Respiratory Quotient (Rq), Exhaust Gas Analyses, CO₂ Emission and Applications in Automobile Engineering

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Development and economic growth throughout the world will result in increased demand for energy. Currently almost 90% of the total world energy demand is met utilizing fossil fuels [1]. Petroleum and other liquid fuels include 37% of the total fossil reserves consumed for transportation and other industrial processes [1]. Emission of harmful gases in the form of nitrogen oxides, sulphur oxides and mercury are the major concerns from the combustion of conventional energy sources. In addition to these pollutants, huge amount of carbon dioxide is liberated into the atmosphere. Carbon dioxide is one of the greenhouse gases which cause global warming. Though technology is being developed to sequester the CO₂ from stationary power generating sources, it is difficult to implement such a technology in non-stationary automobile IC engines.

Some of the methods which has been studied to reduce the amount of CO₂ being released from the IC engines include blending ethanol with gasoline. Ethanol produced from corn, sugarcane bagasse and lignocellulosic biomass is considered to be carbon neutral. It is assumed that the carbon released during combustion of ethanol will be readily absorbed by the plants and will be recycled and hence the carbon released in such a process will not be accounted in the carbon footprint. But such an approach with biomass is being challenged by a number of recent studies. Land use change, use of electrical energy and fossil based energy for collection, and transportation and processing of biomass, energy conversion efficiency and productivity of forest land impacts the decision on carbon neutrality of biomass based fuels [2]. The use of short rotation woody crops with much higher yield [3] and reduced costs can serve as a source for ethanol production or energy applications.

Recent developments in the IC engines have resulted in reducing the emissions and improving the vehicle efficiency by using different sensors such as oxygen and NOx sensors and utilizing exhaust gas recirculation to lower the oxygen concentration and reduce the temperature within the engines.

The O₂ sensor which operates at about 344°C (650°F) reads 0 volts at lean condition to almost 1.0 volt under rich condition [4]. Typically the ideal A:F for a gasoline engine is 15:1 (by mass). Oxygen sensor serves to maintain a near stoichiometric condition (14.7:1 by mass) and vary the air fuel ratio within the engine for complete combustion of fuel and hence reduce the emission of unburnt hydrocarbons (HC) and CO [5]. Ideal O₂% in exhaust is less than 1.5%. A high amount of HC and CO may indicate problems in combustion and appropriate A: F ratio. x It has been found that the higher heating value per unit mass of oxygen burned (HHVO₂) remains approximately the same for all fuels; in fact this approximation is used in biology to determine the metabolic rate (or energy release rate) of humans by measuring O₂ used (=O₂ inhalation rate-O₂ exhalation rate) and using known values of HHVO₂. When renewable fuels (e.g. ethanol, C₂H₅OH) are blended with fossil fuels (gasoline, CHx) and used for combustion in IC engines, same thermal energy input is assured under fixed air flow rate and fuel flow is adjusted such that same O₂% is maintained in exhaust. Thus the oxygen sensor in an IC engine helps to maintain a proper air fuel ratio, similar heat input rate (or power) and excess air %. 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 O₂% is maintained the same when fuel is switched from gasoline to blend [6,7].

Recently CO₂ based motor vehicle tax has been introduced in European Union countries to promote the utilization of renewable fuels in automobiles [8]. Taxes will be levied to the customer based on the emission of CO₂ in g/km. Environmental transport association (ETA) has proposed an empirical rule to determine the CO₂ emission from gasoline and diesel vehicles [9]. If Miles Per Gallon (MPG) is 40, the empirical rule for the SI engine to determine the CO₂ emission is 6760/MPG=6760/40=169 g of CO₂/km. For Diesel engine: 7440/MPG=7440/40=186 g/km. Environment Protection Agency (EPA) has estimated the amount of carbon released on combustion of gasoline and diesel to be around 8887 and 10180 grams CO₂/gallon respectively for each of the fuel [10].

Rather than using the empirical rule, the potential of a particular fuel used in automobile IC engine to produce carbon dioxide can be estimated from the fuel ultimate analysis. A term used in biological literature to determine the basal metabolic rate, Respiratory Quotient (RQ) has been used in Ref [7] to estimate the CO₂ emission potential of fuels. RQ is defined as the ratio of the moles of CO₂ emitted to the moles of O₂ consumed typically for oxidation reaction of a fuel.

RQ factor can also be used to estimate the amount of CO₂ being released on burning fossil fuels. Higher the RQ value of fuel higher the potential to emit CO₂ per unit heat input to the IC engine. Apart from using the fuel chemical formula and fundamental combustion literature, exhaust gas analysis from automobiles can also be used to determine the RQ. The RQ CO₂ emission in tons per GJ of energy input can be estimated from the knowledge of RQ of a particular fuel. The CO₂ in tons per GJ of energy input is given as [7].

Estimation of RQ factor from the empirical chemical formula or fuel ultimate analysis can be performed [7].

\[
RQ = \frac{\text{CO}_2 \text{ moles produced}}{\text{O}_2 \text{ moles consumed}} \left[1 + \frac{H}{2C} \right] = \frac{1}{2} \left( \frac{H}{C} \right) \left( \frac{O}{C} \right) \left( \frac{S}{C} \right)
\]

where C, H, O and S are the number of carbon, hydrogen, oxygen...
and sulphur atoms respectively. Instead of fuel composition, exhaust gas analyses can be used to determine RQ in addition to estimation of air fuel (A:F) ratio used, excess air %, and φ, the equivalence ratio or stoichiometric ratio SR (= 1/φ). If φ<1 or SR>1, it implies lean mixture. General methodology is to formulate the following reaction equation, assume complete combustion and use atom conservation assuming the fuel to be CHxOy where x=H/C and y=O/C.

\[ CH_4 + O_2 \rightarrow CO_2 + H_2O \]  (2)

There are 8 unknowns for C-H-O fuel: x, y, a, b, c, d, e and f. Thus one needs 8 equations. Four equations are obtained from an 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 as 3.76; the percent of O\(_2\), CO\(_2\), and H\(_2\)O are known from the exhaled gas composition. One can derive the following formula for RQ from exhaust gas analysis [7]:

\[ RQ = \frac{CO_2 \text{ moles produced}}{O_2 \text{ moles consumed}} = \frac{X_{CO_2,i} \left( \frac{X_{CO_2,e}}{1 - X_{N_2,e} - X_{O_2,e}} - X_{CO_2,e} \right)}{X_{O_2,i} - X_{O_2,e} \left( \frac{X_{CO_2,i}}{1 - X_{N_2,e} - X_{O_2,e}} - \frac{X_{CO_2,i}}{1 - X_{O_2,i} - X_{CO_2,e}} \right)} \]  (3)

Where \( X_{N_2}, X_{CO_2} \) and \( X_{O_2} \) are the mole fractions of nitrogen, carbon dioxide and oxygen which could be either on dry or wet basis and subscripts i and e refer to inlet and exit of combustion chamber respectively. The fuels gasoline, Diesel and Kerosene have chemical formula to be CHx and as such one needs only 7 equations and hence need only % of 2 species in exhaust (e.g.: O\(_2\), CO\(_2\), and O\(_2\)% and N\(_2\)%). Typically N and S in fuels are trace species and hence one may apply the above analysis even for CHxOyNzSs fuels. From the exhaust gas data for a gasoline engine [6] (HC: 750 ppm; NOx: 1050 ppm; CO: 0.68%; H\(_2\): 0.23%; CO\(_2\): 13.5%; O\(_2\): 0.51%; H\(_2\)O: 12.5%; N\(_2\): 72.5%); and dumping small amounts of H\(_2\) and CO with N\(_2\), the RQ of the fuel was estimated to be 0.71 (if CO and H\(_2\) remain in exhaust, O\(_2\)% = 0.51) to determine the RQ from available exhaust gas data. EXCEL based software had been developed to estimate all unknown in Equation (2). CO\(_2\) emission in tons per GJ of engine input can be estimated from the knowledge of RQ of a particular fuel. The CO\(_2\) in tons per GJ of energy input is given as [7]

\[ CO_2 \text{ in tons per GJ energy input} \approx RQ \times 0.1 \]  (4a)

\[ CO_2 \text{ in short tons per mmBTU} \approx RQ \times 0.116 \]  (4b)

If one uses the fuel composition, RQ value for motor gasoline (CH2.02 with C mass %=84.5, [14]) was found to be 0.68 (or 0.66 tons of CO\(_2\) per GJ heat input); the RQ for diesel is 0.68, and biodiesel 0.70 and alcohols have a RQ of 0.67 [7]. Note that RQ seems to fluctuate from 0.66 to 0.73 even for gasoline and as such exhaust gas analyses provide more reasonable values of RQ during operation of automobiles. More details are given in [7].

An empirical formulae for flue gas volume is given in ref 13 and it can be used to estimate NOx in kg/GJ. Thus

\[ NOx \text{ in g of NOx/GJ} = [NOx \text{ in ppm}] \times 1.88 \times 10^{-4} \times \text{Flue gas volume in m}^3/GJ \]  (5)

**Flue gas volume in m}^3/GJ = (3.55+0.131 O\(_2\)%+0.018*(O\(_2\)%)^2) \times 27.664+1.019 O\(_2\)%+0.140*(O\(_2\)%)^2 \times (H/C)+279.12+10.285 O\(_2\)%+1.416*(O\(_2\)%)^2**  (6)

Using exhaust gas analyses presented before, O\(_2\)% = 0.51% (φ = 0.97), the estimated flue gas SATP volume is 246 m3/GJ. With NOx=1050 ppm, the formula (5) yields 480 g/GJ.

For NO emissions, the RQ and X\(_{CO_2,e}\) in exhaust can also be used to convert the NO in ppm into GJ or lb per mmBTU[11]. See Ref [13] for reporting emissions in different forms

\[ NO \text{ in g per GJ} = 0.102 \times NO \text{ in ppm} \times [RQ/X_{CO_2,e}] \]  (7)

Using Equation. (7), X\(_{CO_2,e} = 0.135, RQ = 0.71, NO = 1050 ppm, the NO in g/GJ is 496 g/GJ. As X\(_{O_2}\) decreases, NO in g per GJ increases for same NO in ppm due to higher mole or volume flow rate of exhaust gases for the same energy released.

It should also be noted that the production of renewable fuels such as ethanol will consume some fossil resources which will emit CO\(_2\). Hence, in addition to RQ for oxidation, one must define an equivalent RQ\(_{\text{fuels}}\) which should take into account the amount of CO\(_2\) released during processing of the fuel (e.g. ethanol production from corn) and net RQ=RQ+RQ\(_{\text{fuels}}\).

Equations (4) can be modified to determine the total amount of CO\(_2\) emitted per unit distance travelled by an automobile while consuming different fuels [7]. With heat value of 123,361 BTU/gallon (34,383 kJ/L) or 45844 kJ/kg assuming ρ = 750 kg/m\(^3\) for gasoline, Equations (4) transform to

\[ CO_2 \text{ in lb/mile} = 28.62 \times \frac{RQ}{\text{MPG}} \]  (8a)

\[ CO_2 \text{ in kg/km} = 3.44 \times \frac{RQ}{\text{km per L}} \]  (8b)

Using Equations (8) the amount of CO\(_2\) emitted on using gasoline were estimated to be around 0.47 lb per mile or 0.13 kg per km assuming 40 MPG (16.9 km per L). Net CO\(_2\) emitted for a blend of 85:15 (vol. %) gasoline: Ethanol was 0.12 kg/km or 0.42 lb per mile (including CO\(_2\) from both gasoline and ethanol) assuming same 40 MPG [7]. Two points need to be noted for blends: Firstly, the MPG will not be the same for the blend (CHxOy) since the amount of energy in a gallon will be less for the blend. Hence Equation (4) which gives the CO\(_2\) emission in kg/GJ would be a better representation for determining the CO\(_2\) emission, taxing the vehicle and ranking fuels based on CO\(_2\) emitting potential. Secondly one must not include CO\(_2\) from ethanol oxidation in gasoline: ethanol blend since ethanol is renewable fuel; excluding CO\(_2\) from ethanol, the CO\(_2\) in kg per km is reduced to 0.11 kg per km or 0.39 lb per mile.

With recent developments in sensor technology and engine controls, the data from the gas sensors at the engine tail pipe can be used to keep track of the total CO\(_2\) being emitted while driving an automobile. The formulas presented here can be included in an algorithm in the engine Onboard Diagnostics (OBD) to calculate the cumulative CO\(_2\) emitted from an automobile during its life time. Including this number in an automobile dashboard will enable continuous monitoring and logging of CO\(_2\). With ongoing research to increase the production of short rotation woody crops for ethanol production, more efficient ways of converting biomass to renewable liquid fuels will be identified and implemented.

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