

A Simple Method to Predict Knock Using Toluene, N-Heptane and Iso-Octane Blends (TPRF) as Gasoline Surrogates

Gautam Kalghatgi, Hassan Babiker, and Jihad Badra
Saudi Aramco

ABSTRACT

The autoignition resistance of a practical gasoline is best characterized by the Octane Index, OI, defined as RON-KS, where RON and MON are respectively, Research and Motor Octane Numbers, S is the sensitivity (RON-MON) and K is a constant depending on the pressure and temperature history of the fuel/air mixture in an engine. Experiments in knocking SI engines, HCCI engines and in premixed compression ignition (PCI) engines have shown that if two fuels of different composition have the same OI and experience the same pressure/temperature history, they will have the same autoignition phasing. A practical gasoline is a complex mixture of hydrocarbons and a simple surrogate is needed to describe its autoignition chemistry. A mixture of toluene and PRF (iso-octane + n-heptane), TPRF, can have the same RON and S as a target gasoline and so will have the same OI at any given K value and will be a very good surrogate for the gasoline.

In this paper, a method to define the composition of a TPRF to match both RON and MON of a target gasoline is presented. The appropriate TPRF as a surrogate for a particular gasoline, which has been extensively tested in a knocking SI engine, is identified using this method. A chemical kinetic model is used to calculate ignition delays at different pressures and temperatures for this surrogate TPRF. From these data, a simple Arrhenius type equation with a pressure correction to predict ignition delays is identified. This equation is used to find the ignition delay as a function of crank angle and calculate the Livengood-Wu integral, I, for a number of individual knocking cycles covering a wide range of operating conditions using the gasoline in a single cylinder engine. Knock is predicted to occur at the crank angle when the integral, I, reaches unity. The crank angle at which knock is predicted to occur using the simple equation for ignition delay for the surrogate TPRF agrees very well with the experimentally observed value for the gasoline for all the cases considered. Finally, using the chemical kinetic model for TPRF, simple equations which can be used to estimate ignition delay are presented for a range of RON and sensitivity. Such equations can be used to predict when knock occurs during the cycle for these gasolines if the pressure and temperature development with crank angle is known.

CITATION: Kalghatgi, G., Babiker, H., and Badra, J., "A Simple Method to Predict Knock Using Toluene, N-Heptane and Iso-Octane Blends (TPRF) as Gasoline Surrogates," *SAE Int. J. Engines* 8(2):2015, doi:10.4271/2015-01-0757.

1. INTRODUCTION

The efficiency of SI engines is fundamentally limited by knock, an abnormal combustion phenomenon caused by the autoignition of the end-gas ahead of the flame front [1, 2, 3]. Knock depends on the pressure and temperature history of the end-gas as well as on the anti-knock quality of the fuel.

The autoignition chemistry cannot be adequately quantified for practical fuels because of their complexity. Hence, fuel anti-knock quality has to be described by empirical measures and it is traditionally specified by Research and Motor Octane Numbers, RON and MON, of the fuel used. These tests are run in a single-cylinder CFR (Cooperative Fuels Research) engine in accordance with the procedures set in [4] - ASTM D2699 for RON and ASTM D2700 for MON. The RON test is run at an engine speed of 600 rpm and an intake temperature of 52° C while the MON test is run at 900 rpm and with a higher intake temperature of 149°C.

The octane scale is based on two paraffins, n-heptane and iso-octane. Blends of these two primary components are referred to as primary reference fuels (PRF) and define the intermediate points in the RON or MON scale. However, the autoignition chemistry of non-paraffinic components in gasoline differs from that of PRF and RON or MON describes the anti-knock behavior of the gasoline only at the RON or MON test condition. The true anti-knock quality of a gasoline is best described by an Octane Index, OI [3, 5, 6, 7] which is defined as

$$OI = (1-K)RON + KMON = RON - KS \quad (1)$$

where K is an empirical constant which depends on the pressure and temperature history of the unburned mixture in the cylinder and S is the sensitivity (RON-MON). OI is the octane number of the PRF that matches the knock behavior of the gasoline that is of interest, at the conditions of the particular engine test. The temperature of the unburned gas increases as pressure increases in the engine cylinder

and pressure and temperature in the end-gas are determined by engine design and operating conditions. Practical fuels have $S > 0$, typically around 10 and S can be taken as a measure of how different the fuel autoignition chemistry is compared to PRF, which by definition, have zero sensitivity.

The value of K has to be determined empirically by measuring a quantity dependent on fuel autoignition quality, such as the Knock Limited Spark Advance, KLSA, at a fixed operating condition for fuels of different RON and MON [3, 5, 6]. K is a measure of how different the pressure and temperature regime is compared to the RON test condition. If the temperature of the unburned gas for a *given* pressure is above that in the RON test condition $K > 0$; otherwise $K < 0$.

The value of K and hence OI for a given fuel depends on the design and operating condition of the engine. Measures aimed at improving the efficiency of a SI engine, such as increasing the compression ratio and turbocharging (aligned with downsizing) increase the maximum pressure and the temperature of the charge making autoignition and knock more likely. Fuel anti-knock quality becomes more important.

Moreover, with increase in efficiency, in the unburned gas, for a *given* pressure, the temperature decreases or alternatively, for a *given* temperature, the pressure increases. This happens with turbocharging in down-sized engines and if the compression ratio is increased, because the amount of hot residual charge at the end of the exhaust stroke is reduced. In [5], T_{comp15} , the unburned mixture temperature when the pressure is 15 bar (1.5 MPa) was introduced and helps to place the operating condition of interest in relation to the RON test condition. If T_{comp15} is less than that for the RON test, the condition is said to be “beyond RON” and K in Eq. 1 is negative so that for a given RON, a lower MON fuel has higher OI, i.e. higher anti-knock quality. Modern engines and downsized turbocharged SI engines of the next generation have negative values of K at the conditions where their performance is limited by knock [5, 6, 7, 8, 9, 10, 11, 12, 13] so that for a *given* RON, a fuel with greater sensitivity has more resistance to autoignition. Studies in HCCI engines have helped greatly in understanding autoignition and the dependence of K on T_{comp15} in pre-mixed mixtures [3].

Thus, as the unburned mixture pressure increases with the temperature held constant (T_{comp15} decreases), the value of K decreases, and non-PRF fuels ($S > 0$) become relatively more resistant to autoignition compared to PRF. This observation is consistent with shock tube measurements of ignition delay for different types of fuels. The ignition delay, τ_i , can be expressed as a function of temperature, T , and pressure, P , in general as

$$\frac{\tau_i}{\tau_{i0}} = f(T) \left(\frac{P}{P_0} \right)^{-n} \quad (2)$$

Here, τ_{i0} is the ignition delay measured at a pressure of P_0 at a given temperature, T , and n is a constant. In IC engines at each point during the cycle the mixture will have a different value of τ_i . It is then hypothesized that auto-ignition occurs when the integral (Livengood-Wu integral) of the reciprocal of τ_i with time, t , reaches unity (Eq. 3).

$$I = \int_0^{te} \frac{dt}{\tau_i(P,T)} = 1 \quad (3)$$

Shock tube experiments show that in the region where ignition delay is low enough to contribute significantly to the Livengood-Wu integral, n is much smaller for non-PRF fuels compared to PRF [3]. In other words, τ_i decreases less (knock resistance increases) for non-PRF fuels compared to PRF fuels as pressure increases for a fixed temperature.

Multiple studies in knocking SI [5, 6, 7, 8], HCCI [14, 15] and PCI [16] engines show that if two fuels of different composition are exposed to the same pressure/temperature history and have the same OI, they will have the same autoignition phasing. The OI of practical fuels ($S > 0$) will change as the value of K changes, unlike for PRF. Hence PRF are not appropriate as surrogates for practical gasolines. A blend of toluene and n-heptane, toluene reference fuel (TRF) which has the same RON as a practical gasoline would have a comparable, though not the same, sensitivity and would be a better surrogate than a PRF. If the scale in the anti-knock rating system was based on toluene and n-heptane, rather than PRF, a single “Toluene Number”, TN, the volume percent of toluene in the toluene/n-heptane mixture, can describe anti-knock behavior of real gasolines reasonably well at different conditions, unlike RON or MON [17]. More importantly, such a system would also enable fuels such as ethanol mixtures, with higher anti-knock quality than iso-octane, to be rated quantitatively within the scale.

However a proper surrogate should match *both* RON and MON of the gasoline. The simplest such surrogate fuel would require three components - iso-octane, n-heptane and toluene (TPRF fuels) [18]. Dryer and co-workers [19, 20] have also suggested that such fuels can be appropriate surrogates for gasoline. In this paper, a method to define the composition of a TPRF to match both RON and MON of a target gasoline is first presented.

We then focus on experimental results on knock in a single cylinder engine running on a Saudi market gasoline with RON of 95.1 and MON of 86. The appropriate TPRF as a surrogate for this gasoline is first identified. A chemical kinetic model is used to calculate ignition delays at different pressures and temperatures for this surrogate TPRF. From these data, a simple Arrhenius type equation with a pressure correction to predict ignition delays (< 15 ms) is identified. This simple equation is used to find the ignition delay as a function of crank angle and calculate the Livengood-Wu integral, I , for a number of individual knocking cycles covering a wide range of operating conditions for which pressure was measured and the temperature was estimated. Knock is predicted to occur at the crank angle when the Livengood-Wu integral (Eq. 3) reaches unity. The crank angle at which knock is predicted to occur using the simple equation for ignition delay for the surrogate TPRF agrees very well with the experimentally observed value for gasoline for all the cases considered. Finally, using the chemical kinetic model for TPRF, simple equations which can be used to estimate ignition delay are presented for a range of RON and sensitivity. Such equations can be used to predict when knock occurs during the cycle for gasoline.

2. DEFINING THE COMPOSITION OF A TPRF TO MATCH BOTH RON AND MON

Previous work in this regard was published by Morgan et al. [18] and Knop et al. [21]. However in the current paper the model is based on measurements of RON and MON over a more extensive range. The model equations are fundamentally correct in that the sensitivity goes to zero when the toluene concentration goes to zero. Model predictions agree extremely well with other data not used in developing the model

The RON and MON values were measured for mixtures of PRF of different octane numbers with different concentrations of toluene. Blends with RON or MON greater than 100 were not considered for developing the model. The extension of the RON scale beyond 100 provided by ASTM is an extrapolation based on using octane enhancers within the scale e.g. by adding a known amount of lead to a lower octane PRF, measuring the increase in RON and assuming that the same increase in RON will be obtained if the same amount of lead is added to isooctane. However we cannot be certain that such an extrapolation is valid quantitatively for other fuels. For fuels with RON > 100, the actual head position of the CFR engine during the RON test is a physical measurement but the RON number associated with this is based on an extrapolation. A fuel with RON greater than 100 cannot be actually compared with a PRF since such a PRF cannot exist. Hence the current method to assign RON values to fuels that are more resistant to autoignition compared to isooctane, is not quantitatively reliable. If RON is greater than 100 we can say that the fuel is more resistant to autoignition compared to isooctane in the RON test but not quite by how much. In contrast, a TRF (toluene/n-heptane) can be found to match such a fuel in the RON test and a Toluene Number (TN) assigned to it [17].

The upper half of Table 1 (non-shaded) lists the data used to develop the model. Also listed in the shaded bottom half of Table 1 are data for TPRF with RON < 100, mostly from [4, 18, 19] which were not used in developing the model but were compared to the model - see below. In Table 1, Vi, Vn and Vt are respectively, the volume percentages of iso-octane, n-heptane and toluene in the blend. TMF is the toluene mole fraction in the blend. In calculating TMF, the density (g/cc)/molecular weight used for toluene, iso-octane and n-heptane are respectively 0.867/92.1, 0.692/114.2 and 0.684/100.2. With these assumptions, TMF is given by

$$TMF = \frac{V_t}{V_t + 0.6437V_i + 0.72515V_n} \quad (4)$$

PRF in Table 1 is the octane number of the PRF used so that

$$\frac{PRF}{100} = \frac{V_i}{V_i + V_n} \quad (5)$$

Of course,

$$V_i + V_n + V_t = 100 \quad (6)$$

Also shown in Table 1 are TN from Eq.s 8 and 11 in [17]. TN is the volume percent of toluene in a toluene/n-heptane mixture which matches the fuel under consideration in the RON test (has the same RON).

In addition to these data, the data for TPRF with RON > 100 are available and are listed in Appendix A for completeness. For RON > 100, the position of the head in the RON test expressed as the DCR (Digital Counter Reading) can be found from Table A4.1 in [4]. Then using Eq. 4 from [17], the equivalent TN can be found and this is also listed in Appendix A.

In general, even when blending rules for RON on a volumetric basis are non-linear, blending rules on a molar basis are linear [17, 21, 22]. Figure 1 shows measured RON plotted against TMF (data from Table 1) at different PRF levels.

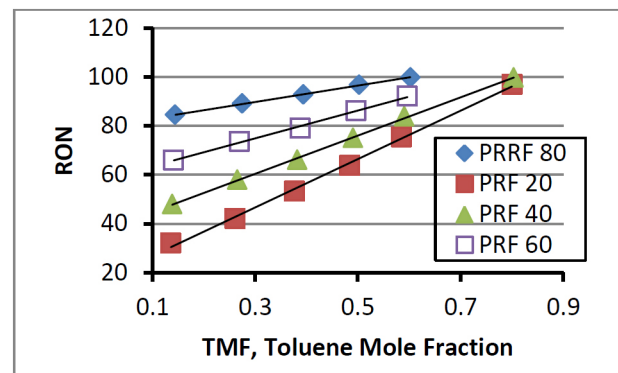


Fig. 1. RON vs TMF at different PRF levels

With a fixed PRF, as the toluene concentration is increased, RON increases linearly with TMF so that RON can be related to the toluene mole fraction, TMF, by

$$RON = aTMF + b \quad (7)$$

Both the constants, a and b are listed in Table 2 and are different for each PRF level. Table 2 also lists the Rsq value for each linear fit shown in Fig. 1. Also listed in Table 2 is the result for PRF zero, i.e. the blends of n-heptane and toluene from Eq. 11 in [17] which was based on a large number of measurements. This equation, rather than Eq. 9 in [17], has the right format in that with TMF = 0, RON is zero, the value for n-heptane. The constants a and b in Eq. 7 are linear functions of PRF as shown in Fig. 2 and represented in Eq.s 8 and 9. Once again the linear fit is excellent with Rsq values of 0.9968 and 0.9978 for a and b respectively.

$$a = 118.09 - 1.0355 PRF \quad (8)$$

$$b = 1.0023PRF - 1.7774 \quad (9)$$

From Eq.s 7, 8 and 9 we can write

$$RON = (1.0023 - 1.0355TMF)PRF + 118.09TMF - 1.777 \quad (10)$$

Figure 3 shows the sensitivity, S from Table 1 plotted against TMF. For PRF zero, Eq.s 11 and 12 from [17] give $S = 13.9TMF$. It can be seen that, not surprisingly, S seems to be independent of PRF. The

linear model forced to go through the origin is given by Eq. 11 and the Rsq value of the fit with this model is 0.957. Equation 11 has the right format because when the toluene concentration is zero, the sensitivity should be zero regardless of the PRF value.

$$S = 14.07TMF \quad (11)$$

Table 1. Experimental data for TPRF with RON < 100. The data in the non-shaded area used for developing the model to determine the composition of TPRF to match target RON and MON

Source	Vi, vol % iso-oct	Vn, vol % n-hep	PRF	Vt, vol % tolu	TMF	MON	RON	S	TN from Eq.s 11, 8 [17]
Current	18	72	20	10	0.136		32.0		21.7
Current	16	64	20	20	0.261		42.0		29.2
Current	14	56	20	30	0.377	48.0	53.2	5.2	38.1
Current	12	48	20	40	0.485	58.0	63.7	5.7	46.9
Current	10	40	20	50	0.585	68.0	75.5	7.5	57.5
[4]	5	21	19	74	0.800	85.2	96.9	11.7	78.7
[4]	10	16	38	74	0.804	88.7	99.8	11.1	81.8
Current	36	54	40	10	0.138		48.0		33.9
Current	32	48	40	20	0.265		58.0		42.1
Current	24	36	40	40	0.490	68.0	75.1	7.1	57.2
Current	20	30	40	50	0.591	76.2	83.8	7.6	65.4
Current	28	42	40	30	0.382	61.0	66.1	5.1	49.0
Current	54	36	60	10	0.141	64.4	66.0	1.6	49.0
Current	48	32	60	20	0.270	70.0	73.6	3.6	55.8
Current	36	24	60	40	0.496	79.6	86.2	6.6	67.8
Current	30	20	60	50	0.597	82.9	92.1	9.2	73.7
Current	42	28	60	30	0.388	74.0	79.0	5	60.8
Current	64	16	80	20	0.275	85.6	89.1	3.5	70.7
Current	56	14	80	30	0.394	86.9	92.8	5.9	74.4
Current	48	12	80	40	0.503	88.7	96.7	8	78.5
Current	40	10	80	50	0.602	90.9	99.8	8.9	81.8
Current	72	18	80	10	0.144	82.0	84.5	2.5	66.1
[4]	0	42	0	58	0.656	66.9	75.6	8.7	57.6
[4]	0	34	0	66	0.728	74.8	85.2	10.4	66.8
[4]	0	30	0	70	0.763	78.2	89.3	11.1	70.9
[4]	0	26	0	74	0.797	81.5	93.4	11.9	75.1
Current	10	30	25	60	0.680	75.2	85.3	10.1	66.9
Current	20	20	50	60	0.687	83.7	95.0	11.3	76.7
[18]	17	64	21.0	19	0.251	37.0	39.0	2	26.9
[18]	0	50	0.0	50	0.580	57.7	65.9	8.2	48.9
[18]	33	33	50.0	33	0.423	70.9	76.2	5.3	58.2
[18]	67	17	79.8	16	0.229	84.0	87.0	3	68.6
[18]	17	17	50.0	67	0.744	87.4	98.0	10.6	79.9
[21]	0	27	0.0	73	0.792	80.7	92.3	11.6	73.9
[21]	72	10	87.9	18	0.250	90.3	93.7	3.4	75.4
[21]	44	17	72.5	40	0.500	85.8	93.0	7.2	74.7
[21]	52	15	77.8	34	0.436	86.7	93.0	6.3	74.7
[21]	0	21	0.0	79	0.840	86.2	97.7	11.5	79.6
[21]	65	10	86.7	25	0.337	90.5	95.2	4.7	76.9
[21]	35	15	70.0	50	0.599	87.3	96.3	9	78.1
[21]	69	17	80.7	14	0.201	84.2	86.6	2.4	68.2
[21]	74	16	82.1	10	0.140	84.6	85.7	1.1	67.3
[21]	43	14	75.8	44	0.537	88.3	96.3	8	78.1

*Data for TPRF with RON > 100 are given in Appendix A. Shaded numbers not used to develop model.

Table 2. Constants a and b in Eq. 7 from Fig. 1

PRF	a	b	Rs _q
0*	115.9	0	0.989
20	98.978	16.945	0.9976
40	78.181	36.996	0.9993
60	56.892	57.853	0.9973
80	33.395	79.773	0.995

*From Eq.11 in [17]

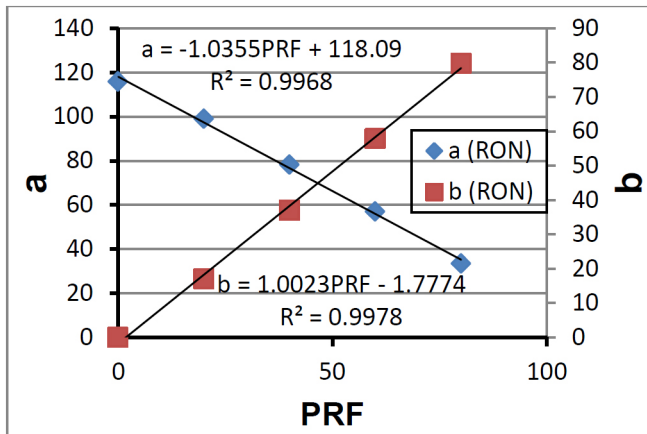


Fig. 2. The constants a and b (Eq. 7) plotted against PRF. Data from Fig. 1, Table 2

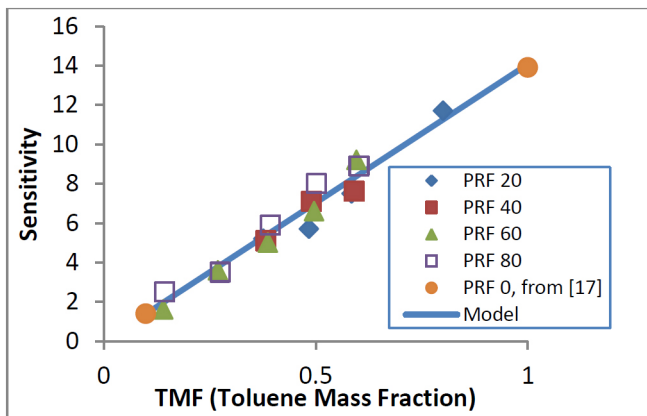


Fig. 3. Sensitivity vs Toluene molar fraction for different PRF in TPRF blends

If we have a target RON and S, we first find the value for TMF using Eq. 11 and then, using Eq. 10, find the appropriate PRF for the blend. Then by solving Eqs. 4, 5 and 6, the individual volume percentages in the blend of iso-octane (V_i), n-heptane (V_n) and toluene (V_t) can be found.

Figures 4 and 5 compare the predicted values using Eqs. 10 and 11, with the measured values for RON and MON respectively. There is excellent agreement between predicted and measured values (R_{sq} of

0.9998 for RON and 0.9976 for MON) even when cases which were not used to develop the model (the shaded numbers in the lower half of Table 1) are included.

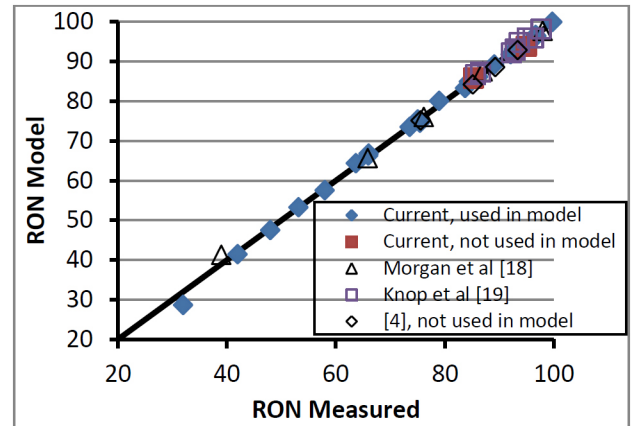


Fig. 4. Predicted RON from Eq. 10 vs Measured RON

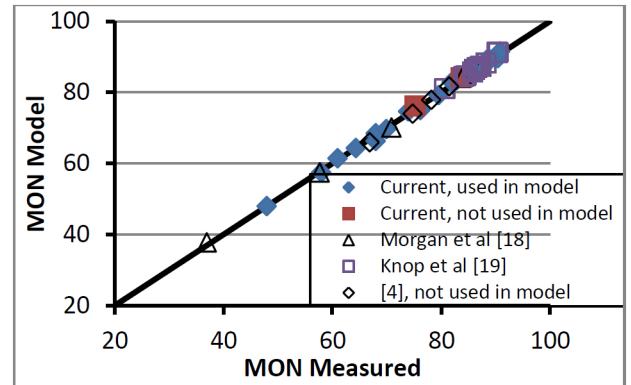


Fig. 5. Predicted MON from Eqs. 10 and 11 vs Measured MON

Figure 6 shows the PRF needed in the TPRF blend vs the target sensitivity for different target RONs. Clearly with TPRF, maximum sensitivity is obtained when PRF is zero i.e. with toluene/n-heptane blends. The lower the target RON, the lower is the maximum sensitivity attainable. As we lower RON, the blend heads towards n-heptane.

3. A SIMPLE MODEL FOR IGNITION DELAY FOR A GASOLINE USING A TPRF SURROGATE

A Saudi Arabian market gasoline with 95.1 RON and 86 MON was tested in a single cylinder port fuel injected (PFI) research engine at different operating conditions in [17]. The fuel contains 12.3% MTBE and further details about the fuel can be found in [17] - also Appendix B. From the procedure described above, the TPRF that matches this gasoline for both RON and MON is made up of 55.3% vol toluene, 27.6% vol iso-octane and 17.1% vol n-heptane.