

Extensional Viscosity and a Single Phenomenological Basis for the GTA Fuel Additive

1. Approach

We begin with the equations for Newtonian viscosity as a function of concentration and molecular weight. Then we look at the parameters influencing the extensional viscosity. Finally, we look at the parameters governing the evaporation of a liquid from the surface of an evaporating drop. The extensional viscosity relationship is then overlaid on the equation for evaporation of a liquid drop. Calculated values will be given in the next discussion paper.

2. Resting Viscosity of a Dilute Polymer Solution

The Newtonian (resting) viscosity of a very dilute polymer solution is close to that of the solvent. This is a consequence of the following two equations:

$$\begin{aligned} \text{(I)} \quad & [\eta] = KM^{1/2} \text{ and} \\ \text{(II)} \quad & \eta_{sp} = [\eta]c + k'[\eta]^2c^2 \end{aligned}$$

where $[\eta]$ is the intrinsic viscosity of the polymer - solvent system, M is molecular weight, and K is the constant of proportionality. Note that $[\eta]$ is weakly dependent on molecular weight, thus the specific viscosity of a given solution concentration is also little increased by M . This is especially the case when the polymer concentration, c , is also small as it is for fuel additive at 10 ppm, or 0.0010 grams per deciliter. c is 1×10^{-3} g/dl and c^2 is 1×10^{-6} g²/dl². Thus the treated fuel is not very different from untreated fuel at rest. References for this are 1) Billmeyer and 2) Flory.

3. Extensional Viscosity

The ratio of viscosity of stretched, elongated of extended polymer solution to the viscosity of the unperturbed solution is given by

$$\text{(III)} \quad \bar{\eta}/\eta_o = 3 + \epsilon c \eta_o K^2 M^{(1+2\alpha)}/RT$$

The extensional viscosity, $\bar{\eta}$, is strongly dependent on the molecular weight. The term $M^{(1+2\alpha)}$ becomes M^2 for the case of worst solvent for the polymer, and M^3 for the best possible solvent. Polyisobutylene and fuel are ideally compatible and the term more closely approaches M^3 than M^2 . Despite the strong dependencies of $\bar{\eta}/\eta_o$ on the molecular weight, $\bar{\eta}/\eta_o$ approaches the low limiting value of 3 when c approaches 0. This

is why the ratio can be "tuned" to a particular type of engine or burning condition, (further discussions will be postponed to the next section). The rate of strain, $\dot{\epsilon}$ is a measure of elongation per unit length per second, or $\Delta L/L\Delta t$. This parameter changes when the solution is sheared, stretched, or deformed. Physically the large polymer chains are deformed from a random coil conformation to a stretched chain conformation. In the absence of the strain, the chains thermally relax to the random coils. Often the strain induces a stress which breaks some of the extended molecules in the middle (mid-point break theory). However, in undergoing a break, the fluid is also most rigid. In other words $\Delta L/L\Delta t$ was very large and $\bar{\eta}/\eta_0$ was also maximized. Regions where $\Delta L/L\Delta t$ are large include turbulent liquid flow regions (drag reduction effect), injection from a nozzle (cohesive effect), the interaction of a liquid stream or droplets with high velocity air. These conditions exist in most modern engines, especially when conditions are changing in the millisecond to microsecond domain. K in this equation is obtained in the laboratory by plotting the log of the intrinsic viscosity against the log of the molecular weight and taking the slope of the line. K is constant for a particular polymer solvent system. The K for polyisobutylene in Benzene is 1.07×10^{-3} at 297°K. T enters the expression for $\bar{\eta}/\eta_0$ in the term $1/RT$ where R is the gas constant. T has little effect on $\bar{\eta}/\eta_0$ since there is usually little displacement from 298 degrees (25°C). T could be 273 (0°C) or perhaps 325 degrees, but the effect on $\bar{\eta}/\eta_0$ is very small.

4. Effects on Fuel Properties

Under some conditions $\bar{\eta}/\eta_0$ can approach 10,000. When this is too large for an optimal effect on combustion or volumetric efficiency, or delayed vaporization, or suppression of vapor-like particles, the concentration can be decreased toward zero. This it is always possible to tune the fuel for 2 cycle spark ignition, 4 cycle spark ignition, compression ignition, turbine or other combustion scenarios. c can also be changed for different carburetor or fuel injection systems. High molecular weight is an advantage because it generates large $\bar{\eta}/\eta_0$ values at low concentrations where "at rest" fuel properties are virtually unaffected. There is no doubt that 5 to 10 ppm concentrations of 7.2×10^6 M PIB decreases energy loss in turbulently flowing fuels, resulting in flow rate increase of more than 20%. There is also no doubt that the formation of vapor-like particles is suppressed at low concentrations of high molecular weight PIB. These two effects are related to $\bar{\eta}/\eta_0$.

However, $\bar{\eta}/\eta_0$ is also related to transient increases in the "solidity" and surface tension of particles produced by shear at surfaces or in turbulent air. The following relationships have been derived in "Physical Chemistry", by Moelwyn - Hughes p. 1213. The derivation will not be repeated here. Consider a sphere of isolated liquid in an inert atmosphere at constant temperature and pressure. Let the radius be larger than 10^{-6} cm. The number of molecules vaporizing from the surface of the sphere per second is given by

$$(IV) \quad dN/dt = 4\pi r D n^{\circ}$$

r is the radius of the droplet and D is the diffusion coefficient of molecules within the droplet. n° is the saturation vapor pressure at the interface of the drop with the gaseous atmosphere. r_m is the molecular radius. The link between D and η is via the Stokes relationship or

$$(V) \quad D = RT/n_o 6\pi n r_m$$

accumulating the constants and the radius of a molecule equation V becomes

$$D = k/\eta, \text{ or for extensional viscosity } \bar{\eta}$$

$$(VI) \quad D = k/\bar{\eta}$$

Substitution of VI into V we get

$$dN/dt = 4\pi r k n^{\circ} / \bar{\eta}$$

Thus during periods close to those where $D\Delta L/L\Delta t$ is large, the rate of vaporization, dN/dt is very depressed. Simultaneously the droplet is very rigid and solid like, and the surface is equally tense or hardened. When $\bar{\eta}$ subsequently approaches $3\eta_o$, the rate of evaporation increases sharply. During the "hardened" phase both the surface tension and bulk viscosity of the droplet favor transport without coating or premature vaporization. This leads to improved performance in gasoline and diesel engines.

Another equation incorporates D and γ , or surface tension into the expression for the lifetime of a spherical droplet. This equation is,

$$(VII) \quad t = (r^2 n_L / 2Dn^{\circ}) (1 - 4\gamma/n_L r k_c T)$$

where n_L is the number of molecules per cm^3 in the liquid and r is the radius of the droplet.

again replacing D by $k/\bar{\eta}$ we get

$$(VIII) \quad t = (r^2 \bar{\eta} n_L) / (2k n^{\circ}) (1 - 4\gamma/n_L r k_c T)$$

In equation (VIII) the surface tension approaches 0 when saturated vapor is present above the droplet interface and γ approaches 0. The droplet lifetime equation (VIII) then becomes proportional to $\bar{\eta}$.

Relaxation of PIB and η

$\bar{\eta}$ becomes larger as ϵ increases. Similarly $\bar{\eta}$ decreases as ϵ approaches zero. When the stretching force is released the extensional or elongational viscosity decreases. The

increase or decrease in $\bar{\eta}$ depends on the product of the strain ϵ and the reciprocal of the time it takes for the molecule to thermally relax to the unstretched conformation. The units of the stretching rate or elongation rate are reciprocal seconds and the units of polymer relaxation times are seconds. The product of the two factors is dimensionless. The following equation links $\bar{\eta}$ to ϵ and θ .

$$\bar{\eta} = 3\eta_o + (3cRT/M) \sum_p (\theta_p / (1 - 2\epsilon\theta_p)(1 + \epsilon\theta_p))$$

θ_p is the relaxation time of the p th normal mode of chain response. Note that as $\epsilon \rightarrow 1/2\theta_1$, where θ_1 is the longest relaxation time, the $(1 - 2\epsilon\theta_1)$ term approaches zero. As the denominator approaches zero, $\bar{\eta}$ approaches infinite elongational viscosity. The relaxation time θ_1 is proportional to

$$[\eta]M\eta_o/RT$$

where $[\eta]$ is itself equal to KM^α and α is between 0.5 (θ solvent = poor solvent) and 1.0 (perfect solvent). Thus the relaxation time is proportional to $M^2\eta_o/RT$ in a good solvent. Relaxation time increases with M^2 and therefore a state of high $\bar{\eta}$ will exist longer than it would for the case of a lower molecular weight. The mist particles would retain a high $\bar{\eta}$ for a desirable period during engine operation. Since $\bar{\eta}$ approaches ∞ when ϵ approaches $1/2\theta$ a high molecular weight polymer in a good solvent will develop an extensional viscosity that approaches infinity at lower extension rates than a low molecular weight polymer in a poor solvent. The former is the case for the GTA fuel additive in gasoline and diesel fuels. Concentration then provides the final tuning for the desired $\bar{\eta}$ at a particular ϵ .

Summary

1. The large $\bar{\eta}/\eta_o$ possible using low concentrations of 7.2×10^6 M PIB in gasoline and diesel fuels influences pre-combustion events and thus affects combustion.
2. Through c , $\bar{\eta}/\eta_o$ can be tuned to improve the operation of several types of engines.
3. $\bar{\eta}/\eta_o$ changes are linearly dependent on concentration and $\Delta L/\Delta t$ and this provides another dimension for engine tuning.
4. Through c , $\bar{\eta}/\eta_o$ can be tuned to:
 - a) eliminate vapor-like burning
 - b) promote diffusive burning (diesel)
 - c) develop a uniform cloud mix for improved combustion (diesel)
 - d) improve volumetric efficiency by slightly delaying vaporization (2-stroke and 4-stroke spark ignition engines)
 - e) negate undesirable surface coating effects through momentary

- increases in surface and bulk rigidity
- f) promote diesel fuel jet penetration prior to ignition and diffusive burning
- g) decrease the extent of vapor explosion before TDC in a diesel
- h) prevent droplet agglomeration and surface wetting after TDC in a diesel.