Thermodynamic CO_2 Upper Bound Forcing Estimates

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Abstract

We have developed a new method to assess CO_2 forcing estimates using a thermodynamic framework. We study the available work in the CO_2 atmospheric system which is bounded by its free energies. This is estimated by assessing the CO_2 byproduct due to fossil fuel consumption from 1950 to 2019. This available work must be less than the total CO_2 accumulated double bond enthalpy and is further bounded by the single bond dissociation energy. We also add in 15% more CO_2 from other sources. As well we consider altitude factors. Our thermodynamic model indicates a total mean forcing of about 0.9W/m^2 which is about 51% of IPCC anticipated estimates.

Key Words: Fossil fuel consumption, CO_2 byproduct, CO_2 forcing estimates, CO_2 available work, CO_2 atmospheric enthalpy, CO_2 free energy

1. Introduction

In this approach, we use a novel thermodynamic framework to make CO_2 forcing estimates in the atmospheric system. This methodology offers the advantage of simplicity over complex environmental modeling. As an aid in this new approach, we find it helpful at times to refer to a space heater analogy. The heater consists of its heating elements; these are rated often by wattage and generate heat proportional to the current supplied. The space heater increases the temperature in a room by the amount related to the wattage rating and allowed current flow. This is the general concept in this paper for estimating CO_2 forcing capabilities due to the 1) thermodynamic available work expressed in wattage per year over the Earth's area and 2) re-radiation IR 'current' with single bond enthalpy constraint.

- We assert that the thermodynamic free bond enthalpies bound the available re-radiation work for CO_2.

Thus, our findings are for re-radiation thermodynamic re-radiation work capability and are therefore upper bound estimates. More specifically, we determine the atmospheric CO_2 system due to fossil fuel consumption for oil, coal, and natural gas from 1950 to 2019. This provides an estimate of the CO_2 accumulated double bond enthalpy in the atmospheric system analogous to the space heater's wattage. The current flow in the space heater is analogous to the IR re-radiation flow that can be utilization constrained by the molecule's dissociation energy. We also added into our conclusions an estimated 15% increase in CO_2 from other non-fossil fuel sources [1]. Additionally we provide atmospheric altitude considerations.

The assessment for the amount of forcing that we compare to from 1950 to 2019 comes from NOAA/IPCC estimates for GHG warming of 2.38W/m^2 and specifically for CO_2 of 1.78 W/m^2 [2]. We note that an increase of 2.38W/m^2 can be equated to a temperature rise of 0.44^{o}K. The actual global warming with feedback from 1950 to 2019 is about 0.95^{o}K.

Method and Data

In this section, we first look at the fossil fuel consumption followed by an estimate of the total double bond enthalpy in the atmospheric system. Then we consider the maximum utilization due to the single bond dissociation energy for the active dipole modes.

2.1 Fossil fuel distribution from 1950 to 2019

The global fossil-fuel consumptions are graphed in figures 1 and 2 with the data presented in Appendix 1. From 1950 to 2019, the total consumption is 5,266,589 TWh [3]. This consists of coal, oil, and natural gas total for each year, then summed from 1950 to 2019. We convert to TWatts by dividing by 8760 hours per year and then divide this by the surface area of the Earth (5.1E14 m^2) to provide an estimate of equal distribution across the globe to make comparisons to the global warming energy and also in kJ units. The result is

$$Total\ Fossil\ Fuels\,(W/m2) = 5,246,890\,TWh/8760\,Hrs/5.1E14\,m^2 = 1.17\,W/m^2 = 4.23kJ/m^2/year \tag{1}$$

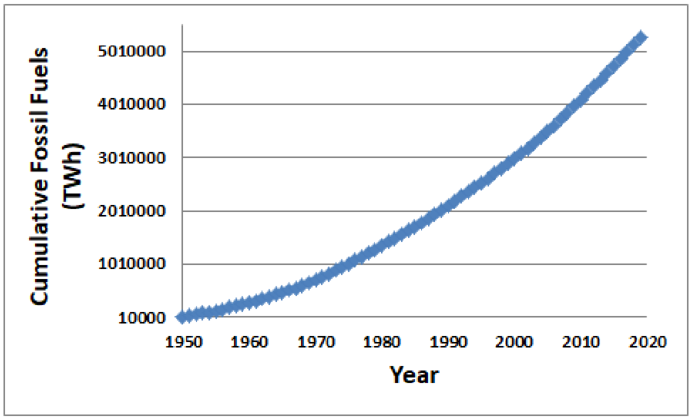

Figure 1 Cumulative Fossil Fuel Consumption from 1950 to 2019 [3] in TWh consisting of the sum of coal, oil, and gas

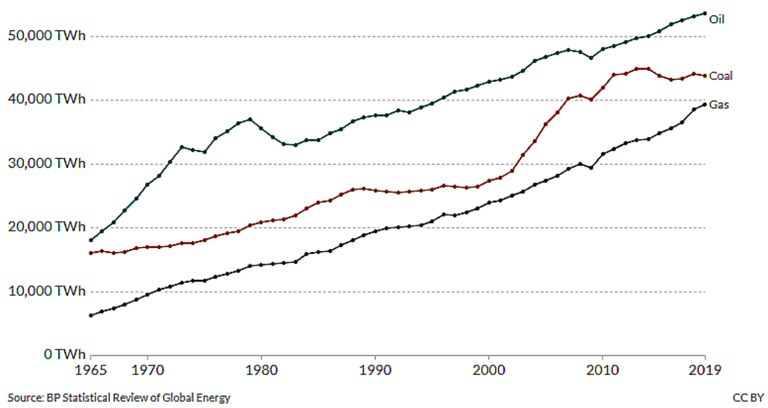

Figure 2 Fossil Fuel Consumption from 1950 to 2019 [3] in TWh for coal, oil, and gas

2.1 Fossil Fuel Combustion Energies

Different fuels produce different amounts of CO_2. Table 1 illustrates the primary fuels creating CO_2 on a large scale reviewed in this study.

Table 1 Amount of CO2 produced for Gas, Oil, and Coal [4, 5]

Fuel	Average CO_2 Per BTU	Ratio Per Energy Units
Natural Gas	117	1
Oil, Gasoline	157	1.34
Bituminous Coal	206	1.76

2.1.1 Methane and CO_2 Free Energies

Fossil fuels are composed primarily of hydrocarbons. During the combustion reaction with oxygen, the hydrocarbon molecules are converted to carbon dioxide and water. The combustion of methane natural gas is the simplest of fossil fuel analysis where

$$CH_4 + 2O_2 \xrightarrow{\Delta H} CO_2 + 2H_2O \tag{2}$$

The bond enthalpy free energy of the reaction is given by

$$\Delta H = \sum Energy\ of\ bonds\ broken - \sum Energy\ of\ bonds\ made \tag{3}$$

The estimated energy release is given in Table 2.

Table 2 Estimated bond enthalpies in methane fossil fuel reaction [6,7]

Molecule	Bond	Bond Energy Released kJ/mol
CH_4	C-H	4 @ 410 = 1640
O_2	O=O	2 @ 494 = 988
CO_2	C=O	2 @ 799= 1598
H_2O	O-H	4 @ 460 = 1849
ΔH		-810

The bond enthalpy energy released is [6]

$$\Delta H = (1640 + 988) - (1598 + 1840) = -810\, kJ / mol \tag{4}$$

The ratio of the double bond enthalpy of CO_2 relative to the reaction enthalpy is

1598/810=1.97 BE/ME : C=O Ratio of Bond enthalpy (BE)/methane reaction enthalpy (ME) (5)

2.1.2 Oil

Oil and gasoline chemical reactions releases, from Table 1, about 34% more CO_2 per unit of energy [4,5] compared to methane combustion. From Eq. 5 and Table 1 this yields an additional factor relative to methane of

1.97 x 1.34=2.64 (BE/OE) CO_2 Bond Oil Enthalpy Ratio (BE/OE) x CO_2 Oil Factor (6)

2.1.3 Coal

Coal chemical reaction releases from Table 1 about 76% more CO_2 per unit of energy [4,5] compared to methane combustion. From Eq. 5 and Table 1 this yields an additional factor relative to methane of

1.97 x 1.76=3.47(BE/CE) CO2 Coal Bond Enthalpy Ratio $(BE/CE)_C$ x CO_2 Coal Factor (7)

2.2 Total CO_2 Fossil Fuel Available Work

The total CO_2 fossil available work can be obtained relative to the methane combustion analysis. We can partition the percentages from the factors above. The percentages of fossil fuels are 22.9% for natural gas, 33.5% for coal, and 43.6% for oil as indicated in Table 5 (bottom) in Appendix 1 and as illustrated in Fig 2. The cumulative total results in Equations 1, 5, 6, and 7 yields

$$\begin{aligned} CO_2\ Available Work / m^2 / Year &= 4.23\, kJ / m^2 / year\, x (1.97 \frac{kJBE}{kJME} x0.229_{Gas} + 2.64 \frac{kJBE}{kJOE} x0.436_{Oil} + 3.47 \frac{kJBE}{kJCE} x.335) \\ &= 4.23 kJ / m2 / year\, x\, 2.76 \frac{kJBE}{kJ} = 11.7 kJBE / m^2 / year = 3.24\, W / m^2 \end{aligned} \tag{8}$$

This is the available total bond enthalpy per year over the area of the Earth that has increased each year from 1950 to the current year 2019. It is analogous to the wattage ratings for a space heater.

2.1.4 CO_2 Normal Modes, Associated Energies, and Estimated Maximum Utilization

Lastly, we look at CO_2 normal mode spectral energies per mol. This is similar to the electricity for the space heater. We note from Figure 4 the main dipole modes are at 665 cm^{-1} and 2349 cm^{-1}.

Figure 4 CO_2 Absorbance Spectrum [8], strongest absorption is at 2349 cm^{-1} having intensity 665 kJ/mol [9]

The main contributing IR CO_2 normal dipole modes and intensities are listed in Table 3 with experimental intensity data [9].

Table 3 CO_2 active IR normal modes and intensity

CO_2 Modes cm^{-1}	Spectral Energy kJ/mol [9]
667	54.2
2349	665

We note that the single bond stretching mode enthalpy at 2349 cm^{-1}, which plays a minor role in CO_2 absorption in the IR black body region, in the experimental data [9] shows a capability of 665 kJ/mol without molecular dissociation.

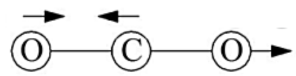

Figure 3 Stretching normal CO_2 mode at 2349 cm^{-1}

The normal mode at 667 cm^{-1} which plays a major role in IR atmospheric absorption, also may be capable of 665kJ/mol intensity. Comparing this to the enthalpy bond energy yields a ratio of

$$665/1598=42\% \quad CO_2 \text{ Ratio: Normal Mode Spectral Energy/Bond C=O energy} \tag{9}$$

It is important to recognize that the maximum kJ/mol needs to be considered for the single C-O bond. This is because some authors have reported that the thermochemical bond dissociation energy of CO_2 has been estimated as low as 532kJ/mol [10]. This is lower than the single bond enthalpy of 799 kJ/mol in Table 2 and yields ratio of

$$532/1598=33.3\% \quad CO_2 \text{ Ratio: Bond dissociation energy/ Bond C-O energy} \tag{10}$$

Certainly, the maximum utilization ratio is due to the single bond enthalpy per mol with a ratio

$$799/1598=50\% \quad CO_2 \text{ Ratio: C-O Bond Strength/ Bond C=O energy} \tag{11}$$

We see the spectral energy reported in CCCBDB [9] exceeds the bond dissociation energy [10] but does not exceed the reported C-O bond enthalpy per mol shown in Table 2. This may be indicative of experimental variability or the ways assessments are made. In any event, we would not anticipate higher utilization energy per mol than 50% in Equation 11.

3. Fossil Fuel and CO_2 Available Work for Forcing

For a comparative analysis, we need to take into account the average global mean re-radiation percent. For example, on average, about 62% of infrared is re-radiation back to Earth and 38% is radiated into outer-space [11]. In addition, we consider a small CO_2 nonlinear forcing factor of 0.975 occurring from 1950 to 2019 as detailed in Appendix 2. Table 4 provides the comparative analysis with these factors shown in Column 3.

The estimated global warming due to CO_2 forcing is assessed by IPCC/NOAA as 1.78W/m^2 [2]. Table 4, Column 4 provides the CO_2 atmospheric forcing from 1950 to 2019 years from fuel consumption and its associated enthalpies. The relative comparison to forcing needed is in Column 4 and the total normal mode utilization is in the last column. In the last row, we added 15% more CO2 which is estimated to come from other sources [12].

From the table, we first note that the double bond available work/m^2/year has an adequate rating at 1.96W/m^2 greater than the IPCC/NOAA estimate for this time period of 1.78W/m^2. This is similar to a space heater having adequate wattage capability. However, from Column 4, the re-radiation model 'space heater current' utilization is limited by the single bond enthalpy per mol found to bound forcing to a mean value of 1.04W/m^2 which is about 58% of IPCC/NOAA [2] estimates. Exceeding these kJ/mol energies indicated possible bond dissociation (Sec. 2.1.4).

Table 4 CO2 available work for global warming forcing

Energy Type	**Total Energy 1950 to 2019 W/m^2**	**Effective Ratings W/m^2** (re-radiation x CO2 nonlinear factor 0.62 x 0.975=0.605 times the total energy) 2019	**CO_2 Normal Modes Max Utilization**	**Estimated CO_2 Forcing (%Relative to 2.35W/m^2) [% Relative to 1.78W/m^2]**
Fossil Fuel Consumption	1.17	-		
CO_2 Bond Enthalpy per year per m^2	3.24	1.96	42%-50%	0.82-0.98W/m^2 (35%-41%) [46%-55%]
Estimates when 20% CO_2 is added from other sources				
CO_2 Bond Enthalpy Per year per m^2 with 15% CO_2 added from other sources [12]	3.73	2.26	42%-50%	0.95-1.13 W/m^2 (40%-48%) [53%-64%]

3.1 Atmospheric Altitude Considerations

In the troposphere, CO_2 normal modes at 667 cm^{-1} competes with water-vapor, especially in humid climates. This will cause some attenuation of its warming capability. There is little guidance on this; we derate conservatively by 20% to provide an informal estimate. In the stratosphere and mesosphere, where water vapor is frozen out, CO_2 absorption modes are non-competitive with water-vapor. However, we need to subtract out the CO_2 volume from the troposphere. CO_2 has increased by 400ppm from 1950-2019. To make an assessment and simplify, we consider this concentration as evenly distributed over the lower and upper atmosphere. The troposphere extends to about 10km while the top of the mesosphere is about 80km. Therefore, we subtract out 1/8 of the CO_2 volume in the upper atmosphere, a reduction of 12.5%. The weighted average (20% x 0.125 + 12.5% x 0.875=13.4%) between the lower and upper atmosphere yields a re-radiation reduction of 86.3%. Table 4 summarizes showing a mean estimate of 0.9W/m^2. This is 51% and 38% mean forcing relative to 1.78W/m^2 and 2.38W/m^2 IPCC/NOAA [2] value respectively from 1950 to 2019.

Table 5 CO_2 available work for forcing with atmospheric considerations

Energy Type	**Total Energy 1950 to 2019 W/m^2**	**Effective Ratings W/m^2** (re-radiation x CO2 nonlinear factor 0.62 x 0.975=0.605 times the total energy) 2019	**CO_2 Max Utilization**	**Troposphere loss due to Water Vapor & Upper Atmosphere Concentration Change**	**Estimated CO_2 Forcing (%Relative to 2.38W/m^2) [% Relative to 1.78W/m^2]**
CO_2 Bond Enthalpy per year per m^2	3.73	2.26	42%-50% (0.95-1.13 W/m^2)	86.3%	0.82-0.98W/m^2 (35%-41%) [46%-55%]

4. Conclusion

In this paper, we provide a new way to estimate CO_2 forcing using a thermodynamic framework by considering the total double bond enthalpy in the CO_2 atmosphere and its utilization capability. This was assessed from the cumulative fossil fuel consumption and CO_2 byproduct evaluated for oil, coal, and natural gas from 1950 to 2019. Then the thermodynamic work which is limited by its bond-free energies was used as a relative measure of their re-radiation potential. We converted to friendly forcing units. Then forcing capability was measured relative to the IPCC/NOAA [2] CO_2 values of 1.78 Watt/m^2 and total GHG estimate of 2.38 Watts/m^2 from 1950 to 2019. Our thermodynamic model's initial forcing results indicated 0.82W/m^2 -0.98W/m^2 capability. Then we added about 15% more CO_2 from other sources scaling this up to 0.95W/m^2 -1.13W/m2. In addition, we gave an overview of what one might expect when atmospheric effects were considered. This attenuated the results down to 0.82W/m^2 – 0.98W/m^2 with a mean of 51% of IPCC/NOAA CO_2 estimates. Our model's findings describe capability for the available CO_2 re-radiation work, as such are upper bound thermodynamic estimates. While these results are lower than IPCC/NOAA values in this time period, they are higher that the author's Urban Heat Island and land cover/land use forcing estimates of 11-20% [13,14].

Conflict of interest

The author declares that he has no conflicts of interest.

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Appendix 1

The table below [3] provides the global estimated fuel consumption broken down by coal, oil, and gas in TWh. The values from 1951-1959 and 1961 to 1964, were extrapolated, as these were not included in the original data [3].

Table 5 Fossil fuel consumption by year and cumulative in TWh [3]

Year	Coal	Oil	Gas	Total	Cumulative
1950	12603	5444	2092	20139	20139
1951	13122	5784	2244	21150	41289
1952	13322	6265	2419	22007	63295
1953	13522	6786	2609	22917	86212
1954	13723	7350	2813	23886	110098
1955	13923	7962	3033	24918	135016
1956	14123	8624	3271	26018	161034
1957	14323	9341	3527	27192	188226
1958	14523	10118	3803	28445	216671
1959	14723	10960	4101	29785	246456
1960	15442	11097	4472	31011	277467

1961	15124	12859	4769	32752	310219
1962	15324	13929	5142	34395	344614
1963	15524	15087	5545	36156	380770
1964	15724	16342	5979	38046	418816
1965	16140	18109	6303	40552	459368
1966	16324	19496	6869	42689	502057
1967	16061	20891	7375	44327	546384
1968	16301	22675	8044	47020	593404
1969	16799	24577	8833	50209	643613
1970	17059	26708	9614	53381	696994
1971	16966	28205	10292	55463	752457
1972	17154	30378	10861	58393	810850
1973	17668	32746	11378	61792	872642
1974	17682	32272	11656	61610	934252
1975	18025	31948	11661	61634	995886
1976	18688	34030	12356	65074	1060960
1977	19241	35215	12761	67217	1128177
1978	19458	36426	13294	69178	1197355
1979	20364	37024	14119	71507	1268862
1980	20858	35577	14239	70674	1339536
1981	21150	34296	14394	69840	1409376
1982	21384	33198	14469	69051	1478427
1983	22045	32969	14703	69717	1548144
1984	23000	33739	15903	72642	1620786
1985	23986	33789	16261	74036	1694822
1986	24256	34803	16419	75478	1770300
1987	25210	35499	17281	77990	1848290
1988	25965	36703	18089	80757	1929047
1989	26213	37300	18869	82382	2011429
1990	25895	37691	19483	83069	2094498
1991	25643	37691	19975	83309	2177807
1992	25550	38344	20067	83961	2261768
1993	25675	38099	20269	84043	2345811
1994	25774	38935	20394	85103	2430914
1995	25954	39445	21108	86507	2517421
1996	26572	40380	22164	89116	2606537
1997	26527	41413	22033	89973	2696510
1998	26360	41624	22439	90423	2786933
1999	26522	42371	23075	91968	2878901
2000	27417	42897	24000	94314	2973215
2001	27853	43278	24331	95462	3068677
2002	28945	43639	25053	97637	3166314
2003	31497	44610	25753	101860	3268174
2004	33664	46256	26736	106656	3374830
2005	36171	46824	27464	110459	3485289
2006	38071	47367	28175	113613	3598902
2007	40224	47958	29325	117507	3716409
2008	40770	47566	30025	118361	3834770

2009	40149	46654	29411	116214	3950984
2010	41997	48087	31606	121690	4072674
2011	44018	48550	32372	124940	4197614
2012	44185	49157	33219	126561	4324175
2013	44993	49689	33767	128449	4452624
2014	44954	50014	33994	128962	4581586
2015	43844	50892	34781	129517	4711103
2016	43196	51920	35589	130705	4841808
2017	43360	52568	36586	132514	4974322
2018	44109	53181	38517	135807	5110129
2019	43849	53620	39292	136761	5246890
Sums	**1756781**	**2287242**	**1202867**	**5246890**	**5246890**
Percent %	**33.5%**	**43.6%**	**22.9%**	**100.0%**	**100.0%**
-	**Coal**	**Oil**	**Gas**	**Totals**	**Cumulative**

Appendix 2 Nonlinear CO_2 factor

We consider a minor nonlinearity logarithmic CO_2 forcing factor due to its increases in our atmosphere from 1950 to 2019. Other nonlinear estimates may be more appropriate. Here we simply consider $\ln(400_{2019}/300_{1950})$ and compare the deviation to the linearity ratio of 400/300. The linear to logarithmic factor deviation in this method finds $\Delta=1-(0.333-0.288)/1.78=0.975$ where $1.78W/m^2$ is the anticipated IPCC/NOAA forcing in 2019. We note that the 0.975 factor should not have much effect in our assessment (Table 4 and 5) and is provided as a way to conservatively recognize the logarithmic nonlinearity.