

# Application of the Ideal Gas Law to Determine the Average Molecular Weight of Real Fuel Complex Mixtures

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## 1. INTRODUCTION

The rise of environmental concerns regarding global warming along with the prediction of decreasing oil reserves have forced the scientific community to explore alternative fuel sources. The use of biomass to produce a more “environmentally friendly fuel” has shown promising results for gasoline, petrol and jet fuel [e.g. 1-2]. Similar to petroleum derived fuel, biofuel needs to pass a series of technical and safety assessments in order to obtain an ASTM standard of approval, guarantying the performance and reliability of the fuel for commercial use. Due to the high costs attributed to the fuel standardization procedure along with the high rate of failure, the prediction of the fuel’s intrinsic properties is crucial. Quantitative modeling of the fuel’s behavior is based on physical and chemical properties (typically: density, viscosity, boiling point, H/C ratio, aromatic % ...). Recently, Dooley et al. have successfully predicted the properties of a jet fuels surrogate based on empirically derived chemical group fragment properties [3].

The mixture averaged molecular weight of a fuel is an important fundamental parameter toward important practical combustion properties. The molecular weight of the fuel infers the size of the comprising molecules. Molecule size is a directly proportional scaling term to the vaporization, diffusion and viscosity behavior of liquid fuels. Each of these are very important phenomena in allowing the liquid fuel to vaporize and mix with oxidizing gas, this is the critical process for non-premixed combustion that characterizes diesel, and gas turbine combustion modes. In addition it is well know that fuel molecule size is also proportional to the temperature-extent in chemical reactivity which a fuel exhibits. Large molecules can form alkylperoxy radicals with transition state rings of low enough energy to allow the radical to isomerize, creating reactivity enhancing hydroperoxide functionalities. Moreover, the fuel (average) molecular weight is required parameter with which to determine commonly used combustion/fuel property metrics, such as the threshold sooting index. More importantly, the fuel (average) molecular weight is a legally required parameter involved in the EURO VI emissions certifications calculations.

Despite the fundamental and applied importance of the fuel (average) molecular weight, to date there remains no tried and tested, reliable and accurate method for its determination, let alone a methodology that is fundamental in nature. The available range of options include but are not limited to, vapor pressure osmometry, freezing point suppression and gas-chromatography–FID/MS. The former two techniques rely on calibrated parameters to historical petroleum derived fuel experience base, and is unreliable for fluids derived from other feedstocks or by other methods. The later clearly is a very labor intensive challenge, prone to issues with complete peak resolution of all of the chemical species present, and correct identification and accurate quantification of all of the chemical species present.

The reason behind the limited use of the average molecular weight, as a parameter to predict the fuel properties, is the technical difficulties attributed to obtain this information from a

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complex mixture. To overcome this issue, Dryer et al. developed a new methodology to experimentally estimate the average molecular weight of a complex mixture (fuel) with an uncertainty lower than 6 g/mole [4]. In this paper, we demonstrate the applicability and accuracy of this methodology to a range of petroleum distillate type fuels.

## 2. Methodology

The Dryer et al. methodology principle is based on the ideal gas law:

$$PV = nRT \quad \text{Equation 1}$$

with  $P$ : Pressure (Pa),  $V$ : Volume ( $\text{m}^3$ ),  $n$ : Number of moles (mol),  $R$ : Ideal gas constant and  $T$ : Temperature (K). This indicates that this new methodology is applicable to any elements or mixtures even complex, found in the gas phase within the apparatus technical limitation.

From Equation 1, the molecular weight can be express as:

$$MW = \frac{mRT}{PV} \quad \text{Equation 2}$$

with  $MW$ : Molecular weight (g/mol) and  $m$ : mass of sample (g).

By definition, if a specific amount of liquid fuel can be introduce and fully vaporized in a gas chamber, having a constant volume and temperature, a variation of pressure should be observed. If this variation of pressure is measured and recorded, then the  $MW$  can be express as:

$$MW = \frac{\alpha m}{\Delta P} \quad \text{Equation 3}$$

with  $\alpha = \frac{RT}{V}$  ( $\text{K}/\text{m}^3$ ).

## 2. APPARATUS

To execute these determinations, a simple apparatus has been designed and fabricated as presented in Figure 1. It constitutes of the following items:

- A stainless steel cylindrical chamber (H = 300 mm, O.D. = 100 mm) sealed on both ends using conflate flanges.
- Two band heaters (MBH, Omega) attached to the chamber (bottom and top).
- Two RTD sensors (Pt100, TC) to measure the temperature at two different location in the vacuum chamber (bottom and top).
- Two PID controllers (CN32Pt, Omega) each connected to a solid state relay.
- A valve connected to the chamber with two input lines. The first input line is connected to a rotary pump (Edwards) while the second is connected to a nitrogen gas line.
- A pressure transducer (PX409, Omega) able to measure and record the pressure between 0-1 Bar and temperature ranging from -17 to 85 °C with an accuracy of  $\pm 0.08\%$ .
- A enter material septum to allow the introduction of the liquid sample with a syringe injector.
- A PTFE coated magnet inside the vacuum chamber that rotate with the help of a magnetic stirring plate.
- Insulated box to maintain a stable temperature by limiting heat transfer with the surroundings (not represented on the picture).

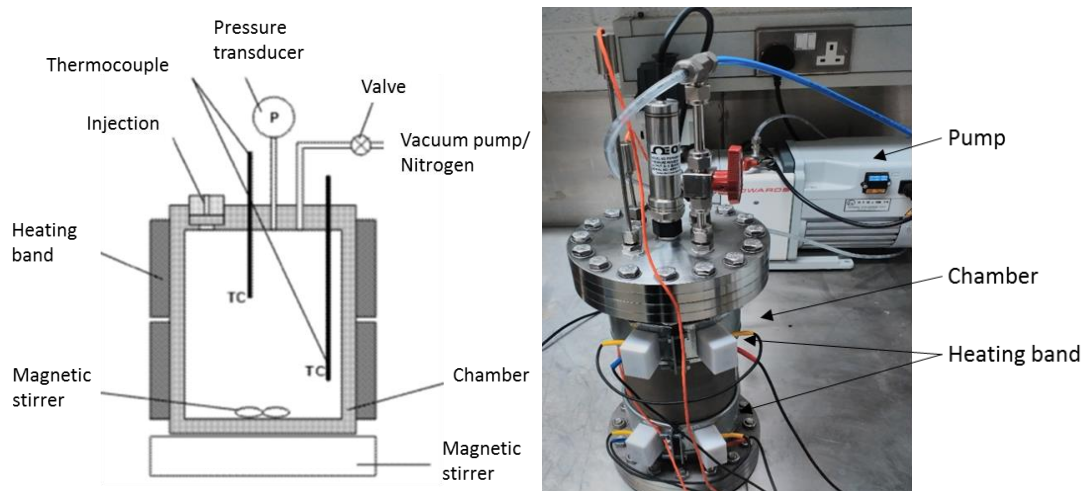


Fig. 1 Molecular weight apparatus.

In the design described above, the apparatus gas chamber is configured to be at constant volume and temperature with the change in gas pressure due to the introduction of the fuel sample set as the determinable parameter. The constant volume is guaranteed by the non-expandable stainless steel chamber sealed on both ends by conflate flanges. The addition of various elements to the gas chamber (RTD sensors, valve, pressure transducer and septum) are connected using non-expandable and leak proof fittings. It is crucial to avoid any variation of volume or leak in the gas chamber as the principle of this methodology is based on a known and constant volume. Any leak or variation of volume within the gas chamber will lead to unreliable results.

It is also critical that the vacuum chamber be of constant and homogenous temperature. A band heater system controlled by the output signal of the PID controller in response to the temperature measured by the RTD sensors are used for this purpose. The homogeneity of the temperature in the chamber is monitored by the two RTD sensors located at two different locations (bottom and top). During the course of the experiment, the typical difference of temperature between the two sensors is  $< 0.5$  K. Another temperature limitation that should not be forgotten is the necessity to avoid the thermal decomposition of the fuel. An insulation box is placed around the gas chamber to keep the temperature stable by limiting heat transfer with the surrounding environment. It is essential to avoid any cold spot in the system which can result in condensation of the sample and impact the final results.

The pressure in the gas chamber is adjusted by opening the valve connected to the pump which has the ability to reduce the vacuum to 0.1mBar. The pressure in the chamber is monitored and recorded by the pressure transducer during the experiments. The introduction of a known mass of liquid sample is made with a gas tight syringe via the septum. The amount of liquid fuel that can be introduced to the gas chamber is dictated by the vapour pressure saturation of the sample to avoid any condensation. The vapour pressure is temperature dependant and to improve the mass range of the apparatus the temperature can be increased to 85 °C.

### 3. RESULTS

#### 3.1 Gas chamber volume estimation

Due to the geometry and combination of peripheral devices connected to the gas chamber (thermocouples, magnetic bar, pressure transducer and pipes) the exact volume is difficult to determine by simple geometric arguments. To precisely determine the volume of the gas chamber, we exploit the ideal gas law again expressed as:

$$V = \frac{nRT}{P} \quad \text{Equation 4}$$

with n: number of moles.

The volume is determined by measuring the variation of pressure due to the introduction of a precise mass of liquid fuel with a known molecular weight into the gas chamber. In our case, two fuels were used, acetone (58.0791 g/mol) and 2-propanol (60.095 g/mol) and the results are presented in Figure 2. The graphs represents the mass of fuel injected vs  $\frac{\Delta pV}{RT}$  for acetone and 2-propanol and show a linear relation. The volume of the gas chamber is determined by solving V, such that the slope of the line corresponds to the known molecular weight of the fuel. If the same volume term can be deduced from a number of pressure measurements performed for a variety of different liquids, we can be confident that the device fully vaporises the introduced fuel without the loss of mass, therefore reliably determining the volume of the chamber.

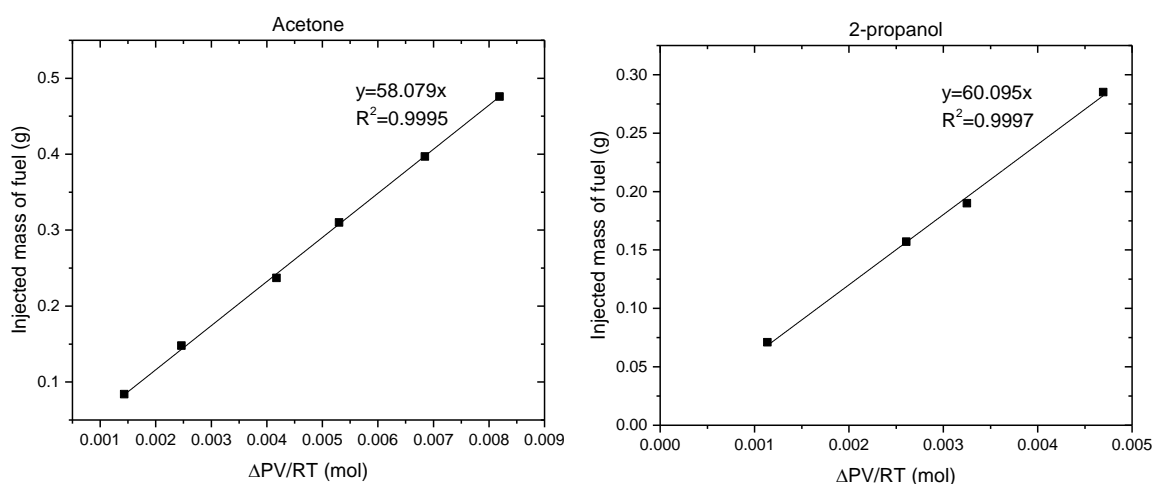


Fig. 2 Mass of fuel injected vs  $\frac{\Delta PV}{RT}$  for acetone and 2-propanol.

Table 1 presents the determination of the gas chamber volume obtained with acetone and 2-propanol. The difference between the two fuels is only 8.33 cm<sup>3</sup> which correspond to 0.4% of the total volume and attributed to experimental error.

	Acetone	2-propanol	$\Delta/\text{cm}^3$
Volume (cm <sup>3</sup> )	2091.27	2099.60	8.33

Table. 1 Estimation of the gas chamber volume with acetone and 2-propanol.

### 3.2 Molecular weight determination of complex mixture

After the estimation of the gas chamber volume, the determination of the molecular weight of a complex mixture is performed. A Reference Gasoline fuel (“Coryton”) is tested using an average of the gas chamber volume estimated previously (2095.44 cm<sup>3</sup>). The results obtained (Figure 3) is a linear relation representing the mass of fuel injected vs  $\frac{\Delta PV}{RT}$  with the slope corresponding to the average molecular weight of the reference gasoline fuel. The average molecular weight of the “Coryton” reference gasoline fuel is estimated to 94.1 ±3 g/mol at 398 K. The results obtained are in line when comparing them with the results obtained using the Detailed Hydrocarbon Analysis (DHA) method which indicate an average molecular weight of 90.7 g/mol.

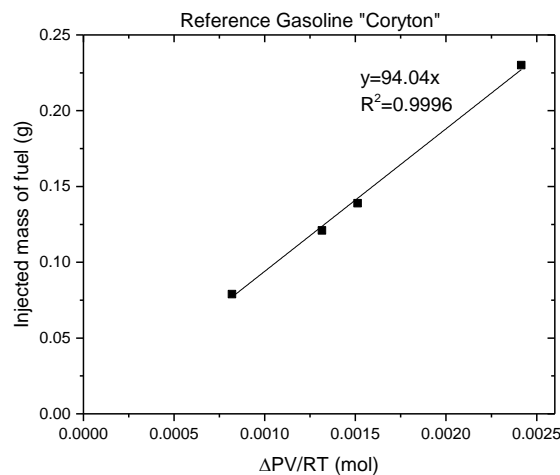


Fig. 3 Mass of fuel injected vs  $\frac{\Delta PV}{RT}$  for Coryton Reference Gasoline Fuel.

## 4. CONCLUSION

A new methodology and apparatus applying the Ideal Gas Law has been described and presented. The average molecular weight of a complex mixture (reference gasoline fuel) determined. Further results will be presented and discussed including a range of Fuels for Advanced Combustion Engines (FACE: A, E, F, I, G and J) and a number of jet fuels.

## 5. REFERENCES

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