has almost certainly been decreasing with time.

The other adjustment for unburned coal has to do with coal which is used for non-fuel purposes. Fig. 3 shows the flow of US coal from the mine to the sectors in which it is ultimately consumed and allows identification of the principal portion which is not used as a fuel. Of coal which is used for cooking, two by-products form the bases for a very large chemical industry—the crude light oil and crude tar of Fig. 3. The quantities of light oil and tar shown in the figure are given in coal equivalents by heating value. Of the coal tar fraction, some 21% is typically used for fuel while benzene (21%), crosote oil (20%), and road tars (17%) are the other principal products (Wainwright, 1977). Benzene, toluene, and xylene typically account for 75% of the crude light oil.

Thus it appears that about 75% of the coal equivalents which are accounted for as light oil and tar represent the coal which ends up in applications where oxidation is long delayed. From US data, Table 10 shows that on average 5.91% of the coal going to coke plants ends up as light oil and crude tar, and 75% of that, or 4.4% has oxidation long delayed. Using this number and statistics for world coke, we can estimate the fraction of the global coal production that does not enter the CO_2 route. This calculation of the mass of US non-fuel coal use agrees within 5% with the numbers compiled by Dupree and West (1972).

There are three other considerations associated with coal production that could affect CO_2 releases. These are burning of wasted coal on abandoned mine lands, methane ventilated from coal mines, and the use of SO_2 scrubbers at coal-burning plants.

Chaiken (1980) cites a 1968 US BOM survey that found 292 waste banks on fire, and in a 1977 survey, 261 coal deposits in the US were classified as burning. The 292 waste banks contained an estimated 49×10^6 t of coal. Even if all of this coal was burned over a 10-year period it would still amount to less than 1% of US coal consumption.

Table 10. *Light oil and tar produced from coal in US coke plants (in 10^6 t coal equivalent by heating value)*

Year	Crude light oil and crude tar	Coal to coke plants	% coal converted to light oil and tar
1980	3.63	60.51	6.00
1979	4.01	69.94	5.74
1978	3.68	64.77	5.68
1977	4.03	70.49	5.72
1976	4.36	76.84	5.68
1975	4.40	75.84	5.80
1974	4.68	81.83	5.71
1973	5.01	85.37	5.87
1972	5.04	79.56	6.33
1971	4.61	75.48	6.11
1970	5.25	87.54	6.00
1969	5.36	84.73	6.33
		12-year mean	5.91

From: US DOE (1982c, 1982d) and US BOM (1973).

Although it is difficult to estimate tonnages involved, burning in coal deposits is probably no greater than burning on waste piles. The US EPA (1977) has estimated that coal refuse burning contributes 0.3% of US carbon monoxide emissions, but because refuse burning occurs in an oxygen-deficient environment, the contribution to carbon monoxide discharge should be a much larger fraction than the contribution to carbon dioxide discharge. Thus much less than 0.3% of the CO_2 emissions can be attributed to this source, and ignoring this as a source of CO_2 seems to be justified.

In considering methane ventilated from coal mines, the content of gas in coalbeds varies considerably but Science Applications, Inc. (1980) estimates an average of 6.25 m^3/t in bituminous coal and anthracite, 2.5 m^3/t in subbituminous coal, and 1.25 m^3/t in lignite. Coal mined in the US in 1979 was composed of 622×10^6 t of bituminous coal, 109×10^6 t of subbituminous, 43×10^6 t of lignite, and 4×10^6 t of anthracite (US DOE, 1981). The ratio among the four types is 0.799/0.140/0.055/0.006 (although this has been changing in recent years with increasing amounts of lower grade coal being used) and using methane emission rates of 6.25/2.50/1.25/6.25 cubic meters per ton respectively, the total methane emissions from US coal mined in 1979 were (at an average of 5.45 m^3/t) 4.24×10^9 m^3. Fully oxidized, this would produce 2.16×10^{12} g C as CO_2. Again this number is a very small fraction of a percent of the emissions from coal burning and will be ignored.

The use of SO_2 scrubbing at coal burning plants is still at a sufficiently small scale that it too can be safely ignored as a source of CO_2 to the atmosphere. Coal with 1.5% S and 29.31×10^9 J/t (12,600 Btu/lb) would discharge 1.025 g SO_2 per J (2.381 lb per 10^6 Btu). If SO_2 emissions were limited to the current 0.258 g/J (0.6 lb $SO_2/10^6$ Btu), scrubbing would have to collect 0.0112 t S per ton of coal or 1.781 lb $SO_2/10^6$ Btu. Approximating the SO_2 scrubbing reaction as a stoichiometric exchange of C for S in the gas phase means that the collection of 0.0112 t S would release 12/32 (0.0112) = 0.0042 t C/t coal. Widespread use of SO_2 scrubbing in the future could result in a small but measurable increase in the CO_2 emission rate.

The conclusion at this point is that from the total mass of coal mined (in tons coal equivalent on a 29.31×10^9 J/t basis) we will subtract 4.4% of the mass which goes to coke plants (about 0.8% of the coal mined) to accommodate long-term non-oxidative uses, and subtract 1% of the remainder to accommodate the fraction which passes through furnaces without being oxidized. Our factor for oxidized fraction of world solid fuel production is thus $FO_s = (1 - 0.008)(1 - 0.01) = 0.982 \pm 0.02$.

5. Carbon content of fuels

The remaining component required to calculate CO_2 emissions is the global average carbon content of each fuel group (C_i in eq. (1)). Because carbon content is correlated with heating value, and because the UN tabulation of gases is in terajoules and of solids in tons of coal equivalent at 29.31×10^9 J/t (7000 calories per gram), the resulting calculations are straightforward.

5.1. *Gases*

Although there are compositional data available for many individual natural gases, we have been unable to locate any statistical summary of the composition of natural gases produced over large geographic areas. From the analytical data for 252 well-head samples of wet gas from 17 states as analyzed by the US BOM in 1976 (Moore, 1977), we eliminated those few samples least likely to be produced as fuels or indicating contamination (i.e., those with heating values less than 33,510 kJ/m^3 (900 Btu/SCF) or oxygen concentrations greater than 0.2%). For the remaining data, a mean composition was calculated for samples from each state having data available; then these state means were weighted according to the marketed production for that state and a "weighted mean" for the United States as a whole was calculated (Table 11, column 1). This we call the 1976 US reference gas. For comparison, a similar "weighted mean" from the 373 samples analyzed in 1970 (Cardwell and Benton, 1971) was calculated and, using their 1970 data, simple unweighted national means and standard deviations were tabulated (Table 11, columns 2, 3, and 4).

Similarly, 174 non-US samples from 18 countries were used to calculate individual country means; data from these 18 countries were combined with the US data by weighting each according to 1970 production statistics to produce a world mean

Table 11. *Composition of natural gas (in volume percent)*

	1976 US reference gas	1970 weighted US mean	1970 unweighted US mean	1970 unweighted US standard deviation	Weighted world mean (circa 1970)	1976 adjusted dry gas
methane	88.32	89.32	86.63	9.63	89.24	92.88
ethane	4.65	4.66	5.02	3.52	4.52	3.91
propane	2.12	2.04	2.57	2.56	1.95	0.62
other Hydrocarbons	1.53	1.56	1.88	—	1.54	—
CO_2	0.92	0.65	0.63	1.11	0.78	—
other	2.46	2.33	3.26	—	2.42	2.59
Higher heating value						
kJ/m³	40,530	40,680	41,250	4,230	40,500	38,090
(Btu/SCF)	(1088)	(1093)	(1108)	(114)	(1088)	(1023)

Table 12. *Mean heating value of dry natural gas*

	US[a] (kJ/m³)	World[b] (kJ/m³)
1980		36,920
1979	37,940	36,980
1978	37,940	37,030
1977	38,020	37,040
1976	38,020	37,090
1975	38,120	37,130
1974	38,020	37,210
1973	38,240	37,330
1972	38,390	37,340
1971	38,390	37,360
1970	38,390	37,470
1969	38,390	
1965–68	38,430	
1964 and before	38,540	

[a] From American Gas Association (1979), except 1979 value from US DOE (1980a).

[b] These values are derived by using a representative (constant) heating value of gas from individual countries as reported in the UN (1982), and calculating a weighted mean, based on annual production statistics. The weighted means are based on the 6 countries that have dominated world gas production over the last decade: US, USSR, Netherlands, Canada, UK, and Romania. The decline in the heating value so determined is a consequence of changing fractions of world total being supplied by the USSR and Netherlands.

composition (Table 11, column 5) (data from Moore (1976)). This aggregation includes countries which represent 75% of the world production, but does not include the USSR.

The 1976 US reference gas composition (Table 11, column 1) should closely describe natural gas reported by the US BOM and US DOE as "marketed production." Marketed production means wet gas and the "extraction loss" shown in the gas flow accounts represents processing to remove liquids which subsequently appear in the accounts as "natural gas liquids." The change in gas composition which occurs during the removal of natural gas liquids results in a reduction of heating value. For dry natural gas delivered to customers in 1976, the American Gas Association (1979) reports 38,020 kJ/m³. Taking the 1976 reference gas, assuming removal of 20% of the ethane, 72% of the propane (Hatch and Matar, 1977b), all of the heavier hydrocarbons, and all of the H_2S, CO_2, and H_2O, the resulting gas (Table 11, column 6), has a calculated heating value of 38,090 kJ/m³. This adjusted "dry gass" should closely resemble the composition of gas delivered to US customers in 1976 and that counted by the UN as gas production. For other years, the composition should be closely approximated by using the same wet gas composition and adjusting to the heating value of delivered gas, as published by the AGA (see Table 12). This is done by removing appropriate amounts of "natural gas liquids," ethane and heavier hydrocarbons, and recognizing that this removal has become increasingly efficient with time.

The 1976 adjusted dry gas contains 0.550 g C/l at 0 °C and, with the separated CO_2 included, would discharge 0.555 g C/l as CO_2 when completely oxidized. Adjusted to 15.6 °C (60 °F), the temperature at which US gas volumes are measured, and assuming ideal gas behavior, this amounts to 525.4 g C/m^3 or 13.81 t C/TJ (tons of carbon per terajoule). Doing similar calculations for the other mean gas compositions, we found that the carbon content per unit of energy could be closely represented by a linear relationship with heating value.

This relationship is expressed by the equation,

$$C_g = 13.708 + 0.0828 \times 10^{-3} (\Delta H_H - 37.234) \quad (3)$$

where C_g is the amount of carbon (in t C/TJ), and ΔH_H is the higher heating value of the gas (in kJ/m^3 at 15.6 °C). Eq. (2) shows that the carbon content per unit of energy of the gas is not very sensitive to the heating value of the gas. Even though the heating value of "average" natural gas has changed slightly with time (as shown in Table 12), little information is lost by assuming a time-averaged heating value. The 1970–80 world average is 37,170 kJ/m^3. For the following reasons we have adopted the upward rounded value of 37,200 kJ/m^3:

1. Heating values for individual countries are not well-known, but the UN reports larger values for most small producers not included in our average,
2. The pre-1970 values were probably higher because US gas made up a larger fraction of the total,
3. The carbon calculation is not very sensitive to small changes in heating value.

The regression equation then gives C_g = 13.7 t C/TJ, and implies that "average" natural gas contains 510 g C per m^3. The value for carbon content of gases obtained by this procedure appears to be accurate to within ±2%.

For flared gas there are no data from which to estimate the carbon content directly. Because flared gas is largely associated gas from oil fields, it seems unlikely that its heating value is as low as is suggested by the heating value we have used for our global mean gas (heavily affected by Soviet gas). Although some gas is flared without processing, in other cases gas liquids are recovered before flaring. In view of these considerations, the assumption that gas flared globally has a carbon content close to that of dry gas marketed in the US (525 g C/m^3) appears reasonable. Because flared gas almost certainly contains more carbon than the "average" global gas (510 g C/m^3), and gas with more than 540 g C/m^3 would be most unusual, the uncertainty on the assumed value of 525 g C/m^3 is taken to be ±3%.

5.2. *Liquids*

Crude oil is a complex collection of hydrocarbons with about 600 individual hydrocarbons identified to date (Hunt, 1979). The American Petroleum Institute's detailed analysis of Ponca City Crude isolated some 295 hydrocarbons which made up 60% of the total crude. "The remaining 40% undoubtedly consists of thousands of compounds many of which will never be identified" (Hunt, 1979, p. 34). Petroleum is the raw material for an estimated 7000 end-use chemicals. Thus the analysis of crude petroleum for CO_2 emissions could be extremely complex.

Variations in petroleum are most often expressed in terms of its specific gravity at 15 °C (60 °F). The API gravity, where

$$\text{API gravity} = \frac{141.5}{\text{specific gravity}} - 131.5, \quad (4)$$

is an indication of the molecular size, carbon/hydrogen ratio, and hence carbon content of a crude oil. Coleman et al. (1978) have assembled analytical data, including API gravity, for 800 important US crudes representing major fields and producing formations. The gravities of this sample varied from 8.9° API (specific gravity = 1.0078) to 62.9° API (specific gravity = 0.7279) with a mean of 34.75° API (specific gravity 0.8511) and a standard deviation of 7.71° API. There is a similar diversity among major world sources of crude and even for the US, the mean of 34.75° API is only indicative because it treats all 800 analyses equally without regard for production rate. According to Carter (1979), the average gravity of world crude varied between 32.0 and 32.9° API for the years 1970–79 and might be expected to drop only slightly lower over the next 5 years. Carter shows North American averages between 31.8 and 32.2 for those years.

For converting volume to mass units, the UN (1982) assumes US crude oil has a specific gravity of 0.848 (35.4° API). We used UN single-country values for specific gravity and took the weighted

average value for the 10 largest crude-producing countries in 1978 (77% of the total). The result was a specific gravity of world crude of 0.857 (33.6° API). Considering this in combination with Carter's conclusion, world average crude appears to have an API gravity of 32.5° ± 2°.

In Fig. 4 we have plotted percent carbon versus API gravity for a few typical North American crudes (Marks, 1978). There is a good correspondence between percent carbon and gravity with 32.5° API suggesting a composition of about 85.25% carbon. Brame and King (1967) give a range of 79.5–87.1% carbon for crudes, with a mean of 84.5% carbon and Hunt (1979) also lists 84.5% as the carbon content of crude oil. The mean carbon content of crude oil will vary slightly from year to year as the distribution of sources changes, and we conclude that $C_1 = 85.0 \pm 1.0\%$ carbon should adequately describe the mean composition of world crude oil during the period of interest here. Because natural gas liquids comprise only 3% of the total liquids, little error can be introduced by applying this factor to the sum of crude petroleum and natural gas liquids, as pointed out above.

5.3. *Solids*

As indicated earlier, the UN now attempts to evaluate coals and tabulates production in the energy units "tons coal equivalent" at 29.31×10^9 J/t (7000 cal/g). The correlation between heating value and carbon content suggests that we can establish estimates for carbon content using the knowledge that the UN has considered the heating value in their published production data. That the correlation between heating value and carbon content is good but not perfect is seen clearly in attempts to write formulas for calculating heating value from chemical analyses. For example, one such attempt arrived at the formula:

$$\Delta H_H = 146.58\,C + 568.78\,H + 29.4\,S - 6.58\,A - 51.33\,(O + N) \quad (5)$$

where ΔH_H is the higher heating value in Btu/lb and C, H, S, A, and $(O + N)$ are weight percents, respectively, of carbon, hydrogen, total sulfur, ash, and oxygen plus nitrogen by difference (all on a moisture-free basis). While this was the most successful of five published equations which were evaluated by the Institute for Gas Technology (1978), when calculated and measured values for 775 US coals (including lignites and subbituminous coals) were compared, the average of the absolute value of the differences was 93 Btu/lb (0.22×10^9 J/t). It is clear that whether or not the precise expression of eq. (4) is used, having the heating value of coal makes it possible to estimate the carbon content.

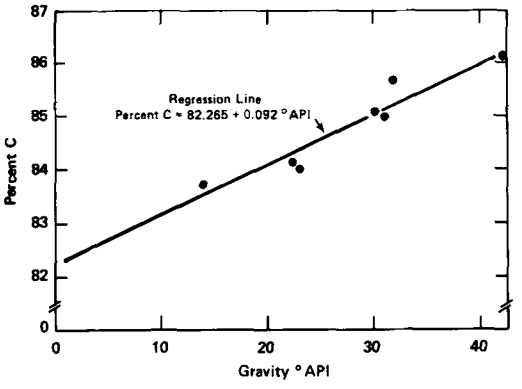

Fig. 4. Percent carbon as a function of specific gravity for samples typical of North American crude petroleum. Data from Marks (1978).

A higher heating value of 29.31×10^9 J/t is a reasonable standard for coal equivalents and until recently it was the standard employed in the UN data tabulations. To determine the factor C_s to be used in eq. (1), it is then necessary to establish the average carbon content of 29.31×10^9 J/t coal. Although the carbon content of solid fuels is variable, for 29.31×10^9 J/t coal, close definition is possible. For the Zubovic et al. (1979) compilation of coal analyses (mean heating value of 29.66×10^9 J/t), the arithmetic mean carbon content was 70.9% for the 491 samples for which ultimate analyses were available. These were samples with heating values varying from 19.69×10^9 J/t to 34.76×10^9 J/t and carbon content from 48.2 to 85.9%. For the 26 samples with heating values between 28.87 and 29.71×10^9 J/t (6900 and 7100 cal/g), the mean heating value was 29.28×10^9 J/t and the mean carbon content 70.7%. "Coal equivalent" is thus assumed to contain 70.7% carbon. We suggest $C_s = 70.7\%$ carbon describes coal equivalent within ±2%, although it does appear that the carbon fraction per unit heating value increases slightly for low grade coals.

The higher heating value of coal is a commonly measured value and most of the discussion above

has been based on higher heating value. However, in its most recent tabulations, the UN has attempted to base coal equivalents on lower heating value ("net heat value" in their terminology) while staying with a 29.31×10^9 J/t (7000 cal/g) basis. Therefore we must make some adjustment. To use the UN data set for coal production with coal composition information based on the higher heating value, the coal composition factor must include a multiplier which simultaneously converts tons of coal equivalent from a lower to a higher heating value basis. Our factor is based on US data and assumes only that the ratio of $\Delta H_H/\Delta H_L$ is the same for average world coal as for US coal. Table 3 shows, by year, the ΔH_H of US coals as reported by the US BOM and US DOE and the heating value assumed by the UN in converting tons of US coal to tons coal equivalent. By including a factor of $\Delta H_H/\Delta H_L$ in the multiplication, we effectively revert to a 29.31×10^9 J/t ΔH_H basis, and this can be regarded simply as a heating value adjustment factor. It should be changed if the UN alters its accounting basis in the future.

From the heating values used by the UN in tabulating US coal production in UN (1982) (Table 3), the mean heating value adjustment factor for 1970–79 data is found to be 1.055. We asume this factor is appropriate for world coal. Combining the composition and heating value adjustment factors, the effective carbon content of world average coal is found to be $C_s = (0.707)(1.055) = 0.746 \pm 0.02$. We emphasize that this factor is uniquely appropriate for the UN coal statistics reported on a "net heat value" basis.

6. Calculation of CO_2 emissions and estimation of error

6.1. *CO_2 emissions from fossil fuel burning*

The computation of CO_2 emissions from fossil fuel burning is accomplished by multiplying the factors developed above and summarized in Table 13. The fuel data taken from UN (1983) and the calculated values for CO_2 emissions are presented and summed in Table 14. A large number of

Table 13. *Factors and units for calculating annual CO_2 emissions from global fuel production data** $CO_{2i} = (P_i)(FO_i)(C_i)$

From natural gas production
- CO_{2g} = CO_2 emissions in 10^6 tons C
- P_g = annual production in thousands of 10^{12} J ($\pm \approx 10\%$)
- FO_g = effective fraction oxidized in year of production = 0.98 ± 1%
- C_g = carbon content in 10^6 tons per thousand 10^{12} Joules = 0.0137 ± 2%

From crude oil and natural gas liquids production
- CO_{2l} = CO_2 emissions in 10^6 tons C
- P_l = annual production in 10^6 tons ($\pm \approx 8\%$)
- FO_l = effective fraction oxidized in year of production = 0.918 ± 3%
- C_l = carbon content in tons C per ton crude oil = 0.85 ± 1%

From coal production
- CO_{2s} = CO_2 emissions in 10^6 tons C
- P_s = annual production in 10^6 tons coal equivalent ($\pm \approx 11.2\%$)
- FO_s = effective fraction oxidized in year of production = 0.982 ± 2%
- C_s = carbon content in tons C per ton coal equivalent = 0.746** ± 2%

From natural gas flaring
- CO_{2f} = CO_2 emissions in 10^6 tons C
- P_f = annual gas flaring in 10^9 m^3 ($\pm \approx 20\%$)
- FO_f = effective fraction oxidized in year of flaring = 1.00 ± 1%
- C_f = carbon content in tons per thousand m^3 = 0.525 ± 3%

* Units are chosen to be consistent with fuel production data compiled in UN (1983). All masses are in metric tons (10^3 kg).

** The 0.746 value includes a heating value adjustment to recognize that the carbon content, developed on a higher heating value basis, must be increased when used with UN production data (UN, 1983) based on "net" or lower heating values.

Table 14. *Summary table of CO_2 emissions from fossil fuels, 1950–82*

Year	Gas fuel production[1] (10^{12} J) (thousands)	CO_2 from gas fuel (10^6 t C)	Liquid fuel production[2] (10^6 t oil)	CO_2 from liquid fuel (10^6 t C)	Solid fuel production[3] (10^6 t coal) (eq.)	CO_2 from solid fuel (10^6 t C)	Gas flared and vented[4] (10^9 m^3)	CO_2 from flared gas (10^9 t C)	Total CO_2 from fossil fuels (10^6 t C)
1950	7,190	97	542	423	1,471	1,077	44	23	1,620
1951	8,560	115	613	479	1,552	1,137	46	24	1,755
1952	9,240	124	646	504	1,538	1,127	50	26	1,781
1953	9,770	131	684	533	1,546	1,132	51	27	1,823
1954	10,250	138	714	557	1,532	1,123	52	27	1,845
1955	11,140	150	801	625	1,659	1,215	58	30	2,020
1956	12,030	161	870	679	1,748	1,281	61	32	2,153
1957	13,250	178	915	714	1,798	1,317	67	35	2,244
1958	14,300	192	938	732	1,834	1,344	66	35	2,303
1959	15,980	214	1,012	790	1,883	1,380	69	36	2,420
1960	17,500	235	1,089	850	1,953	1,430	75	39	2,554
1961	18,870	253	1,161	906	1,831	1,341	79	41	2,541
1962	20,590	276	1,258	981	1,875	1,373	84	44	2,674
1963	22,360	300	1,351	1,054	1,953	1,431	90	47	2,832
1964	24,450	328	1,458	1,138	2,022	1,481	97	51	2,998
1965	26,170	351	1,563	1,220	2,051	1,503	104	55	3,129
1966	28,310	380	1,696	1,323	2,080	1,524	115	60	3,287
1967	30,500	409	1,822	1,421	2,000	1,466	126	66	3,362
1968	33,130	445	1,988	1,551	2,043	1,497	139	73	3,566
1969	36,270	487	2,139	1,669	2,080	1,524	152	80	3,760
1970	38,440	516	2,350	1,833	2,152	1,577	167	88	4,014
1971	41,200	553	2,491	1,944	2,146	1,572	171	90	4,159
1972	43,390	583	2,632	2,054	2,163	1,584	180	95	4,316
1973	45,280	608	2,868	2,238	2,190	1,604	213	112	4,562
1974	45,880	616	2,877	2,245	2,202	1,613	204	107	4,581
1975	46,230	621	2,731	2,131	2,297	1,683	183	96	4,531
1976	48,040	645	2,962	2,311	2,357	1,727	210	110	4,793
1977	49,730	668	3,064	2,391	2,428	1,779	206	108	4,946
1978	51,740	695	3,106	2,423	2,450	1,795	201	106	5,019
1979	54,380	730	3,238	2,527	2,583	1,892	200	105	5,254
1980[5]	53,440	718	3,091	2,412	2,641	1,935	194	102	5,167
1981[5]	54,120	727	2,909	2,270	2,658	1,947	178	93	5,037
1982[5]	54,170	727	2,771	2,162	2,729	1,999	175	92	4,980

[1] Data from UN (1983) and corresponding data tape of UN Energy Statistics.

[2] Data from UN (1983) and corresponding data tape of UN Energy Statistics. Numbers are the sum of crude oil and natural gas liquids, both in mass units.

[3] Data from UN (1983) and corresponding data tape of UN Energy Statistics; in 10^6 t of coal equivalent, where coal equivalent means net heating value of 29.31×10^9 J/t (7000 cal/g).

[4] 1950–70 data from Rotty (1974). 1971, 1972 data from US DOI (1974). 1973 data from US DOE (1979). 1974–78 data from US DOE (1980b). 1979–82 data are estimates by authors.

[5] Data for 1980–82 are from UN (1984, in press, private communication UN statistics office staff).

assumptions and approximations are embodied in these computations but in every case, the values are rather well-bounded. We have tried to draw these approximations in such a way as to acknowledge the uncertainties but to show also that the results cannot lead to large errors in the calculation of CO_2 emissions.

Because liquids probably provide the worst case for accumulation of errors, assembling and contemplating all of the errors and approximations contained in the calculation of CO_2 emissions from liquids provides bounds for other fuels as well. Global production data can be used as a surrogate for annual consumption if identifiable non-oxidative uses are subtracted. Changes in stocks are small compared to production and, over a series of years, must contain positive and negative numbers summing to near zero. Assuming that crude oil and natural gas liquids could be summed on a mass basis introduces little error because of the demonstrated small difference in mean carbon content and the small contribution of NGLs to the total. Global fuel production numbers compiled by the UN are consistent with numbers published elsewhere and represent the best efforts of a staff dedicated to the sole task of bringing together all of the available information. All production data are subject to revision as additional information becomes available, but ultimately all data depend on the reporting of individual nations and production companies. The error estimates for production data ($\pm 8\%$ for liquids) are judgments made after discussing global and some individual country data with the UN staff plus discussions with others more familiar with US data.

The most speculative numbers in our computation are those that relate to how crude oil is ultimately used and the rate at which it is oxidized. It is absolutely clear, however, that over 90% of crude is used for fuels that are burned within a short time of production and errors of only a few percent of total CO_2 emissions are possible as a result of accounting inadequacies within the fraction remaining unoxidized. The fraction not oxidized results from both non-fuel use and combustion inefficiencies. The assumption of $98.5 \pm 1\%$ oxidization effectively recognizes that CO and most unburned or partially oxidized hydrocarbons will soon be oxidized in the environment while soot will remain unoxidized for long periods of time. Although recognizing that we have committed errors of both omission and inclusion, we have listed a variety of non-fuel petroleum products that have long lifetimes before oxidation, and have assumed that the sum closely approximates the fraction of petroleum which is not oxidized each year. Recent year data suggest this is about 6.7% of production and we conclude that errors of greater than $\pm 2\%$ of production are unlikely. One problem is that this fraction (and the combustion efficiency) are functions of time and place and we are forced to rely on recent US data to infer long-term global averages. If the fraction of fuel going into long-lifetime products has been increasing over the last several decades, use of estimates of that fraction based on present data will result in CO_2 emissions that are slightly too low for earlier years. However this will be, at least partially, compensated for by an increase in fuel combustion efficiency with time. The data cited above also suggest that non-fuel uses of coal and natural gas have been decreasing with time while average coal combustion efficiency has been increasing with time. Data are not available to try to discern quantitatively the effect of changing non-fuel uses and increasing combustion efficiencies on the growth rate of CO_2 emissions.

There are enough data published on the composition of world crudes, partly because so much of world crude enters into international commerce, that we can be quite confident in establishing its mean carbon content. Errors in the procedures and the calculations stemming from carbon content or from fraction oxidized are much smaller than those from fuel data.

With present global fuel data, error limits cannot be assigned with scientific precision, but rather the $\pm$ values indicated represent our subjective judgment for an approximate 90% confidence interval over distributions not unlike normal. This is distorted somewhat when we recognize that some of the factors used are dominated by data from the most recent third of the data sequence and that time-dependent biases have been introduced by employing constant multipliers for the entire 1950–82 period. Working largely in energy units should suppress time-dependent, systematic errors in the fuel production and fuel composition data, but fuel combustion efficiency and non-fuel use have almost certainly undergone systematic changes not recognized in our calculation. Since these changes affect quantities which are of the order of a few

percent and the quantities are then subtracted from unity, any adjustments can give only small changes in net CO_2 production or its rate of increase.

We have estimated the overall uncertainty associated with CO_2 emissions by the analysis depicted in Table 15. In 1980, the CO_2 emissions from each fuel group were divided as follows: 14% from natural gas, 47% from liquid fuels, 37% from solid fuels, and 2% from flaring gas. Using these percentages as weighting factors on the uncertainties for each fuel group, this analysis suggests that the estimates on the global total emissions of CO_2 from fossil fuels presented in Table 14 have an uncertainty of between 6 and 10%, depending on how one chooses to aggregate the uncertainties.

The uncertainty in the value used for fuel produced is independent of the uncertainty in the estimate for fraction oxidized and the estimated carbon content. The uncertainty in the product of the three terms is estimated by the square root of the sum of the squares of the uncertainty in each individual component. However, in summing the uncertainties for CO_2 emissions from each fuel type to obtain an overall uncertainty for global CO_2 emissions, independence is not assured. If the data for each fuel type were totally independent, the square root of the sum of the squares would be the appropriate procedure and the estimated uncertainty would be 6.1%. In at least a few cases, it is likely that data for gases, liquids and/or solids are developed and tabulated in the same office or even by the same individual and errors of the same type may occur in data for more than one fuel type. In this case, compensating errors would not occur and the cumulative uncertainty could be as much as $\sum f_i \sqrt{\sum E_j^2}$, 10.2% in this case (see Table 15). The estimated uncertainty in the final emission numbers of between 6 and 10% is based on a 90% confidence interval.

The uncertainty of 6 to 10% is applicable to CO_2 emissions for a given year, but the uncertainty in the relative change from year to year is a different problem. Growth rates are determined by linear least squares fitting of the logarithms of the annual emissions and thus confidence in growth rates can be different from confidence in annual values. There is a memory component in the annual fuel data; that is, fuel production data for a given year are influenced by, and hence not totally independent of, the previous year's data. One of the checks employed by the UN is that reported production data must demonstrate continuity with the previous year's values. In addition, some time-dependent bias may be introduced by the calculative procedure used. However, if we assume that there is a constant exponential growth in CO_2 emissions for a particular period, then we can use some simple statistics to estimate confidence limits on the annual

Table 15. *Uncertainties in CO_2 emissions* (%)

	E_1 fuel produced (P)	E_2 fraction oxidized (FO)	E_3 carbon content (C)	Emissions* $\sqrt{\sum E_j^2}$	Weighted** emissions $f_i\sqrt{\sum E_j^2}$
gases	10	1	2	10.3	1.5
liquids	8	3	1	8.6	4.0
solids	11.2	2	2	11.6	4.3
gas flared	20	1	3	20.3	0.4

Total uncertainty: a. If uncertainties for the individual fuels are mutually independent $[\sum(f_i\sqrt{\sum E_j^2})^2]^{1/2} = 6.1$

b. If uncertainties for the individual fuels are not independent $\sum f_i\sqrt{\sum E_j^2} = 10.2$

* E_j is the uncertainty in the factors P, FO, and C for a given fuel type i.

** Weighted by 1980 weighting factor f_i = 1980 emissions from ith fuel type divided by total 1980 emissions.

growth rate. Assuming that the yearly emissions are independent, and that the statistical deviation from constant exponential growth is the same as the statistical deviation in the individual annual emissions, and that ±8% is the 90% confidence bound on individual values, we calculate that the annual growth rate for the period 1950–73 is 4.44 ± 0.26%. For the period 1973–82 it is 1.46 ± 1.11%.

Because of the memory in the data system, data precision can be much greater than data accuracy; the uncertainty in individual values is not reflected in the difference between successive annual values. Thus, in determining year to year differences, using annual values calculated to four significant figures is not inappropriate.

To reduce the uncertainty in the final result would require that the reliability (or confidence in) the fuel production data be substantially improved. It is shown clearly in Table 15 that most of the uncertainty in calculating CO_2 emissions from fossil fuels comes directly from this source. Developing improved confidence in the UN fuel statistics for even that small group of countries that produce most of the world's fuel, would require a major effort.

We have made no attempt to examine CO_2 emissions prior to 1950. Estimates of Keeling (1973) remain the only source extending back to 1860. There is virtually no difference between the results presented here for the early 1950s and Keeling's values for the same period (e.g., 1618×10^6 t C for 1950 calculated here compares with 1613×10^6 tons carbon calculated by Keeling). Although this apparent agreement makes it easy to combine data for the two periods into a single sequence, we caution that the two series have been developed by different methods from data sets having different uncertainties.

6.2. *CO_2 emissions from other industrial activity*

The only other significant contribution to CO_2 emissions from industrial activities appears to be related to cement manufacture. In cement manufacture, limestone, chalk, oyster shells or some other raw material rich in calcium is a major ingredient. In a cement kiln, calcium carbonate ($CaCO_3$) is broken down into carbon dioxide and the calcium oxide (CaO) which ultimately combines with silicates from other ingredients to form tricalcium and dicalcium silicates.

Portland cements vary as to exact composition depending on the characteristics desired in the product. The common types of cement vary from 62.3 to 65.0% CaO (Helmuth et al., 1979). Type I and Type II cements are the most common and these average 64.0 and 63.6% CaO, respectively. The weighted average of the 1975 cement shipments in the US is 63.8% CaO, and we have accepted 0.638 as an appropriate value for CaO content of the world average cement.

For each mole of CaO produced from $CaCO_3$, one mole of CO_2 must be driven off. Thus in the production of one ton of cement $12.01/56.08 \times (0.638) = 0.137$ t C are released to the atmosphere as CO_2. The annual CO_2 emission from cement manufacture is obtained by multiplying the mass of global cement production by 0.137.

The most consistent series for global cement production that we have been able to identify is that given in the Minerals Yearbooks of the US BOM. Data from the UN Statistical Yearbooks and the UN Monthly Bulletin of Statistics are similar but require some careful interpretation to develop a consistent time series. Table 16 gives world cement production and our estimate of the CO_2 emissions from this source.

7. Conclusions

An important outcome of this exercise is that an independent examination of the full computation of CO_2 emissions from fossil fuels has been completed and no fundamental oversights in the earlier methods of Keeling and of Rotty have been found. Differences from the earlier results are minor, well within the uncertainty limits in the data available. At the same time, we emphasize the uncertainties in the results, and any effort toward a global carbon balance should acknowledge that CO_2 production numbers reported to four significant figures are nonetheless subject to substantial uncertainty.

The CO_2 emissions given in Table 14 are displayed in Figs. 5 and 6. Fig. 5 shows graphically the rate at which CO_2 emissions have been growing and the relative contributions of the various fuels. This figure shows the early dominance of emissions from coal and the rapid increase in emissions from liquids between 1950 and the early 1970s. The disruption of the growth in emissions that ac-

Table 16. *CO_2 emissions from cement, 1950–82*

Year	Cement production[a] (10^6 t cement)	CO_2 from cement (10^6 t C)	Total CO_2 from fuels + cement (10^6 t C)
1950	133	18	1638
1951	150	21	1776
1952	161	22	1803
1953	178	24	1847
1954	195	27	1872
1955	218	30	2050
1956	236	32	2185
1957	247	34	2278
1958	262	36	2339
1959	294	40	2460
1960	317	43	2597
1961	334	46	2587
1962	358	49	2723
1963	377	52	2884
1964	415	57	3055
1965	434	59	3188
1966	464	63	3350
1967	480	66	3428
1968	515	70	3636
1969	543	74	3834
1970	572	78	4092
1971	617	84	4243
1972	657	90	4406
1973	702	96	4658
1974	703	96	4677
1975	702	96	4627
1976	746	102	4895
1977	797	109	5055
1978	853	117	5136
1979	872	119	5373
1980	885	121	5288
1981	892	122	5159
1982	892	122	5102

[a] Cement production data from US BOM Minerals Yearbooks.

companied the dramatic change in energy prices and availability beginning in 1973 is clearly evident and appears to be mostly a consequence of reduced rate of growth in the use of oil and gas.

In Fig. 6, the percentages shown are average exponential growth rates calculated by linear least squares fitting of the logarithms of the annual emissions. Although the trends indicated in Fig. 6 for the period following 1973 are based on only ten points and hence are susceptible to some adjustment as additional years are added to the data, the change in growth rates around 1973 is quite evident. The pre-1973 4.5% annual rate of growth in CO_2 emissions from all fossil fuels has been reduced to less than half that (1.5%). Carbon dioxide emissions from oil and gas show the 1973 change even more clearly. The apparent small increase shown in the growth rate in coal production following 1973 must be considered in terms of the relatively short period over which the 2.59% annual rate was determined. The basic change in total fossil fuel use that occurred in 1973 could be quite important.

Although the estimated uncertainty in the CO_2 emissions is about 10%, the trend of increasing emissions from fossil fuels is firmly established. There may be a small time-dependent error in the emissions calculation but the 1950–73 annual

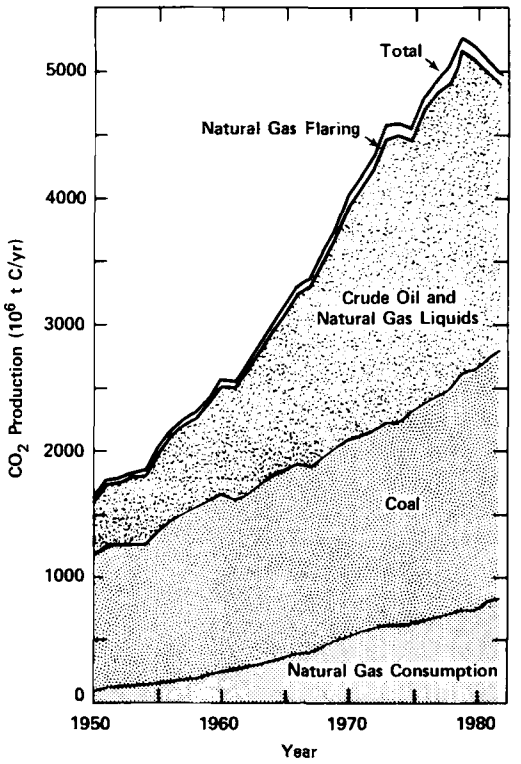

Fig. 5. Annual CO_2 production from fossil fuel burning, 1950–82.

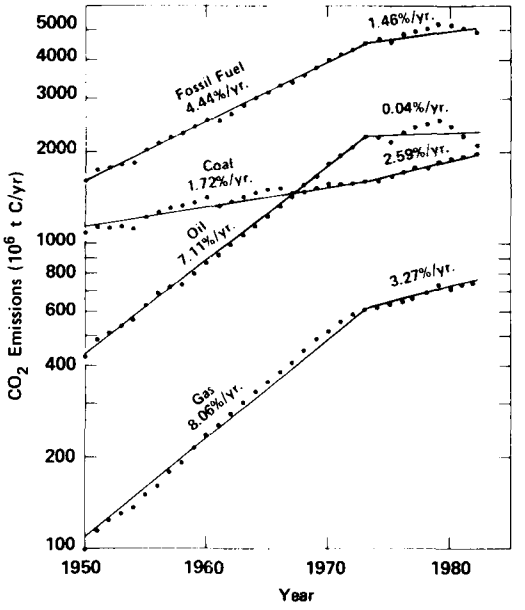

Fig. 6. Annual CO_2 production from each fossil fuel group and total fossil fuels.

growth rate cannot be far from the 4.5% per year calculated here and, although not as well-defined, the growth rate following 1973 is less than half the earlier rate. Even prior to the 1980–82 recession (during which the emissions actually *decreased* for three consecutive years) the reduced growth rate was clearly evident.

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