Research Article

Ranking Renewable and Fossil Fuels on Global Warming Potential Using Respiratory Quotient Concept

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Carbon dioxide (CO₂) is one of the greenhouse gases which cause global warming. The amount of fossil fuels consumed to meet the demands in the areas of power and transportation is projected to increase in the upcoming years. Depending on carbon content, each power plant fuel has its own potential to produce carbon dioxide. Similarly, the humans consume food containing carbohydrates (CH), fat, and protein which emit CO₂ due to metabolism. The biology literature uses respiratory quotient (RQ), defined as the ratio of CO₂ moles exhausted per mole of O₂ consumed within the body, to estimate CO₂ loading in the blood stream and CO₂ in nasal exhaust. Here, we apply that principle in the field of combustion to relate the RQ to CO₂ emitted in tons per GJ of energy released when a fuel is combusted. The RQ value of a fuel can be determined either from fuel chemical formulae (from ultimate analyses for most liquid and solid fuels of known composition) or from exhaust gas analyses. RQ ranges from 0.5 for methane (CH₄) to 1 for pure carbon. Based on the results obtained, the lesser the value of “RQ” of a fuel, the lower its global warming potential. This methodology can be further extended for an “online instantaneous measurement of CO₂” in automobiles based on actual fuel use irrespective of fuel composition.

1. Introduction

Carbon dioxide plays a major role in the climate forcing because of larger quantities of CO₂ being emitted during combustion of fuels [1]. Gases which are considered to have an impact on global warming include CO₂, methane (CH₄), nitrous oxide (N₂O), and chlorofluorocarbons (CFC). Though non-CO₂ based greenhouse gases (GHG) have a higher potential for trapping heat partly due to their higher radiative forcing [2], the amount of non-CO₂ GHG emitted from fossil fuel combustion are much lower. It has been estimated that 356 billion tons of carbon has been released into the atmosphere due to the utilization of fossil fuels since 1751 globally. Around 77% of the total carbon emissions have been due to the solid and liquid fuels while around 18% have been from combustion of gaseous fuels such as natural gas [3]. Biomass and other renewable fuels (e.g., ethanol produced from plant materials) are considered to be carbon

neutral. Typically, the amount of CO₂ released due to the combustion of renewable fuels is not accounted for in carbon footprint. However, this approach has been challenged by many studies. Land use change, energy conversion efficiency, and productivity of forest land impact the decision on carbon neutrality of biomass based fuels [4]. The carbon emitted during the combustion of fossil fuels is automatically accounted for into the carbon footprint. Release of N₂O during the production of biofuels and its effects on negated CO₂ release from biofuels resulting in global warming were studied by Crutzen et al., 2007 [5]. Irrespective of whether the fuel is renewable or nonrenewable, each fuel has its own share to the global warming due to anthropogenic activities.

The fuels for biological species (BS) are mainly from renewable food materials which are converted into carbohydrates (CH), fat (F), and protein (P) using digestion process. The metabolism within BS is slow combustion of these CH, F, and P in the body and emitting CO₂, the product of

metabolism through nasal exhaust. Biology literature defines respiratory quotient (RQ) as the ratio of moles of CO₂ produced (or CO₂ eliminated) to stoichiometric oxygen (O₂) moles consumed typically during oxidation reaction, for example, oxidation of nutrients in the body. The RQ factor for fat, protein, and carbohydrates—the three basic nutrients (Table 1) of the body—are 0.7, 0.8, and 1, respectively [6–12]. Thus, with measured CO₂ and O₂ in nasal exhaust one can determine RQ and determine which nutrient or a mixture of CH:F:P is being oxidized. Typically, the RQ value for human-beings falls between that for fat and glucose with an RQ value 0.85 at rest [10]. During exercise or activity mode, the RQ value is in the range of $0.7 < \text{RQ} < 1$, suggesting a mix of fat and glucose is being oxidized (since metabolism of P is negligible compared to F and CH). In some situations, the RQ is more than 1.0, and it indicates anaerobic reactions (e.g., anaerobic digestion which simply “gasses” the nutrients to produce CO₂ and methane (CH₄) but does not consume O₂). Further, RQ can also indicate energy released per liter of CO₂ produced since O₂ consumed is directly related to energy released. Note that H/C ratio is similar for glucose, fat, and protein.

It has been observed that the heat values of various nutrients expressed on kJ per kg of O₂ consumed (HHV_{O₂}) is approximately constant at about 14,000 kJ/kg of O₂ [11, 12]. Hence, by knowing the O₂ consumption, the amount of energy released in kJ can be readily estimated. Since about 100 W is required for 100 kg person, then, for the same O₂ consumed (7.1 mg of O₂ per s), higher RQ implies more release of CO₂ requiring more CO₂ to be removed from blood. Studies have shown that older people have difficulty in releasing the CO₂ from blood to alveoli in lungs. It also affects transfer of CO₂ from mitochondria (little combustion chamber within a cell). Thus, physicians often prescribe fat-rich diet (RQ = 0.7) and reduce CH-rich diet (RQ = 1) to elderly patients. This warrants a question, if there is a possibility of extending the RQ concept to a thermal power plant for reduction of CO₂ emission.

Consider a power plant which typically consumes C-H-O fuel [12, 13]. For fixed power generation in MW for engineering systems, heat input in MW is fixed. Since HHV_{O₂} is constant, stoichiometric O₂ consumption is fixed for most fuels to achieve the desired power rating. Hence, fuels with

higher RQ value emit more CO₂ for the same power output. In 1984, Marland and Rotty [14] estimated the emission of CO₂ from the combustion of fossil fuels based on the fuel production data and data on carbon oxidized to CO₂ for the time period 1950 to 1982. Global warming potential (GWP) of biofuels from slow growing forests was evaluated by Holtsmark and compared against the impacts from fossil fuels [15]. Impact of residential energy consumption on GHG emissions and policies which can be implemented to reduce the energy utilization was reviewed by Nejat et al. [16]. From the review of literature, it was observed that there were no studies using RQ as a method to rank different fuels on the release of GHG CO₂. Authors believe that this is the first attempt to use the concept of RQ to rank the potential of different fuels (fossil and renewable) to release CO₂.

This paper presents two methods for estimating the RQ factor for different fuels: (a) using standard formulas from combustion literature for known fuel composition and (b) using the exhaust gas analyses for fuels of unknown composition (e.g., metabolism of mix of HC and alcohols in human body). RQ factor enables the estimation of GWP of different fuels and even for new fuels brought into the market for combustion applications. RQ factor of the new fuel can be compared to the conventional fossil fuels in order to evaluate its potential to emit GHG.

2. Analysis and Methods

2.1. Method A: Ultimate Analyses, Empirical Formula for Higher Heating Values Based on Fuel (HHV), and Stoichiometric Oxygen (HHV_{O₂}). Ultimate and proximate analyses can be used to determine the chemical composition of fuels. Different correlations have been developed to estimate the heating value of a fuel from its chemical composition. The gross or higher heating values for coals can be empirically obtained by using the following Dulong equation [17, 18]:

$$\text{HHV (kJ/kg)} = 33800 * Y_C + 144153 * Y_H - 18019 * Y_O + 9412 * Y_S, \quad (1)$$

where Y_C , Y_H , Y_O , and Y_S are mass fractions of carbon (C), hydrogen (H), oxygen (O), and sulphur (S), respectively. Another relation given by Mason and Gandhi is [19]

$$\text{HHV (kJ/kg dry)} = \begin{cases} 33610 * Y_C + 141830 * Y_H + 9420 * Y_S - 14510 * Y_O, & \text{when } O < 15\% \\ 33610 * Y_C + 141830 * Y_H + 9420 * Y_S - \left(15320 - 7200 * \frac{Y_O}{(1 - Y_A)}\right) * Y_O, & \text{when } O > 15\%. \end{cases} \quad (2)$$

Channiwala and Parikh [20] and Sheng and Azevedo [21] studied the accuracy of these correlations in estimating the heating values of different fuels and biomass fuels, respectively. Channiwala and Parikh [20] studied a number of different fuels including biomass and fitted the following equation to the data:

$$\text{HHV (kJ/dry kg)} = 34910 * Y_C + 117830 * Y_H - 10340 * Y_O - 2110 * Y_A + 10050 * Y_S - 1510 * Y_N, \quad (3)$$

where Y_A and Y_N represent dry mass ash fractions and nitrogen (N), respectively. The heating value predicted by

TABLE 1: Properties of macronutrients, adopted from Annamalai and Silva [11].

Nutrients	Formulae	M (kg/kmol)	St.O ₂ (kg/kg)	RQ	HHV (kJ/kg)	HHVO ₂ (kJ/kg O ₂)
Glucose	C ₆ H ₁₂ O ₆	180	1.066	1	15,630	14,665
Fat	C ₁₆ H ₃₂ O ₂	256	2.869	0.7	39,125	13,635
Protein	C _{4.57} H _{9.03} N _{1.27} O _{2.25} S _{0.046}	119	1.54	0.8	22,790	14,705

Multiply HHV in kJ/kg by 0.43 to obtain BTU/lb.

the above correlation had an error of about 1.5% when compared to that of measured heating values [20]. Boie empirical relation for HHV of any fuel is given according to the following equation [17]:

$$\text{HHV} \left(\frac{\text{kJ}}{\text{kg}} \right) = 35160 * Y_C + 116225 * Y_H - 11090 * Y_O + 6280 * Y_N + 10465 * Y_S. \quad (4)$$

These correlations can be applied to study the variation of fuel HHV with respect to fuel chemical composition. For the current study, Boie equation is selected. The HHV predicted by Boie equation had a minimum deviation from the measured HHV for both the biomass fuels and fossil fuels [18, 21]. For a fuel with a given number of C, H, N, O, and S atoms, one can estimate the heating values and the stoichiometric amount of oxygen (ν_{O_2} , kg/kg of fuel) needed for complete combustion using standard atom balance [17]. The C normalized empirical chemical formulae of fuel is given as CH_{*h*}N_{*n*}O_{*o*}S_{*s*} (e.g., C₂H₅OH represents CH₃O_{0.5} on C normalized basis) where

$$\begin{aligned} h &= \frac{H}{C} = \frac{12.01 * Y_H}{1.01 * Y_C}, \\ n &= \frac{N}{C} = \frac{12.01 * Y_N}{14 * Y_C}, \\ o &= \frac{O}{C} = \frac{12.01 * Y_O}{16 * Y_C}, \\ s &= \frac{S}{C} = \frac{12.01 * Y_S}{32.06 * Y_C}. \end{aligned} \quad (5)$$

The formula to determine the stoichiometric amount of oxygen is given below:

$$\begin{aligned} \nu_{O_2} (\text{kg of oxygen/kg of fuel}) \\ = \frac{32 * (1 + h/4 - o/2 + s)}{M_F}, \end{aligned} \quad (6)$$

where M_F is the molecular weight of C normalized empirical fuel. Based on the Boie equation (see (4) and (5)), heating value per unit stoichiometric oxygen can be determined using (6).

$$\text{HHV}_{O_2} (\text{kJ/kg O}_2) = \frac{\text{HHV} (\text{kJ/kg fuel})}{\nu_{O_2} (\text{kg O}_2/\text{kg fuel})} = \frac{(422272 + 117387 * h - 155371 * o + 100480 * n + 335508 * s)}{[32 * \{1 + (h/4) - (o/2) + s\}]}. \quad (7)$$

The RQ factor which is defined as the ratio of amount of carbon dioxide produced for every mole of oxygen consumed can be obtained by using (7).

$$\text{RQ} = \frac{1}{(1 + h/4 - o/2 + s)}. \quad (8)$$

For example, the RQ factor for ethanol (empirical formula of ethanol: CH₃O_{0.5}) can be given as

$$\text{RQ}_{\text{Ethanol}} = \frac{1}{(1 + 3/4 - 1/4 + 0)} = \frac{2}{3}. \quad (9)$$

Note that the RQ depends only on stoichiometric relations and is independent of equivalence ratio.

2.2. Method B: Gas Analysis Method. The RQ factor for any C-H-O fuel can also be determined from the exhaust gas composition. If CO₂% and O₂% are known from dry exhaust

gas analyses, the RQ can directly be determined without the knowledge of fuel composition and air fuel ratio for combustion. The results can be extended to any C-H-O-N-S fuel as long as NO_x and SO₂ are formed in trace amounts. The general methodology is to formulate the following reaction equation. Assuming complete combustion, using atom conservation for fuel CH_{*h*}O_{*o*}, where $h = H/C$ and $o = O/C$, and exhaust gas analyses, RQ can be determined:

If a mix of 25% (mole%) CO and 75% H₂ is fired, the C normalized empirical formula of fuel is CH₆O with $h = 6$ and $o = 1$. Similarly for manure anaerobic digestion gas with 60% CH₄ and 40% CO₂, the C normalized empirical formulae is CH_{2.4}O_{0.8}. Equation (8) shows that there are 8 unknowns for C-H-O fuel: h, o, a, b, c, d, e , and f . Thus, 8 equations

are needed to determine the unknowns. Four equations are obtained using atom balance of C, H, O, and N. The four additional equations are generated as follows. The ratio (b/a) in the intake air is known to be 3.76; the wet percent of O_2 , CO_2 , and H_2O is known from the exhaust gas composition. Thus, all 8 unknowns can be solved. However, if only the dry percent of O_2 , and CO_2 , is known, then the 8 unknowns are solved in terms of “ h ” the hydrogen to carbon atom ratio. For biological applications, h is typically known to be 2 for CH and F. Gasoline typically has H/C atom ratio of 1.94 (mass ratio H/C = 0.16) while ethanol has H/C atom ratio of 3 and O/C ratio of 0.5.

2.3. Solutions with Known Dry Gas $O_2\%$ and $CO_2\%$. The dry exhaust gas composition (either from engine exhaust fired with gasoline, natural gas, diesel, kerosene, and a blend of gasoline and alcohol or from coal/oil/natural gas fired boilers) can be used to determine RQ (hence CO_2 in tons per GJ), equivalence ratio (inverse of stoichiometric ratio: SR), and $A:F_{stoich}$ without knowing “ h ” and “ o .” In the following, atom balance is used for C normalized fuels to derive the results. The Appendix presents simplified method for a blend of C-H-O fuels.

$$RQ = \frac{CO_2 \text{ moles}}{O_2 \text{ stoich moles}} = \frac{1}{\nu_{O_2,stoich}} = \frac{1}{a - e} \quad (11)$$

$$= \frac{1}{(f/3.76) - e},$$

where stoichiometric O_2 moles and $\nu_{O_2,stoich} = 1 + (h/4) - (o/2) = a - e$. Representing X_{N_2} , X_{CO_2} , and X_{O_2} as the dry mole fractions of nitrogen, carbon dioxide, and oxygen, with subscripts i and e referring to inlet and exit of combustion chamber, respectively, $X_{CO_2,e} = 1/N_{dry}$. Thus,

$$N_{dry} = \frac{1}{X_{CO_2,e}} = \frac{f}{X_{N_{2,e}}} = \frac{N_{air,i} * X_{N_{2,i}}}{X_{N_{2,e}}}, \quad (a')$$

where $X_{N_{2,i}}$ is mole fraction of N_2 in and $X_{N_{2,e}}$ is mole fraction of N_2 exit; further $X_{N_{2,e}} = 1 - X_{CO_2,e} - X_{O_{2,e}}$. From (a')

$$\frac{N_{dry}}{N_{air,i}} = \frac{X_{N_{2,i}}}{X_{N_{2,e}}}. \quad (b')$$

Since $\nu_{O_2,stoich} = a - e$, $a = f/3.76$, and $e = X_{O_{2,e}} * N_{dry}$, then

$$\nu_{O_2,stoich} = N_{dry} * \left(\frac{1 - X_{O_{2,e}} - X_{CO_{2,e}}}{3.76} - X_{O_{2,e}} \right)$$

$$= \frac{1}{X_{CO_{2,e}}} * \left(\frac{1 - X_{O_{2,e}} - X_{CO_{2,e}}}{3.76} - X_{O_{2,e}} \right), \quad (12)$$

C normalized fuel.

Since $\nu_{O_2,stoich} = 1 + (h/4) - (o/2)$ then

$$\frac{h}{4} - \frac{o}{2} = \nu_{O_2,stoich} - 1$$

$$= \left\{ \frac{1}{3.76 * X_{CO_{2,e}}} - \frac{4.76}{3.76} * \left(1 + \frac{X_{O_{2,e}}}{X_{CO_{2,e}}} \right) \right\}. \quad (13)$$

If “ o ” = 0 (pure CH_h fuel) h can be evaluated and if $h = 0$ (CO_y fuel), “ o ” can be evaluated, that is, known dry $CO_2\%$ and $O_2\%$ are enough to determine “ h or o .” Dividing numerator and denominator of (9) by $N_{dry} (= 1/X_{CO_2})$

$$RQ = \frac{CO_2 \text{ moles}}{O_2 \text{ stoich moles}} = \frac{X_{CO_{2,e}}}{X_{N_{2,e}}/3.76 - X_{O_{2,e}}}$$

$$= \frac{X_{CO_{2,e}}}{\left((1 - X_{O_{2,e}} - X_{CO_{2,e}})/3.76 \right) - X_{O_{2,e}}} \quad (14)$$

$$= \frac{X_{CO_{2,e}}}{\left((1 - X_{CO_{2,e}})/3.76 \right) - (4.76 * X_{O_{2,e}})/3.76}.$$

As the Appendix shows, this relation for RQ is valid whether the fuel is C normalized or not. Thus, RQ can be readily calculated once dry mole fractions of CO_2 and O_2 are measured from the products irrespective of the composition of C-H-O fuel. A simplified method for any C-H-O fuel is presented in the Appendix. In other words, if an autodriller is driving through various states where gasoline/kerosene/diesel composition keeps changing, an RQ meter (thus CO_2 in tons/GJ) can keep displaying RQ just using exhaust gas analysis irrespective of composition or type of fuel pumped into tank. If fuel is a blend, let us say x mole of gasoline of known formulae (C_8H_{18}) and $(1 - x)$ moles of ethanol (C_2H_6O), then for this example

$$RQ = \frac{CO_2 \text{ moles}}{O_2 \text{ moles}}$$

$$= \frac{8x + 2 - 2x}{\{8x + 18x/4 + 2 - 2x + 6/4 - (6/4)x - 1/2 + (1/2)x\}} \quad (15)$$

$$= \frac{6x + 2}{\{(19/2)x + 6/2\}}$$

$$RQ * \left\{ \frac{19}{2}x + 3 \right\} = 6x + 2 \Rightarrow$$

$$x \left\{ RQ \left(\frac{19}{2} \right) - 6 \right\} = 2 - 3RQ \quad (16)$$

$$\text{or } x = \frac{2 - 3RQ}{\{RQ (19/2) - 6\}}.$$

Thus, knowing RQ from exhaust gas analysis, mole fraction of gasoline and hence mass and volume fraction can be estimated in the blend while combustion is proceeding. The above relation have been verified for known mole fraction of C_8H_{18} in $C_8H_{18}:C_2H_6O$ blended fuels at prescribed equivalence ratio. Equivalence ratio (ϕ) is defined as the

ratio of stoichiometric air flow to the actual air flow for the particular combustion process.

$$\begin{aligned}\phi &= \frac{1}{SR} = \frac{(A:F)_{\text{Stoich}}}{(A:F)} = \frac{\nu_{O_2, \text{Stoich}}}{a} = 1 - \frac{e}{a} \\ &= 1 - \left(\frac{N_2}{O_2} \right)_i \left(\frac{X_{O_{2,e}}}{X_{N_{2,e}}} \right) \\ &= 1 - \left(\frac{N_2}{O_2} \right)_i \left(\frac{X_{O_{2,e}}}{1 - X_{O_{2,e}} - X_{CO_{2,e}}} \right)\end{aligned}\quad (17)$$

$$\text{Excess air\% or excess } O_2\% = 100 * \left(\frac{1}{\phi} - 1 \right). \quad (18)$$

Finally RQ expression can be generalized as follows for any known mixture of N_2 , O_2 , and CO_2 at inlet (e.g., fire condition) instead of pure air. Replacing $(N_2/O_2)_i$ by $X_{N_{2,i}}/X_{O_{2,i}}$ {where $(N_2/O_2)_i$ is nitrogen to oxygen mole ratio at the inlet},

$$\begin{aligned}RQ &= \frac{CO_2 \text{ moles produced}}{O_2 \text{ moles consumed}} \\ &= \frac{X_{CO_{2,e}} - X_{N_{2,e}} (X_{CO_{2,i}}/X_{N_{2,i}})}{X_{N_{2,e}} (X_{O_{2,i}}/X_{N_{2,i}}) - X_{O_{2,e}}} \\ &= \frac{X_{CO_{2,e}} (X_{N_{2,i}}/X_{N_{2,e}}) - X_{CO_{2,i}}}{X_{O_{2,i}} - X_{O_{2,e}} (X_{N_{2,i}}/X_{N_{2,e}})}.\end{aligned}\quad (19)$$

The “ ϕ ” expression can be generalized as

$$\phi = \frac{O_2 \text{ Consumed}}{\text{Inspired } O_2} = 1 - \left(\frac{X_{N_{2,i}}}{X_{O_{2,i}}} \right) \left(\frac{X_{O_{2,e}}}{X_{N_{2,e}}} \right). \quad (20a)$$

For lean mixture, the equivalence ratio in engineering can be called oxygen extraction fraction (OEF) from inspired air for lean mixtures. The medical community defines Z as

$$\begin{aligned}Z &= \frac{O_2 \text{ Consumed}}{\text{Inspired air}} = \frac{O_2 \text{ Consumed} * X_{O_{2,i}}}{\text{Inspired } O_2} \\ &= \phi X_{O_{2,i}} = X_{O_{2,i}} - X_{O_{2,e}} \left(\frac{X_{N_{2,i}}}{X_{N_{2,e}}} \right).\end{aligned}\quad (20b)$$

For power plant, (14) is useful in estimating O_2 consumption rate and hence heat release rate of the plant from measured air intake rate. Most of the results can be obtained without knowledge of “ h ” or “ o ”; particularly the RQ as given by (14) does not require knowledge of “ h ” or “ o .” Thus CO_2 in tons per GJ does not require knowledge of h and o . The RQ must not depend upon excess air% and as such the variation of $CO_2\%$ and $O_2\%$ in exhaust with excess air% must be such that RQ values should remain constant when combustion is complete [12]. Thus the accuracy of instruments in measuring CO_2 and $O_2\%$ can also be checked. The CO_2 mole fraction (not CO_2 in tons per GJ) will reach a maximum value when

FIGURE 1: Estimated variation of HHV with fuel composition using Boie equation. HHV decreases with increase in oxygen content in the fuel. Multiply HHV in kJ/kg by 0.43 to obtain BTU/lb. H/C: hydrogen to carbon atom ratio and O/C: oxygen to carbon atom ratio.

excess air percentage is zero or $\phi = 1$. Thus $X_{O_{2,e}} = 0$ at $\phi = 1$. From (14), with $X_{CO_{2,i}} = 0$ (i.e., pure dry air inlet), one has

$$X_{CO_{2,max}} = \frac{RQ}{((1 - X_{O_{2,i}})/X_{O_{2,i}}) + RQ}. \quad (21)$$

Thus, for dry air $X_{O_{2,i}} = 0.21$, $X_{N_{2,i}} = 0.79$, and $X_{CO_{2,max}} = RQ/(3.76 + RQ)$.

3. Results and Discussion

3.1. Fuel Properties. Properties of different gaseous, liquid, and solid fuels which are commonly used for combustion applications are presented in Table 2.

The major difference which can be observed between conventional fossil fuels and renewable fuels is the amount of oxygen. Biomass fuels have a higher percentage of oxygen, and hence lower amount of oxygen is required for combustion. This results in higher RQ for biomass when compared to oil and gas. Boie equation ((4) combined with (5)) can be used to study the variation of HHV with carbon, hydrogen, and oxygen atoms in the fuel. Figure 1 shows the estimated variation of HHV with fuel composition.

It can be observed from Figure 1 that the HHV of the fuels increases with increase in hydrogen to carbon ratio and decreases with increase in oxygen to carbon ratio. Hydrocarbon fuels with O/C ratio of zero have the highest HHV when compared to other fuels which has some amount of oxygen intrinsically. We can observe a decreasing trend in HHV (Table 2) from pure hydrocarbon fuels (methane,

TABLE 2: Properties of different fuels reported on mass basis.

Fuel	C Mass%	H Mass%	S Mass%	N Mass%	O Mass%	HHV measured (kJ/kg)	HHV, Boie (kJ/kg)	Ref.
<i>Gaseous fuels</i>								
Methane	75	25	0	0	0	55,500*	55,426	[17]
Ethane	80	20	0	0	0	51,100*	51,373	[17]
Propane	81.8	18.2	0	0	0	50,300*	49,914	[17]
Ethylene	80	20	0	0	0	50,300*	51,373	[17]
Acetylene	92.3	7.7	0	0	0	49,900*	41,402	[17]
<i>Liquid fuels</i>								
Gasoline (C_8H_{18})	84.2	15.8	0	0	0	48,500	47,968	[22]
Diesel ($C_{12}H_{23}$)	86.2	13.8	0	0	0	45,000	46,347	[22]
Biodiesel [†]	77.2	12.2	0	0	10.6	35,900	40,147	[22]
Ethanol [†]	52.1	13.2	0	0	34.7	29,700*	29,603	[17]
Methanol [†]	37.5	12.6	0	0	49.9	23,900*	22,168	[17]
Free fatty acid from peanut oil soap stock [†]	80.2	12.2	0.12	0.5	7	39,800	41,645	[22]
Bio oil (wood pyrolysis) [†]	56	6.25	0	0.1	37.5	17,500	22,801	[23]
Heavy oil	85	11	0	0.3	1	40,000	42,579	[23]
Canola oil [†]	80.2	10.9	0.004	0.14	8.62	40,200	39,927	[22]
<i>Solid fuels</i>								
WYO coal	46.5	2.73	0.27	0.66	11.3	18,200	18,347	[24]
TXL coal	37.2	2.12	0.61	0.68	9.61	14,300	14,577	[24]
Hardwood (mesquite) [†]	43.6	4.98	0.03	0.62	33.6	16,700	17,434	[25]
Softwood (juniper) [†]	49.3	5.7	0.01	0.28	37	19,000	19,874	[25]
Fibrous (rice straw) [†]	41.8	4.63	0.08	0.7	36.6	16,300	16,068	[17]
Animal based (LAPCDB) [†]	35.2	3.7	0.43	1.93	18.6	12,800	14,780	[26]

* Estimated from the enthalpy of formation data. [†] Renewable fuels. Multiply HHV in kJ/kg by 0.43 to obtain BTU/lb.

FIGURE 2: Variation of higher heating value of fuels per kg of oxygen consumed with increase in H/C ratio in fuels. It can be seen that HHV_{O_2} almost remains constant for all fuels. Y scale is enlarged to show small deviations; multiply HHV_{O_2} in kJ/stoich kg of O_2 by 0.43 to obtain BTU/stoich lb of O_2 . Multiply HHV_{O_2} in kJ/stoich kg of O_2 by 0.0013 to obtain kJ/SATP liter and multiply kJ/kg by 0.035 to obtain BTU/SATP SCF of O_2 where SATP is standard atmospheric temperature and pressure, 25°C and pressure of 1 atm.

acetylene, etc.) to solid biomass fuels (rice straw) which can be attributed mainly to the O/C ratio in these fuels.

3.2. Higher Heating Value per Unit Stoichiometric Oxygen. Equation (6) was used to determine the HHV_{O_2} (kJ/kg of O_2) for different fuels with $h = H/C$ varying from 0 to 4 and $o = O/C$ varying from 0 to 1. Figure 2 shows the variation of HHV_{O_2} with respect to ratio of hydrogen to carbon atoms (H/C) in the fuel. It is apparent from Figure 2 that HHV per unit mass of oxygen burned is approximately the same of about 14,250 kJ/kg of oxygen (18.6 kJ/SATP L of oxygen) or 3,280 kJ/kg stoichiometric air (3.9 kJ/SATP L of air) for most fuels. For fuels containing oxygen (O/C ratio greater than

zero), HHV will be lower. Further, the amount of oxygen needed for stoichiometric combustion of the fuel will also be lower for these fuels when compared to a pure hydrocarbon (e.g., methane) fuel. This causes the ratio to balance resulting in that HHV_{O_2} stays around 14,250 kJ/kg of oxygen for all the fuels.

It is noted that HHV_{O_2} of nutrients (fuels for body: glucose, fat and protein, Table 1) remains around 14,000 kJ/kg oxygen matching thermal engineering fuels (e.g. coal, oil, gas). It is also noted that $H/C \approx 2$ for both fat and glucose and $H/C \approx 2$ for protein also. For methane, the HHV_{O_2} is 13,550 kJ per kg of O_2 (17.7 kJ/SATP L of O_2) while Boie based equation yields 13,934 kJ/kg of O_2 . For n-octane, the value is 13,640 kJ per kg of O_2 or 17.82 kJ/L of O_2 at standard atmospheric temperature and pressure (SATP) while Boie yields 13,730 kJ/kg O_2 . Medical community uses HHV_{O_2} to estimate metabolic rate in W of any specified organ by measuring input arterial oxygen concentration and exiting venous oxygen concentration. An average value of 20.2 kJ per CSTP liter of oxygen is assumed for the metabolism of mixed diet. The heat released during metabolism is estimated based on the amount of oxygen consumed [27].

Similar $O_2\%$ in exhaust gas after combustion of an arbitrary fuel implies excess air% will also remain approximately similar for most fuels [28]. See (12). Since thermal output = $HHV_{O_2} \times \text{stoichiometric } O_2 \text{ flow rate} = HHV_{air} \times \text{stoichiometric air flow rate} = HHV_{air} \times \text{actual air flow rate} / (1 + x/100)$, where x is % excess air, thus when actual air flow rate is maintained the same, one may switch the fuel and adjust the fuel flow rate such that the same $O_2\%$ is maintained which ensures similar thermal output. In automobiles or gas turbines, when alternate fuels are used for combustion, the same thermal energy input is assured when air flow is maintained the same and fuel flow is adjusted such that the same $O_2\%$ is maintained in exhaust. For example, the heating value of gasoline and ethanol blend is lower than gasoline and hence blend fuel flow rate must be increased until the $O_2\%$ in exhaust is maintained the same when fuel is switched from gasoline to blend.

3.3. CO_2 Emissions in Tons/GJ and RQ Factor. Boie equation can be used to derive an expression for the CO_2 emitted in tons per GJ of energy input from the fuel chemical composition as given in (17).

$$CO_2 \text{ in tons/GJ} = \frac{1 \times 44 \times 1000}{[422270 \times \{1 + (117385/422270) \times h - (177440/422270) \times o\}]}, \text{ known fuel composition.} \quad (22)$$

Alternately the CO_2 in tons per GJ of energy input is given in terms of RQ as

$$\begin{aligned} CO_2 \text{ in tons/GJ of energy input} \\ \approx RQ \times \frac{\text{kg } O_2}{HHV_{O_2} \text{ in GJ}} \times \frac{\text{kmol } O_2}{32 \text{ kg}} \times \frac{44.01 \text{ kg}}{\text{kmol } CO_2} \quad (23) \\ \times \frac{0.001 \text{ Tons}}{\text{kg}}. \end{aligned}$$

Assuming $HHV_{O_2} = 0.014$ GJ/kg O_2 (or 0.448 GJ/kmol of O_2 , 18.3 MJ/SATP m^3 of O_2)

$$\begin{aligned} CO_2 \text{ in tons/GJ of energy input} &\approx RQ \times 0.1 \\ \text{or } CO_2 \text{ in short tons per mm BTU} &= RQ \times 0.116, \end{aligned} \quad (24)$$

where the approximate sign is due to assumption of constant $HHV_{O_2} = 0.014$ GJ per kg of O_2 consumed. For $RQ = 1$ (pure

TABLE 3: Estimated RQ factors for hydrocarbon, alcohol, aromatics, and cycloparaffin fuels. CO_2 in tons per GJ $\approx \text{RQ} \times 0.1$; CO_2 in short tons per MMBtu = $\text{RQ} \times 0.116$; $\text{RQ} = (\text{C, mass\%/12.01}) / \{(\text{C, mass\%/12.01}) + (1/4)(\text{H, mass\%/1.01}) - (1/2)(\text{O, mass\%/16}) + (\text{S, mass\%/32.06})\}$; $\text{HHV}_{\text{O}_2} = 0.014 \text{ GJ/kg O}_2$ or $0.448 \text{ GJ/kmole O}_2$.

Fuel Type	RQ ($=\text{CO}_2/\text{O}_{2,\text{st}}$) relation	Range of RQ	Remarks
Paraffins, $\text{C}_n\text{H}_{2n+2}$	$\frac{1}{\{1 + (1/2 + 1/2n)\}}$	$1/2 < \text{RQ} < (2/3)$	RQ increases slightly with “ n ”; $\text{RQ} = 1/2$ for CH_4 , RQ increases with n and $\text{RQ} \rightarrow (2/3)$ as $n \rightarrow \infty$. HHV_{O_2} ranges from 13,720 kJ/kg O_2 to 13,920 kJ/kg O_2 . (CH_4 to $\text{C}_{20}\text{H}_{42}$)
Diolefins, $\text{C}_n\text{H}_{2n-2}$	$\frac{1}{\{1 + (1/2 - 1/2n)\}}$, $n \geq 2$	$2/3 < \text{RQ} < (4/5)$	RQ decreases slightly with “ n ”; $\text{RQ} \rightarrow (2/3)$ as $n \rightarrow \infty$. HHV_{O_2} ranges from 13,490 kJ/kg O_2 to 13,660 kJ/kg O_2 . (C_2H_4 to $\text{C}_{12}\text{H}_{22}$)
Aromatics, $\text{C}_n\text{H}_{2n-6}$	$\frac{1}{\{(3/2 - 3/2n)\}}$, $n \geq 6$	$2/3 < \text{RQ} < (4/5)$	RQ decreases slightly with “ n ”; RQ , $\text{RQ} \rightarrow (2/3)$ as $n \rightarrow \infty$. HHV_{O_2} ranges from 13,585 kJ/kg O_2 to 13,620 kJ/kg O_2
Olefins, naphthenes, or cycloparaffin, C_nH_{2n}	$(2/3)$	$(2/3)^*$	RQ constant
Alcohols, $\text{C}_n\text{H}_{2n+2}\text{O}$	$(2/3)$	$(2/3)^*$	RQ is constant

*The RQs for olefins, naphthenes, cycloparaffins, and alcohols are same; thus a blend of these fuels will not change RQ values and dry gas percentage will remain the same for both pure fuels and blends of arbitrary percentage at given equivalence ratio (refer to the Appendix). On the other hand, RQ for a blend of, say, CH_4 (Fuel 1) with RQ of 0.50 with glucose or carbon monoxide (Fuel 2) for which RQ is 2 will change with proportion of Fuel 1 in the blend of Fuel 1 and Fuel 2 and dry exhaust gas percentage will change for blends with change in % Fuel 2 in the blend and vice versa. Biology literature uses the change in RQ to determine the proportion of Fuel 1 (glucose) in the blend of glucose and fat (Fuel 2) being metabolized.

carbon), CO_2 is about 0.1 tons per GJ or 100 g per MJ. In order to validate approximate expression for CO_2 , actual measured heating values of fuels for which compositions are well known (e.g., CH_4 , C_8H_{18} , $\text{C}_{12}\text{H}_{23}$, $\text{C}_2\text{H}_5\text{OH}$, coal, and biomass) are used to estimate CO_2 in tons per GJ. Results are shown in Figure 3. It is apparent from Figure 3 that CO_2 in tons per GJ of energy input has a slope of 0.1 which confirms the approximation [13].

3.4. RQ Factor from Known Fuel Composition. The RQ factor for fuels can be estimated (i) using (8) when C normalized chemical formula is known (e.g. ethanol: $\text{C}_2\text{H}_6\text{O}$, C normalized formulae: $\text{CH}_3\text{O}_{0.5}$), (ii) using equation presented in Table 3 and (iii) when ultimate analysis is known (e.g. Coal, biomass). Table 3 shows the variation of RQ factor for hydrocarbon (HC), alcohol, aromatics, and cycloparaffin fuels. In general, the RQ factor increases with decrease in hydrogen to carbon ratio. The increasing CO_2 emission in tons with year is usually interpreted by using energy consumption model; but it is also affected by change in type of fossil fuel consumed in power generation. Methane which has an H/C ratio of 4 has the lowest RQ factor for pure fuels with $\text{RQ} = 0.5$.

The RQ factors along with the O/C and H/C obtained for the common gaseous, liquid, and solid fuels are presented in Table 4. It can be observed from Table 4 that the solid fossil and biomass fuels have comparatively higher oxygen content. Higher oxygen content results in higher RQ factor for solid fuels. Gasoline and diesel fuels which are used in the automobiles have a lower RQ when compared to that of solid fuels.

FIGURE 3: CO_2 emitted in tons per GJ of energy input for fuels with different RQ factors. Fuel measured heating value and composition data were used to estimate CO_2 released (for fuels listed in Table 2). Slope of both the trend lines (actual heating value and heating value estimated using Boie equation) was approximately 0.1 [13]. $y = \text{CO}_2$ in tons per GJ, $x = \text{RQ}$.

It is seen that most solid fuels (pure carbon $\text{RQ} = 1$, biomass fuels $\text{RQ} = 0.94$ – 0.97 , most sweet sorghum sources = 0.98 to 1.0 [29], coals $\text{RQ} = 0.92$ – 0.93 , and animal wastes

TABLE 4: RQ factor for different fuels along with their respective O/C and H/C ratios.

Fuel	"o" or O/C	"h" or H/C	RQ	HHV, Boie (kJ/kg)
<i>Gaseous fuels</i>				
Methane	0.00	4.00	0.50	55,426
Ethane	0.00	3.00	0.57	51,373
Ethylene	0.00	3.00	0.57	51,373
Propane	0.00	2.67	0.60	49,914
Acetylene	0.00	1.00	0.80	41,402
<i>Liquid fuels</i>				
Methanol [†]	1.00	4.00	0.67	22,168
Ethanol [†]	0.50	2.99	0.67	29,603
Gasoline (C ₈ H ₁₈)	0.00	2.25	0.64	47,968
Diesel (C ₁₂ H ₂₃)	0.00	1.92	0.68	46,347
Biodiesel [†]	0.10	1.90	0.70	40,147
Free fatty acid from peanut oil soap stock [†]	0.07	1.83	0.70	41,645
Canola oil [†]	0.08	1.63	0.73	39,927
Heavy oil	0.01	1.55	0.72	42,579
Bio oil (wood pyrolysis) [†]	0.50	1.34	0.92	22,801
<i>Solid fuels</i>				
Softwood (Juniper) [†]	0.56	1.39	0.94	19,874
Hardwood (mesquite) [†]	0.58	1.37	0.95	17,434
Fibrous (rice straw) [†]	0.66	1.33	1.00	16,068
Animal based (LAPCDB)*	0.40	1.26	0.89	14,780
Wyoming coal	0.18	0.70	0.92	18,347
Texas Lignite coal	0.19	0.68	0.93	14,577

[†] Renewable fuels. * LAPCDB: low ash partially composted dairy biomass.

RQ = 0.92–0.95) have an RQ factor of around 0.95. Gaseous and liquid fuels have RQ between 0.50 and 0.80. Figure 4 shows the plot for variation of "RQ" with H/C and O/C ratio of different fuels (see (8)). It is noted that renewable biomass fuels have a slightly higher RQ compared to coal. Fuels having higher RQ have a lower HHV as observed in Table 4. Higher RQ also implies lower amount of oxygen required for complete combustion of a given fuel. This would cause a fuel with higher RQ and lower HHV to emit more CO₂ in order to meet the desired heat input for a given application. Since HHV_{O₂} is constant for most fuels, then, for given thermal input, the O₂ moles consumed will remain the same. Hence, a fuel with higher RQ (lower HHV) would result in more fuel being consumed producing more CO₂ for the same thermal heat input, that is, more tons of CO₂ per GJ.

For pure carbon, the RQ is 1 since each C atom requires one O₂ to burn. For CO, RQ = 2. RQ scaling must be applied to oxidation processes. For example, RQ tends to ∞ for anaerobic digestion which produces CH₄ and releases CO₂ since no O₂ is consumed. It does not imply that it has highest global warming potential. Here the production of CH₄ becomes important. Even in human body, old people seem to have a higher RQ compared to young adults [30] due to anaerobic digestion which produces CH₄ and CO₂ and no oxygen is consumed.

Using Boie equation, carbon dioxide emitted on a mass basis (g/MJ or kg/GJ) determined for different fuel compositions is shown in Figure 5. Solid biomass fuels with higher RQ will emit more CO₂ per GJ when compared to existing conventional gaseous and liquid fossil fuels. Just as Environmental Protection Agency (EPA) sets limit on NO_x in lb per MMBtu or kg/GJ, the CO₂ amount must be estimated in kg per unit GJ or lb per MMBtu rather than kg of CO₂ per kg fuel since heat input must be maintained the same to generate the same power when fuel is switched. Both Figures 4 and 5 follow the same trend in terms of increased emissions with increase in oxygen content and C/H ratio in the fuel. From results on RQ factor and carbon dioxide emissions from fuels, it can be seen that the liquid fuels currently used in automobiles have the least RQ factor next only to natural gas. Biofuels produced from renewable energy sources are limited by the energy density and oxygen content. If the oxygen content can be reduced by using torrefaction of biomass [25, 31] and catalytic cracking and hydrotreating [32, 33] of bio-oils, the energy density of the biomass and bio-oils can be improved and in turn will also reduce the RQ factor of the fuels. But such a process also reduces the yield of bio-oil.

3.5. RQ Factor from Exhaust Gas Composition. Equations (11), (12), (13), (14), (15), (17), and (19) (refer to the Appendix

FIGURE 4: Variation of RQ with H/C ratio and O/C ratio of the C-H-O fuel. Gaseous and liquid fuels have lower RQ factor when compared to that of solid fossil and renewable fuels. CO_2 in tons per GJ $\approx \text{RQ} * 0.1$; CO_2 in short tons per MMBtu $\approx \text{RQ} * 0.116$.

FIGURE 5: Effect of H/C and O/C on the CO_2 emission from fuels. Fuels with higher RQ factor emit higher amounts of carbon dioxide. Note g/MJ = kg/GJ; multiply kg/GJ by 2.326 to obtain lb per MMBtu.

for any C-H-O fuel) which give the relation between $\text{O}_2\%$, $\text{CO}_2\%$, and RQ factor of the fuel can be used to present the variation of RQ for different exhaust oxygen concentrations. The resulting plot is shown in Figure 6. This plot will serve as an important tool to determine the RQ factor for C-H-O fuels

FIGURE 6: Variation of RQ and equivalence ratio {called OEF in biology} with respect to dry carbon dioxide with oxygen mole fraction in the flue gas as parameter (see the Appendix for relations). Solid lines: RQ with X_{O_2} as parameter; dashed lines: ER with X_{O_2} as parameter. As $\text{CO}_2\%$ in exhaust increases, it implies increasing RQ for given $\text{O}_2\%$. At given $\text{CO}_2\%$, increase in $\text{O}_2\%$ in exhaust implies increasing RQ.

of unknown composition (e.g., blended fuels like gasoline: alcohol, solid fuels in power plants) from the exhaust gas composition measurements. Particularly (11) can be used to determine RQ. In order to illustrate this, nasal exhaust gas analyses have been used with composition as given in Table 5.

From Figure 6, it can be inferred that, for an exhaust CO_2 concentration of 12% with O_2 of 0%, RQ is 0.5. Substituting the CO_2 , O_2 , and N_2 inhaled concentration (Table 5) in (14) with $X_{\text{CO}_{2,i}} = 0$ yields RQ as 0.79. Since RQ for glucose = 1, RQ for fat 0.7 (Table 1), then RQ of 0.79 indicates that a mix of fat and glucose is burned in the body. Since an average person of 70 kg releases about 80 W or 0.0069 GJ per day [10], with RQ = 0.79, CO_2 emitted by 70 kg human who consumes renewable fuels is $0.1 * 0.79 * 0.0069 * 1000 = 0.55 \text{ kg/day}$.

3.6. RQ Factor for Blended Fuels

Known Chemical Formula and % Volume/Mass/Mole of Each Fuel. Gasoline (a fossil fuel): ethanol (a renewable fuel) blends are used in automobiles while coal (a fossil fuel): biomass (a renewable fuel) blends are used in power plants. Thus, it is of interest to estimate RQ of blended fuels. Consider blended fuels of Fuel 1 and Fuel 2. Since CO_2 in tons per GJ $\approx \text{RQ} * 0.1$ which assumes that the HHV_{O_2} (kJ/kg O_2) is the same for all fuels, then

CO_2 in tons per GJ of blended fuel

$$\begin{aligned} &\approx \text{RQ}_{\text{blend}} * 0.1 \\ &= (\text{RQ}_1 * 0.1) (\text{tons/GJ of fuel-1}) \\ &\quad * (\text{GJ of fuel-1/GJ of blended fuel}) \\ &\quad + (\text{RQ}_2 * 0.1) (\text{tons/GJ of fuel-2}) \\ &\quad * (\text{GJ of fuel-2/GJ of blended fuel}) + \dots \end{aligned} \quad (25)$$

TABLE 5: Nasal gas analysis, adopted from Kimball, 2013 [34].

Composition of ambient air and expired air in a normal human (table modified to present dry basis values; assumed CO ₂ at inlet = 0)		
Component	Atmospheric air (%)	Expired air (%)
N ₂ (plus inert gases)	79.05	79.85
O ₂	20.95	16.31
CO ₂	0.0	3.84
H ₂ O	0.0

FIGURE 7: Heat fraction contributed by gasoline and RQ of mixture for known volume fractions of gasoline. Assume the following mixture burned: gasoline (C₈H₁₈) and ethanol (C₂H₆O). HHV_{O₂} = 14,200 kJ/kg of O₂ consumed.

Let heat fraction (HF)—HF₁ = (GJ of Fuel 1/GJ of blended fuel)—be a fraction of heat released by Fuel 1 from blend. Since HHV_{O₂} is the same for all fuels, then HF₁ ≈ (GJ due to Fuel 1/GJ of blended fuel) = (O₂ consumed by Fuel 1/O₂ consumed by blend). If Fuel 1 is gasoline and Fuel 2 is ethanol,

$$RQ_{\text{blend}} \approx RQ_{\text{gasoline}} * HF_{\text{gasoline}} + RQ_{\text{ethanol}} * HF_{\text{ethanol}} \quad (26)$$

RQ_{ethanol} and RQ_{gasoline} can be used to estimate the RQ value for the blend of gasoline and ethanol. Figure 7 shows a plot of RQ and heat fraction versus volume fraction of gasoline. Table 6 summarizes the results for 85:15 (volume%) gasoline (Fuel 1, represented by surrogate fuel C₈H₁₈): ethanol (Fuel 2, C₂H₅OH) blend. The 85:15 gasoline:ethanol blend has a heat fraction: HF_{gasoline} = 0.9 and HF_{ethanol} = 0.1.

From Table 6 it can be seen that RQ_{blend,net} for 85:15 blend of gasoline and ethanol is 0.584 by assuming ethanol to be carbon neutral. It is less than RQ_{gasoline} of 0.64 which is the desired criterion to reduce the GWP. Thus CO₂ in tons per GJ is reduced from 0.064 tons to 0.0584 tons or a reduction of 8.74%. It is noted that a gallon of gasoline has a heat value of 0.138 GJ while a gallon of 85:15 blend has a heat content of 0.130 with a reduction of 5.4% in heat content.

Known Exhaust Gas Analysis and Chemical Formula of Each Fuel. If each fuel percentage and fuel composition are

unknown, then exhaust gas analyses can be used to estimate RQ_{blend} and hence CO₂ in tons per GJ for such blend directly using exhaust gas composition (Appendix).

$$RQ = \frac{X_{\text{CO}_{2,e}} (N_2/O_2)_i}{X_{N_{2,e}} - X_{O_{2,e}} (N_2/O_2)_i} \quad (27)$$

Equation (21) enables determination of RQ for any C-H-O fuel of unknown composition and RQ. Hence, CO₂ in tons can be easily estimated. If fuel is a blend of gasoline and ethanol with RQ₁ for gasoline (e.g., 0.64) and RQ₂ (e.g., 0.67) for ethanol, the CO₂ contributed by gasoline only is needed. The appendix or (26) shows that RQ of blend is related to heat fraction contributed by gasoline and ethanol.

$$\begin{aligned} RQ &= HF_1 * RQ_1 + (1 - HF_1) * RQ_2 \\ &= RQ \text{ contributed by fossil fuel} \\ &\quad + RQ \text{ contributed by renewable fuel,} \end{aligned} \quad (28)$$

where RQ₁ and RQ₂ can be determined for each fuel if each fuel is fired alone and exhaust gas analyses are performed (i.e., using Figure 6). Solving for HF₁

$$HF_1 = \frac{RQ - RQ_2}{RQ_1 - RQ_2} \quad (29)$$

Figure 8 plots X_{CO_{2,e}} and energy released per liter of air input versus gasoline volume fraction with X_{O_{2,e}} as parameter. It should be noted that the RQ values for this blend have a narrow range of 0.64 to 0.67 and as such X_{CO₂} curves are almost flat. The product 0.1 * (HF₁ * RQ₁) provides CO₂ in tons contributed by gasoline per GJ of total energy released. For X_{CO₂} = 0.0702 and X_{O₂} = 0.11, RQ = 0.643 (from Figure 6), gasoline volume fraction is 0.85, and HF₁ = 0.90 (Figure 8). When RQ₁ and RQ₂ are close to each other as in this case (RQ₁ = 0.64 and RQ₂ = 0.67), the error from charts may be high. For blends of C₈H₁₈ and C₂H₆O fuels one might have to use equation to determine HF₁ rather than charts. Thus effective RQ for gasoline alone is 0.9 * 0.64 indicating 0.57 due to gasoline alone which is less than RQ of gasoline 0.64 with a reduction of 11%.

The Energy Released per L Air in. Energy released per L air can be determined using the following equation:

$$\begin{aligned} \text{Energy released per L air in} &= O_2 \text{ consumed per L of air} \\ &\quad * HHV'_{O_2} \text{ in kJ/L } O_2 \\ \text{Energy released per L air in} &= \left(\frac{O_2 \text{ consumed in kg}}{O_2 \text{ consumed in kg}} \right) \\ &\quad * O_2 \text{ supplied in kg per L of air} * HHV_{O_2} \text{ in kJ/kg } O_2 \\ \text{Energy released per L air in} &= \varphi * Y_{O_{2,i}} * \rho \text{ (kg/L air)} \\ &\quad * HHV_{O_2}, \end{aligned} \quad (30)$$

where Y_{O_{2,i}} is typically 0.23 for dry air. The secondary y-axis in Figure 8 presents the results.

TABLE 6: RQ values for pure gasoline, pure ethanol, and for 85 : 15 (vol%) gasoline: ethanol blend. Blend: volume%, gasoline: 85 and ethanol: 15; mass%, gasoline: 84.6 and ethanol: 15.4; heat%, gasoline: 90 and ethanol: 10; $RQ_{\text{process,ethanol}} = 0.09$; $RQ_{\text{Blend,total}} = RQ_{\text{Blend}} + RQ_{\text{process,ethanol}}$; $RQ_{\text{blend,net}} = RQ_{\text{Blend,total}} * HF_{\text{gasoline}}$; CO_2 in tons per GJ $\approx RQ * 0.1$.

Fuel	Pure gasoline	Pure ethanol	(85 : 15) blend
Formula (empirical formula)	$\text{C}_8\text{H}_{18}(\text{CH}_{2.25})$	$\text{C}_2\text{H}_5\text{OH}$ ($\text{CH}_3\text{O}_{0.5}$)	
Density (kg/m^3)	750	785	785
HHV (kJ/kg)	48500	29700	
CALCULATED			
C normalized empirical formula	$\text{CH}_{2.25}$	$\text{CH}_3\text{O}_{0.5}$	$\text{CH}_{2.33}\text{O}_{0.051}$
Molecular weight-empirical	14.283	23.04	15.182
HHV, kJ/kg	-	-	45569
ν_{emp} (stoichiometric O_2 moles/empirical mole)	1.563	1.5	1.556
St O_2 kg/kg fuel	3.501	2.083	3.28
HHV O_2 , kJ/kg O_2	13854	14256	13894
RQ_{blend}	0.640	0.667	0.643
$RQ_{\text{blend total}}$	-	-	0.652
$RQ_{\text{blend,net}}$ (ethanol being carbon neutral)	-	-	0.584

FIGURE 8: Using dry mole fractions of CO_2 and O_2 in the exhaust to estimate the gasoline volume fraction (solid lines) and energy released in J per L of air input (dashed line). Assume gasoline to be C_8H_{18} .

3.7. RQ Factor from Fuel Blend Exhaust and CO_2 Tax. If exhaust analyses are known for any volume blends of unknown C-H-O fuel₁ and C-H-O fuel₂ with different RQ values (RQ_1 and RQ_2 , $RQ_2 \neq RQ_1$), all the above parameters including RQ (which is useful for CO_2 taxation) can be evaluated, that is, without the knowledge of “h” and “o” (see the Appendix). Figure 8 shows the plots for energy released per SATP L of air input (secondary axis). For example, if 85% (vol%) gasoline: ethanol blend is used and if $X_{\text{CO}_2} = 0.0702$, $X_{\text{O}_2} = 0.11$, and $\phi = 0.5$ (Figure 6) energy released per SATP L of air is $1.95 * 1000 = 1950$ J/L of inlet air (Figure 8); if the inlet air rate is 60 LPS for an engine, then the energy release rate can be estimated to be 117 kW out of which $117 * 0.90 = 105$ kW from gasoline. Even though ethanol is about 15% on volume basis ($\approx 30\%$ on mole basis) for the given exhaust gas composition, most of the energy released comes from

gasoline due to its high heat value. With known RQ_1 and RQ_2 the heat fraction is computed. However if RQs are the same for main fuel (MF) and renewable fuel (RF), dry exhaust gas analysis method will not yield heat fraction in blend (refer to the Appendix) and knowledge of volume or mole or mass fraction of RF in the blend is required. As in the previous section, $RQ_{\text{blend,net}} = RQ_{\text{blend total}} * HF_{\text{gasoline}}$.

Carbon Fraction Method. When RQs are approximately the same for Fuel 1 and Fuel 2 in blend, exhaust gas analysis method may not yield % contribution by, say, Fuel 1 in the blend to CO_2 . Thus if volume or mole or mass fraction of RF is known, the carbon fraction method can be used as indicated below. Carbon atom fraction due to main fuel (MF) (=ratio of C atom contribution by main fuel to total C atoms of fuel blends or mass ratio of carbon) must be estimated. It can be shown that, for a volumetric blend of MF and RF, the carbon atom fraction in the final blend due to main fuel (MF) is given as

C fraction due to MF

$$= \frac{(1 - \nu_{\text{RF}}) * \rho_{\text{MF}} * \text{mf}_{\text{C,MF}}}{(1 - \nu_{\text{RF}}) * \rho_{\text{MF}} * \text{mf}_{\text{C,MF}} + \nu_{\text{RF}} * \rho_{\text{RF}} * \text{mf}_{\text{C,RF}}} \quad (31)$$

$$= \frac{1}{1 + (\nu_{\text{RF}} * \rho_{\text{RF}} * \text{mf}_{\text{C,RF}}) / ((1 - \nu_{\text{RF}}) * \rho_{\text{MF}} * \text{mf}_{\text{C,MF}})},$$

where ν_f represents volume fraction which is either known from specification at gas station. If MF = gasoline, volume fraction of main fuel (ν_{MF}) = 0.85 (density $750 \text{ kg}/\text{m}^3$, C (mass): 84%) and the rest is RF = ethanol (fraction of $\text{C}_2\text{H}_6\text{O}$: 15%, C: 52.13%, and density $785 \text{ kg}/\text{m}^3$), then C due to gasoline in blend is 0.90 and hence RQ obtained from exhaust of car fired with 85% gasoline and 15% ethanol (vol%) needs to be multiplied by 0.90 for levying CO_2 tax. Figure 9 shows the variation of C atom fraction contributed by gasoline as a function of ethanol volume fraction. From gas analysis

FIGURE 9: Carbon fraction (atom or mass) contribution by gasoline in gasoline: ethanol blend. x -axis: ethanol volume percentage; y -axis: carbon atom fraction contributed by gasoline in blend. The curve is almost linear for small ethanol volume fraction. Gasoline is assumed to be $\text{CH}_{2.25}$. RQ from exhaust analysis needs to be multiplied by C fraction from gasoline to estimate CO_2 contribution by gasoline.

method, it was illustrated that the measurements of CO_2 and O_2 can yield mole% and mass% of the main fuel.

Recently CO_2 based motor vehicle tax has been introduced in European Union countries [35]. Based on the emission of CO_2 in g/km, taxes will be levied to the customer. An empirical rule to determine the CO_2 emission from gasoline and diesel vehicles has been proposed by the Environmental Transport Association (ETA) [36]. If miles per gallon (MPG) value is 40, the empirical rule for the Spark Ignition (gasoline) engine to determine the CO_2 emission in g per km is $6760/\text{MPG} = 6760/40 = 169$ g of CO_2/km . For diesel engine, $7440/\text{MPG} = 7440/40 = 186$ g/km.

Using the formula derived in the current work to estimate the CO_2 emitted by fuel in tons/GJ (see (24)), CO_2 emitted in g per km can be determined as follows:

$$\begin{aligned}
 \text{CO}_2 \text{ in } \left(\frac{\text{tons}}{\text{gallon}} \right) &= \left(\text{CO}_2 \text{ in } \frac{\text{tons}}{\text{GJ}} \right) * \left(\text{heat value in } \frac{\text{GJ}}{\text{m}^3 \text{ of fuel}} \right) \\
 &\quad * \left(\frac{\text{m}^3 \text{ of fuel}}{\text{gallon}} \right) \\
 \text{CO}_2 \text{ in } \left(\frac{\text{g}}{\text{km}} \right) &= \left(\text{CO}_2 \text{ in } \frac{\text{tons}}{\text{gallon}} \right) * \left(\frac{10^6}{\text{MPG}} \right) * \left(\frac{\text{mile}}{\text{km}} \right) \quad (32) \\
 &= \left(\text{CO}_2 \text{ in } \frac{\text{tons}}{\text{GJ}} \right) * \left(\text{heat value in } \frac{\text{GJ}}{\text{m}^3 \text{ of fuel}} \right) \\
 &\quad * \left(\frac{\text{m}^3 \text{ of fuel}}{\text{gallon}} \right) * \left(\frac{10^6}{\text{MPG}} \right) * \left(\frac{\text{mile}}{\text{km}} \right) \\
 &\approx \frac{5445}{\text{MPG}}, \text{ gasoline}
 \end{aligned}$$

Gasoline with HHV ≈ 0.132 GJ/gallon.

Using the above formulae and heat values (Table 2), CO_2 emitted on using gasoline as a fuel was 136 g/km at 40 MPG and for diesel it is 145 g/km based on empirical chemical formulae of fuels. Note that the empirical CO_2 formula used by ETA also shows the increased amount for diesel. For the same MPG, CO_2 -net for 85:15 gasoline:ethanol blend = 118.2 g/km assuming the same 40 MPG. But the MPG may not be the same for the blend since the amount of energy in a gallon is less for a blend and less distance will be travelled. Hence the present method of determining the online CO_2 emission in kg per GJ would be a better representation for the CO_2 emission rather than presenting the results on g per km basis.

4. Conclusions

(1) Respiratory quotient (RQ = ratio of CO_2 moles produced per unit mole O_2 consumed) used in the biological literature is applied to combustion of fossil and biomass fuels in order to rank their potential in producing global warming CO_2 (CO_2 in tons per GJ $\approx \text{RQ} * 0.1$ and CO_2 in short tons per MMBtu = $\text{RQ} * 0.116$). RQ depends only on stoichiometric relations and is independent of equivalence ratio. Such relation is based on the assumption that the higher heat value in kJ per kmol or kg of O_2 consumed remains constant at around 14,000 kJ/kg of oxygen consumed (or 6019 BTU/lb mass of oxygen consumed).

(2) Two methods were presented to determine the RQ factor of fuels: (i) chemical formulae of fuel or known ultimate analyses of fuel and (ii) exhaust gas analyses from automobile, trucks, kitchen stoves, gas turbines, and boilers in case fuel composition and heat values are not known.

(3) Since RQ must not depend upon excess air% and as such the variation of $\text{CO}_2\%$ and $\text{O}_2\%$ in exhaust with excess air% must be such that RQ values should remain constant when combustion is complete. This enables checking the instrumental accuracy.

(4) The higher the RQ value, the higher the amount of CO_2 produced in tons per GJ (or short tons/MMBtu) for the oxidation processes.

(5) It was observed that the carbon emission potential and hence the global warming potential were considerably low for gaseous fuels which typically have low RQ values (RQ for $\text{CH}_4 = 0.5$). Conventional liquid fuels such as gasoline and diesel are around 0.7 and solid fossil and biomass fuels with comparatively higher oxygen content had higher RQ (0.93–1.0).

(6) The current method enables a direct measurement of CO_2 in tons over a period with a “ CO_2 Odometer” which is operated with known $\text{CO}_2\%$ and $\text{O}_2\%$ in exhaust of automobile either for main fuels such as gasoline and diesel or blends of main fuels with renewable fuels such as ethanol.

(7) All C-H-O fuels having the same RQ will have the same CO_2 and $\text{O}_2\%$ based on dry gas analysis at given equivalence ratio or excess air%

(8) For blended fuels with a large difference in RQ values (e.g., for CO: CH_4 blend, CO with RQ = 2, CH_4 with RQ = 0.5), one can estimate the CO_2 contribution by each fuel by measuring RQ of blended fuels. However when RQ values are

close to each other, one may use carbon fraction method to estimate the CO_2 contribution by each fuel.

Appendix

Consider a mixture of x moles of Fuel 1 and $(1 - x)$ moles for Fuel 2. When this mixture undergoes stoichiometric oxidation,

With an equivalence ratio of φ

For dry analysis,

$$\text{N}_{\text{dry}} = a_{\text{st}}\text{RQ} + a_{\text{st}}\left(\frac{1}{\varphi} - 1\right) + \left(\frac{a_{\text{st}}}{\varphi}\right)\left(\frac{\text{N}_2}{\text{O}_2}\right)_i. \quad (\text{C})$$

But

$$\text{N}_{\text{dry}} = \frac{a_{\text{st}}\text{RQ}}{X_{\text{CO}_{2,e}}}. \quad (\text{D})$$

Thus using (C) noting CO_2 moles = $a_{\text{st}}\text{RQ}$ and solving for $X_{\text{CO}_{2,e}}$

$$X_{\text{CO}_{2,e}} = \frac{a_{\text{st}}\text{RQ}}{(a_{\text{st}}\text{RQ} + a_{\text{st}}(1/\varphi - 1) + (a_{\text{st}}/\varphi)(\text{N}_2/\text{O}_2)_i)}. \quad (\text{E})$$

Simplifying

$$X_{\text{CO}_{2,e}} = \frac{\text{RQ}}{(\text{RQ} + (1/\varphi - 1) + (1/\varphi)(\text{N}_2/\text{O}_2)_i)}. \quad (\text{F})$$

Similarly

$$\begin{aligned} X_{\text{O}_{2,e}} &= \frac{\text{supplied O}_2 - \text{used O}_2}{\text{N}_{\text{dry}}} \\ &= \frac{(1/\varphi - 1)}{(\text{RQ} + (1/\varphi - 1) + (1/\varphi)(\text{N}_2/\text{O}_2)_i)}. \end{aligned} \quad (\text{G})$$

Equations (F) and (G) can be used to solve for “RQ” and φ if $X_{\text{CO}_{2,e}}$ and $X_{\text{O}_{2,e}}$ are known from exhaust analyses

$$\begin{aligned} \varphi &= \frac{a_{\text{st}}}{a} = 1 - \frac{X_{\text{O}_{2,e}}}{X_{\text{N}_{2,e}}}\left(\frac{\text{N}_2}{\text{O}_2}\right)_i \\ \text{RQ} &= \left(\frac{X_{\text{CO}_{2,e}}(\text{N}_2/\text{O}_2)_i}{X_{\text{N}_{2,e}} - X_{\text{O}_{2,e}}(\text{N}_2/\text{O}_2)_i}\right), \\ X_{\text{N}_{2,e}} &= 1 - X_{\text{CO}_{2,e}} - X_{\text{O}_{2,e}}. \end{aligned} \quad (\text{H})$$

Note that the ratio $1/\text{RQ}$ represents stoichiometric O_2 moles supplied per C atom in fuel since

$$\begin{aligned} \frac{\text{stO}_2}{\text{C atom in fuel}} &= \frac{a_{\text{st}}}{\text{CO}_2 \text{ moles produced}} = \frac{a_{\text{st}}}{a_{\text{st}}\text{RQ}} \\ &= \frac{1}{\text{RQ}} = \left(\frac{X_{\text{N}_{2,e}} - X_{\text{O}_{2,e}}(\text{N}_2/\text{O}_2)_i}{X_{\text{CO}_{2,e}}(\text{N}_2/\text{O}_2)_i}\right). \end{aligned} \quad (\text{J})$$

Now consider a blend of Fuel 1 and Fuel 2:

If excess air is used and equivalence ratio is φ , $\text{RQ} = \text{CO}_2$ moles/ a_{st} , and $\text{N}_2 : \text{O}_2$ ratio at inlet is $(\text{N}_2/\text{O}_2)_i$, then

So for the blend

$$\text{RQ} = \frac{a_{\text{st},1}\text{RQ}_1 * x + a_{\text{st},2}\text{RQ}_2 * (1 - x)}{a_{\text{st},1} * x + a_{\text{st},2} * (1 - x)}. \quad (\text{K})$$

The heat fraction of fuel 1 is given as

$$\begin{aligned} \text{HF}_1 &= \frac{(a_{\text{st},1} * x * \text{HHV}_{\text{O}_2})}{(a_{\text{st},1} * x + a_{\text{st},2} * (1 - x)) * \text{HHV}_{\text{O}_2}} \\ &= \frac{(a_{\text{st},1} * x)}{(a_{\text{st},1} * x + a_{\text{st},2} * (1 - x))}, \\ &\quad \frac{\text{Moles of O}_2 \text{ consumed by fuel 1}}{\text{Moles of O}_2 \text{ consumed by blend}}. \end{aligned} \quad (\text{A.3})$$

Thus (K) becomes

$$\text{RQ} = \text{HF}_1 * \text{RQ}_1 + (1 - \text{HF}_1)\text{RQ}_2. \quad (\text{L})$$

Then, for $\text{RQ}_1 \neq \text{RQ}_2$,

$$\text{HF}_1 = \frac{(\text{RQ} - \text{RQ}_2)}{(\text{RQ}_1 - \text{RQ}_2)}, \quad \text{RQ}_2 \neq \text{RQ}_1. \quad (\text{M})$$

Note that (M) does not require knowledge of fuel composition except for RQ_1 and RQ_2 which can be determined from exhaust analyses of pure fuels.

Equation (K) yields mole fraction of fuel 1 as

$$\begin{aligned} x &= \frac{a_{\text{st},2}(\text{RQ}_2 - \text{RQ})}{\{\text{RQ}(a_{\text{st},1} - a_{\text{st},2}) + a_{\text{st},2}\text{RQ}_2 - a_{\text{st},1}\text{RQ}_1\}}, \\ &\quad \text{RQ}_2 \neq \text{RQ}_1. \end{aligned} \quad (\text{N})$$

“ x ” can be estimated provided “ a_{st} ” and RQ of both fuels are known. Once “ x ” is known, mass fractions and hence volume fractions can be computed for fuels of known densities.

$$Y_{F1} = x * \frac{M_{F1}}{M_{mix}}, \quad (O)$$

where $M_{mix} = \{x * M_{F1} + (1 - x) * M_{F2}\}$.

$$\frac{1}{\rho_{mix}} = \left(\frac{Y_{F1}}{\rho_1} + \frac{Y_{F2}}{\rho_2} \right) \quad (P)$$

$$v_{f1} = \frac{Y_1 * \rho_{mix}}{\rho_1}.$$

If $RQ_1 = RQ_2$ (e.g., blends of naphthenes and alcohols), (N) does not yield “ x ” since RQ is independent of Fuel 1 mole fraction in blend. The dry mole fractions of products do not change with composition of blend at specified ϕ when $RQ_1 = RQ_2$.

Abbreviations

a_{stoich} :	Oxygen required for stoichiometric combustion
A : F:	Air fuel ratio
BTU:	British Thermal Unit
CH ₄ :	Methane
CO:	Carbon monoxide
CSTP:	Chemist standard temperature ($T = 0^\circ\text{C}$) and pressure ($P = 101\text{ kPa}$)
CO ₂ :	Carbon dioxide
EPA:	Environmental Protection Agency
ETA:	Environmental Transport Association
FC:	Fixed carbon or fully composted (context dependent)
GHG:	Greenhouse gas
GJ:	Gigajoule
GWP:	Global warming potential
HF:	Heat fraction
HHV:	Higher or gross heating value, kJ/kg fuel
HHV _{O₂} :	Higher or gross heating value expressed in heat units per kg stoich O ₂
$\overline{\text{HHV}}_{\text{O}_2}$:	Higher heating value expressed in heat units per kmol stoich O ₂
MMBTU:	Million BTU
mf:	Mass fraction
MPG:	Miles per gallon
N ₂ :	Nitrogen
OEF:	Oxygen extraction fraction
RF:	Renewable fuel
RQ:	Respiratory quotient
SATP:	Standard Atmospheric temperature (25°C) and pressure (101 kPa)
SR:	Stoichiometric ratio
VM:	Volatile Matter
Vf:	Volume fraction
X:	Mole fraction in gas mixture
Y:	Mass fraction.

Greek Symbols

ϕ :	Equivalence ratio
ρ :	Density
$v_{\text{O}_2, \text{stoich}}$:	Stoichiometric oxygen.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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