

Effects of High Molecular Weight Condensed Molecules on Catalyzed Combustion Reaction Rates

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In 1995 SFA discovered that a combination of oil-soluble compounds of iron and magnesium gave a greater reduction in particulate matter in the exhausts of combustion turbines and boilers than was expected from the literature. SFA studied this phenomenon and found that the catalyst was very effective in reducing fuel consumption in compression ignited (Diesel) engines. We observed a wide range of changes in fuel efficiency ranging from 1% to 20%. We accumulated a large amount of data with some of these tests run under rigorous conditions. We found an unexpected correlation between percent reduction in fuel consumption and logarithm of parts per million sulfur content. Sulfur content in petroleum fuels is correlated with the presence of high molecular condensed aromatic molecules. The original version of this paper was presented at the American Chemical Society, Fuels Division, Fall Meeting, Philadelphia, PA, August 2008.

The purpose of this paper is to extend the mechanism developed to explain the above observations to fuels containing high levels of condensed molecules such as solid fossil fuels (coal).

Test Data

SFA has data for six tests of the catalyst in Diesel engines with known sulfur content. All of these are “old” Diesel engines predating computer controls. Fuels are all in the ASTM No. 2 fuel range. These data are summarized in Table I.

Southwest Research Institute. SFA received a grant from the Texas Commission on Environmental Quality (TCEQ) for a “Test of Concept” evaluation. TCEQ required that the tests were run under a predetermined protocol with fuel containing 0.6 ppm sulfur. Because of the TCEQ protocol, the reference engine horsepower was determined for only the first day of the tests that extended over 6 days. We were able to compare mass emissions from each test and found a fuel efficiency improvement of 1.89%.

Eco-Mission Inc. Truck. A 2000 Ford F-250 Diesel truck has used the catalyst since February 2006. While “Pick-Up Truck” trials are not generally given much credibility, this test is different in that the owner of the truck is a chemical engineer; Data were taken with great care and over a long period removing variations due to driving conditions. It also demonstrated that the catalyst is harmless in the engine over the longest period we have used the catalyst in a Diesel engine.

Data from the period beginning January 2007 through July 2007 with catalyst were compared with non-catalyst use in August – September of 2007. This part of the test began when Tx-LED 15 ppm sulfur fuel (or less) became available.¹

TransGlobal Solutions Railroad Locomotive. This test was run in a 1980’s vintage GP-9 1,500 hp two-cycle locomotive. The engine load was measured on a load box allowing us to gather information on power output. We used flow meters to measure fuel flowing toward and away from the engine yielding fuel consumption. Base load conditions were measured and catalyst was added for three weeks. During this period the engine consumed about 1,200 gallons fuel. The catalyst effect was measured at the end of this period. The fuel was Off-Road Diesel with about 350 ppm sulfur. We measured a 9.54%

improvement in engine efficiency. This combines fuel efficiency improvement and increase in horsepower at the test throttle setting.

Lincoln and Plymouth Railroad. The Lincoln and Plymouth is a railroad in central New Hampshire with tourist operations, private car storage and passenger car renovations. We tested two months on regularly scheduled trains at two stations. We measured 12.0% and 12.8% reduction in fuel consumption between July and August 2005. Fuel was home heating oil in the kerosene range with about 0.3% sulfur (3,000 ppm).

Automobile Research Association of India. Road driving and dynamometer tests were conducted on a 1.4 liter Padmini sedan. An average of data from the test yielded 13.5% reduction of fuel consumption with fuel averaging 1.12% (11,200 ppm) sulfur.

Bahrain Bus Trial. Emission Control Products wll, an SFA distributor, ran a trial on three identical buses in Bahrain in 2002. Catalyst and fuel addition and distances driven were carefully logged. There was no control of driving conditions other than these buses were used on the same routes. The result was an average of 13.87% fuel reduction. The fuel had approximately 2% (20,000 ppm) sulfur.

Correlation of Fuel Efficiency and Sulfur Level

Observation of a wide range of fuel efficiency improvements with our catalyst raised the question of why there are large variances in the observations. We plotted fuel efficiency vs. sulfur level and found a strong correlation between fuel efficiency and logarithm of parts per million sulfur in the fuel as shown in Figure 1. This Figure shows the actual data with the best-fit line from linear regression analysis. The slope and intercept of this line are given in Table I. The correlation coefficient is almost 1.0 indicating a near perfect correlation between the two sets of data.

Hydrocarbon Fuel Combustion Reactions

Distillate fuels in the ASTM No. 2 range contain two types of compounds: aliphatic and aromatic. Aliphatic compounds combust easily. Aromatic compounds are condensed hydrocarbons that contain sulfur, have higher molecular weights and lower vapor pressures, and are generally more difficult to combust. Hydro-desulfurization (HDS) processes carried out as part of the refining operation remove sulfur and breakdown high molecular weight aromatic species. From this premise, it seemed appropriate to explore separate competing reactions to get a better understanding of the effects of varying reaction rates on fuel efficiency results.

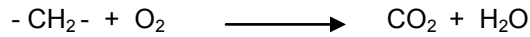
Engine and Fuel Parameters

The test work at Southwest Research Institute was carried out with a Cummins Model 60 truck style Diesel engine². Parameters for this engine are given in Table II. This engine at full power and 1,800 rpm consumed 254 Kg/Hr fuel. From this we were able to calculate the moles fuel for each power stroke. From the displacement of the engine and an estimated 10 to 1 compression ratio, we were able to calculate piston volume. This allowed us to compute moles oxygen in the cylinder when fuel was injected and ignition occurred. It became obvious from this calculation that turbo-charging is required to introduce sufficient oxygen for the reaction to go to completion.

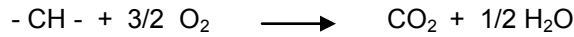
Competing Reactions

We proceeded on the hypothesis that aliphatic and aromatic compounds in the fuel reacted with oxygen in separate, competing reactions with different reaction rates. Examples of these reactions are:

Aliphatic Compounds



Aromatic Compounds



Kinetics for 2nd order reactions are expressed as follows^{3,4}:

$$dx/dt = k_2 (a - x) (b - x)$$

Rearranging yields the differential equation:

$$dx / [k_2 (a - x) (b - x)] = dt$$

Integrating this equation with partial fractions yields:

$$k_2 t = [1 / (a - b)] \ln [b (a - x) / a (b - x)]$$

Conversion to exponential form yields:

$$e^{(a-b)k_2 t} = [b (a - x) / a (b - x)]$$

Solving for x, the finished product, results in the following expression:

$$x = [a (1 - e^{(a-b)k_2 t})] / [1 - (a/b) e^{(a-b)k_2 t}]$$

Table III presents calculations for second order competing reactions with a common reactant. We calculated yields of carbon dioxide at various crank angles to 180°. We estimated reaction rates based on all aliphatic hydrocarbon reacting to 99% with oxygen by the end of the power stroke. This required a rate of 12,000 per mole – second. We based our competing reaction on aromatic fuel burning to 15% completion at the end of the power stroke with a reaction rate of 1,200 per mole – second.

We then calculated the total amount of carbon dioxide in the two reactions for 1% through 25% aromatic content. This yielded a rate of completion ranging from 99.04% to 78.81%. A plot of unreacted fuel vs. percent asphaltene content is given in Figure 2.

A difference in reaction rate of 10² is large. Combustion reactions approach the kinetics of explosions. In consideration of the very high reaction rates, it is not unreasonable to postulate this size difference in reaction rates between easily combustible compounds and those that are more difficult to combust. We do not have data to estimate Activation Energies for these reactions. We can assume that they will be very high based on high quench temperatures.

Catalysis and Competing First Order Reactions

The two laws of catalysis require that the rate of reaction is proportional to catalyst concentration and the reaction order is reduced by one. We examined the catalyzed reaction with first order kinetics.

Kinetics for 1st order reactions are expressed as follows:

$$dx/dt = k_1 (a - x)$$

Rearranging yields the differential equation:

$$dx / (a - x) = k_1 dt$$

The integrated form of the expression is:

$$k_1 t = \ln(a - x)$$

Conversion to exponential form yields:

$$e^{k_1 t} = a - x$$

Solving for x, the finished product, results in the following expression:

$$x = a - e^{-k_1 t}$$

We applied a reaction rate that gave the same level of completion as was found for aliphatic compounds in the 2nd order reaction study. We then applied a reaction rate for aromatic compounds that yielded 96.4% completion for the catalyzed reaction. This was based on actual observations of fuel efficiency. These rates yielded the data presented in Table IV. The result is that the reaction goes to more than 98% completion with the time of the power stroke.

Note that the reaction rates for the first order are 10² smaller than for second order reactions. This is caused by the more complex expression for product for the 2nd order expression compared with the 1st order expression. Reaction rates for 2nd and 1st order reaction kinetics should be viewed as comparisons and not in terms of absolute values.

Sulfur Levels in Fuels after Hydro-Desulfurization (HDS)

Ranges of organic sulfur compounds that may be found in asphaltenic fuels are presented in Table V. The relation between asphaltene content and sulfur is shown in Figure 3. The HDS process reduces sulfur by removing asphaltenic compounds including those containing sulfur. Compounds presented in Table V range as high as 17% sulfur by weight^{5,6,7}.

Comparison of Iron-Magnesium Catalysts with Iron Catalysts

Use of iron in the form of ferrocene and other soluble forms as fuel catalysts is well known. A study was carried out on a railroad locomotive using kerosene type fuel that yielded 10% in switcher duty and 5% road duty improvement in fuel efficiency with an oil-soluble ferrocene catalyst. The fuel was estimated to contain 3,000 ppm sulfur⁸. We measured 12.0% and 12.8% on a similar fuel from the same area of the United States with our iron-magnesium catalyst.

It is logical to assume that oil-soluble iron dissolves in the hydrocarbon and forms iron oxides in the combustion process⁹. The source of iron in the catalyst influences catalyst performance only in regard to solvency and dissolution in the fuel. The major difference in the catalyst used in the SFA test is the presence of magnesium.

It is known from the literature that magnesium has no catalytic effect on the combustion reaction¹⁰. Earlier works published by SFA present data for particulate matter in combustion turbine exhausts demonstrating 90% reduction compared with 50% reduction with iron alone¹¹.

Table VI presents major spectra line positions and intensity for iron and magnesium from 2,000 to 6,000 Angstroms. There are few iron spectra lines below 4,000 Angstroms whereas most of the strong lines for magnesium are below 4,000 Angstroms. A possible reason for the synergy between iron and magnesium as catalysts is that excited magnesium atoms with strong, high energy lines in the shorter wave length ultraviolet area release energy that excites the iron electron structure to produce high energy electron distribution over a longer time. This will produce the increased catalysis seen with both metals. This mechanism can be compared to a capacitor releasing stored electrical energy¹¹.

Comparison of results with Aromatics in Low Emission Diesel Fuels

Fuel specifications for Texas Commission on Environmental Quality Registration Requirements may be found in Rule/Citations: 30 TAC, Subchapter H, Division 2, Paragraph 114.315¹². Comparison fuels in reference testing specified by this Rule are limited to maximums of sulfur at 15 ppm, total aromatic hydrocarbon of content 10% and polycyclic aromatic hydrocarbon content of 1.4%.

Data presented in Table III show that 10% aromatic content yield 8.5% un-reacted hydrocarbon by the second order competing reactions hypothesis presented here. In actual practice, we see a 6% increase in fuel efficiency in Texas Low Emission Diesel fuel with catalyst use. This is remarkably good agreement between our hypothesis and actual practice.

Catalyst Mechanism

In the past we have thought of the catalyst mechanism as release of energy as electrons decay to degeneracy following excitement at combustion temperature. We have been led to consider a somewhat modified alternative mechanism based on comparison with the HDS process.

Iron exists in four valence states; +1, +2, +3 and +6¹³. While +1 and +6 are not well represented at ambient temperatures, the $3d^6, 4s^2$ electron structure of iron leads to the possibilities of existence of these valence states, possibly simultaneously, at combustion temperatures (2,500° C). As a result, iron can react with oxygen to activate the molecule and make it more reactive toward the hydrocarbon moieties.

It seems reasonable to suggest that the catalyst forms high-energy free radicals from high molecular weight and complex structure hydrocarbon molecules that break up the molecules and improve reaction with oxygen leading to more complete reaction and improved fuel efficiency. Electron-rich basic magnesium oxide can be a Lewis Base that further enhances free-radical formation.

This type of mechanism is more in line with the HDS process in which sulfur is removed from condensed molecules such as benzothiophenes leading to free radical formation. This occurs because of electron donation from molybdenum and tungsten oxide catalysts at high temperatures in a hydrogen rich atmosphere.

A mechanism for the synergy of iron and magnesium as combustion catalysts is proposed above.

Conclusions

This study of hydrocarbon combustion catalysis indicates that the hypothesis for competing reactions is a reasonable approach to resolving levels of reaction completion. It demonstrates that field results for fuel efficiency can be stated in terms of competing combustion reactions for aliphatic and aromatic compounds with widely varying reaction rates. Comparison of results from this work with actual aromatic hydrocarbon in TCEQ reference fuels was in remarkably good agreement.

A mechanism hypothesis is presented based on enhanced free radical formation. This mechanism also takes into account the synergistic role of magnesium enhancing iron as a combustion catalyst.

Coal is a condensed carbon structure that is aromatic in structure and resembles graphite. Carbon present in coal is in similar high-molecular weight condensed aromatic molecules. Coal can be pictured as an extreme example of a highly asphaltenic petroleum fuel. The effect of SFA's iron-magnesium catalyst system has been well demonstrated in petroleum fuels. Use of the catalyst with coal is a logical extension because of the similarity of coal to the portions of petroleum fuels where the catalyst is most effective.

References

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Table I. Catalyst Performance and Fuel Sulfur Content

Data Source	Old Engine	SwRI	EcoMission	TGS Locomotive	L&P RR	ARAI	ECP Bus Trial
Fuel Source		Chevron-Phillips	Tx-LED	Off Road Dyed Fuel	Kerosene	India	Bahrain
% Sulfur		0.00006%	0.0010%	0.0027%	0.3000%	1.1200%	2.0000%
Sulfur, ppm		0.6	10.0	360.0	3,000.0	11,200.0	20,000
Log Sulfur, ppm		(0.22)	1.00	2.56	3.48	4.05	4.30
Fuel Efficiency		1.89	5.30	9.54	12.40	13.50	13.87

Data Source	New Engine	U of H
Fuel Source		La-LED
Diesel		80%
% Sulfur		0.0010%
Biodiesel,		20%
Sulfur, ppm, Blend		8.00
Log Sulfur, ppm		0.90
Fuel Efficiency		2.50

Correlation Equation

$$\text{Fuel Savings} = 2.70 \times \log \text{ ppm S} + 2.59$$

Correlation Coefficient = 0.999

Table II. Engine and Fuel Parameters

Engine	Cummins Model 60	
Displacement	12.70	Liters
Cylinders	6	
Rated Power @ 1,800 rpm	365	bhp
Fuel	254.0	Kg/Hr.
Cylinder	2,328	Liters
Compression Ratio	10	
rpm	1,800	
rps	30	
seconds/revolution	3.333E-02	
seconds/degree	9.259E-05	
Inlet Air Temperature	25	deg. C.
gm fuel per power stroke	0.7839	
moles fuel per power stroke	0.0560	
moles oxygen	0.0840	
moles gas per power stroke	0.3999	

Table III. Second Order Competing Reactions

Estimated Rates of Reaction		mole ⁻¹ sec ⁻¹						
Aliphatic		12,000						
Asphaltenic		120						
Crank Angle	Time	(a-b)k ₂ t	Aliphatic		CO ₂	Asphaltenic		Total CO ₂
			(a-b)k ₂ t	e		(a-b)k ₂ t	e	
Degrees	Seconds							
0.0	0.0000							
30.0	0.0028	1.40	4.05	3.608E-02	0.02	1.02	3.855E-04	3.647E-02
45.0	0.0042	2.10	8.16	3.925E-02	0.03	1.04	5.737E-04	3.983E-02
60.0	0.0056	2.80	16.44	4.067E-02	0.05	1.05	7.588E-04	4.143E-02
90.0	0.0083	4.20	66.64	4.167E-02	0.07	1.07	1.120E-03	4.280E-02
120.0	0.0111	5.60	270.15	4.191E-02	0.09	1.10	1.470E-03	4.338E-02
150.0	0.0139	6.30	543.95	4.195E-02	0.10	1.11	1.641E-03	4.359E-02
180.0	0.0167	7.00	1,095.24	4.197E-02	0.12	1.12	1.809E-03	4.378E-02

% Asphaltenic	Aliphatic		Aromatic		Competing Reactions	
	Reacted	Unreacted	Reacted	Unreacted	Reacted	Unreacted
1%	99.89%	0.11%	15.45%	84.55%	99.04%	0.96%
5%	99.92%	0.08%	15.42%	84.58%	95.70%	4.30%
10%	99.95%	0.05%	15.39%	84.61%	91.50%	8.50%
15%	99.97%	0.03%	15.35%	84.65%	87.28%	12.72%
20%	99.98%	0.02%	15.31%	84.69%	83.05%	16.95%
25%	99.99%	0.01%	15.28%	84.72%	78.81%	21.19%

Table IV. First Order Competing Reactions

Estimated Rates of Reaction		sec ⁻¹								
Aliphatic		150								
Asphaltenic		100								
Crank Angle	Time	(a-b)k _{2t}	Aliphatic		CO ₂	Asphaltenic		CO ₂	Total CO ₂	Total Gas
			(a-b)k _{2t} e	CO ₂		(a-b)k _{2t} e	CO ₂			
Degrees	Seconds									
0	0.00000									
30	0.00556	0.833	2.30	1.35E-02	0.556	1.74	3.38E-03	1.68E-02	0.1113	
45	0.00833	1.250	3.49	1.70E-02	0.833	2.30	4.49E-03	2.15E-02	0.1159	
60	0.01111	1.667	5.29	1.93E-02	1.111	3.04	5.32E-03	2.46E-02	0.1191	
90	0.01667	2.500	12.18	2.19E-02	1.667	5.29	6.44E-03	2.83E-02	0.1227	
120	0.02222	3.333	28.03	2.30E-02	2.222	9.23	7.08E-03	3.00E-02	0.1245	
150	0.02778	4.167	64.50	2.34E-02	2.778	16.08	7.44E-03	3.09E-02	0.1253	
180	0.03333	5.000	148.41	2.36E-02	3.333	28.03	7.65E-03	3.13E-02	0.1257	
% Asphaltenic	Aliphatic		Aromatic		Competing Reactions					
	Reacted	Unreacted	Reacted	Unreacted	Reacted	Unreacted				
1%	99.33%	0.67%	96.43%	3.57%	99.30%	0.70%				
5%	99.33%	0.67%	96.43%	3.57%	99.18%	0.82%				
10%	99.33%	0.67%	96.43%	3.57%	99.04%	0.96%				
15%	99.33%	0.67%	96.43%	3.57%	98.89%	1.11%				
20%	99.33%	0.67%	96.43%	3.57%	98.75%	1.25%				
25%	99.33%	0.67%	96.43%	3.57%	98.60%	1.40%				

Table V. Sulfur Compounds in Petroleum Fuels

Atomic Weights	Formula	Mol. Wts.	% S	Boiling Point °C
Thiophene	C ₄ H ₄ S	84.142	38.1%	84
Benzothiophene	C ₈ H ₆ S	134.202	23.9%	221
Dibenzothiophene	C ₁₂ H ₈ S	184.262	17.4%	332
Anthracene	C ₁₄ H ₁₀	178.234		354
Chrysene	C ₁₈ H ₁₂	228.294		448
Thiochrysene	C ₁₇ H ₁₁ S	247.341	13.0%	
Dithiochrysene	C ₁₆ H ₁₀ S ₂	266.388	24.1%	
Trithiochrysene	C ₁₅ H ₁₁ S ₃	285.435	33.7%	

% Asphaltenes	CO ₂ from Aliphatic		CO ₂ from Asphaltenes		CO ₂ from Competing Reactions		ppm S	log ppm
	% of Total	% of Completion	% of Total	% of Completion	% of Total	% of Completion		
1%	99.29%	0.71%	15.19%	84.81%	98.45%	1.55%	0.26	(0.59)
5%	99.52%	0.48%	15.15%	84.85%	95.30%	4.70%	2.69	0.43
10%	99.71%	0.29%	15.11%	84.89%	91.25%	8.75%	46.3	1.67
15%	99.83%	0.17%	15.07%	84.93%	87.12%	12.88%	728	2.86
20%	99.90%	0.10%	15.02%	84.98%	82.93%	17.07%	10,232	4.01
25%	99.94%	0.06%	14.98%	85.02%	78.70%	21.30%	128,000	5.11

Table VI. Major Atomic Spectra Lines for Iron(III) and Magnesium(II)

Iron		Magnesium	
Wavelength	Intensity	Wavelength	Intensity
2,151.78	15		
2,174.66	15		
		2,795.53	1,000
		2,825.70	600
		2,852.13	6,000
3,013.17	15		
		3,832.30	300
		3,838.29	50
3,954.33	16		
4,164.73	18		
4,296.85	16		
4,304.78	18		
4,310.36	20		
4,372.81	18		
5,243.31	18		
5,276.48	15		
5,282.30	16		
5,833.93	18		
5,891.91	15		
5,929.69	18		
5,999.54	18		
6,032.59	16		

Figure 1. Fuel Efficiency and PPM Sulfur

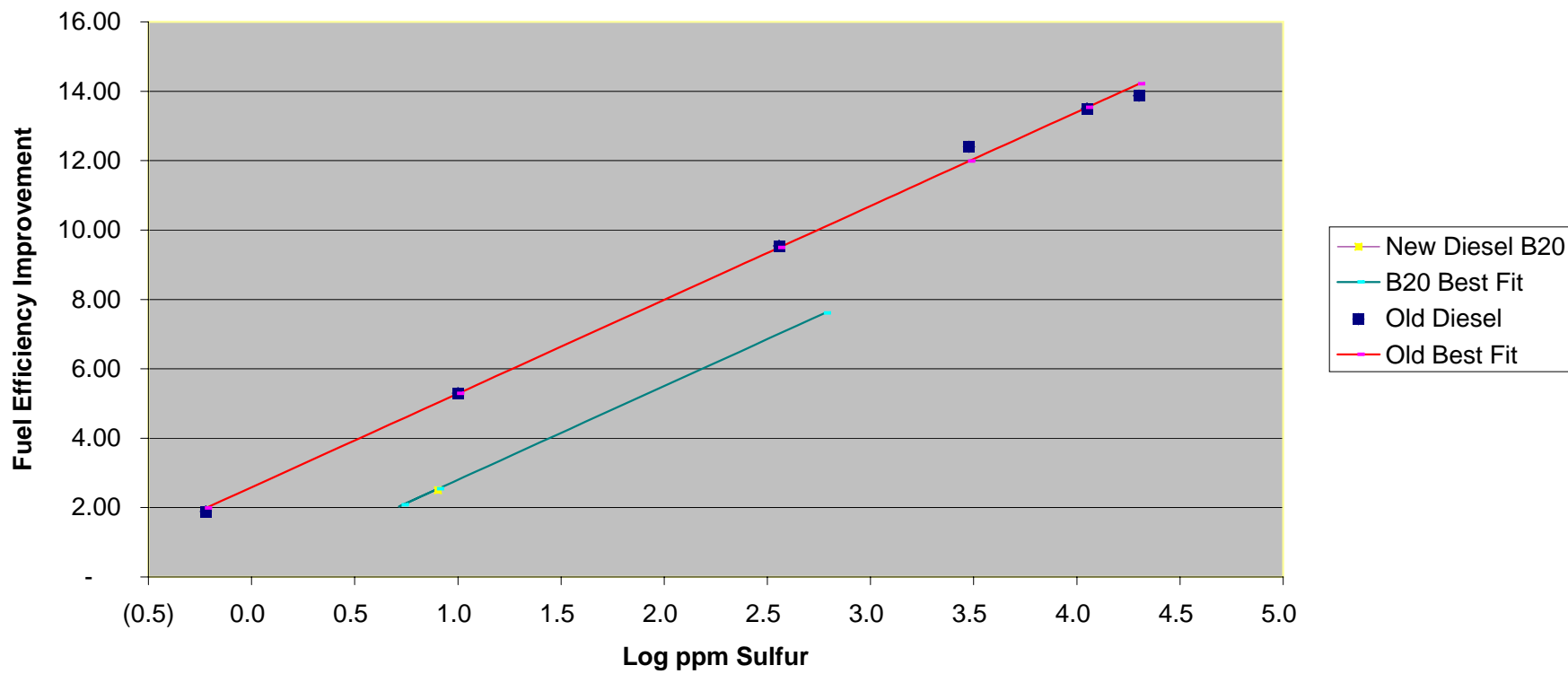


Figure 2. Unreacted Fuel vs. Asphaltenic Content
2nd Order Competing Reactions

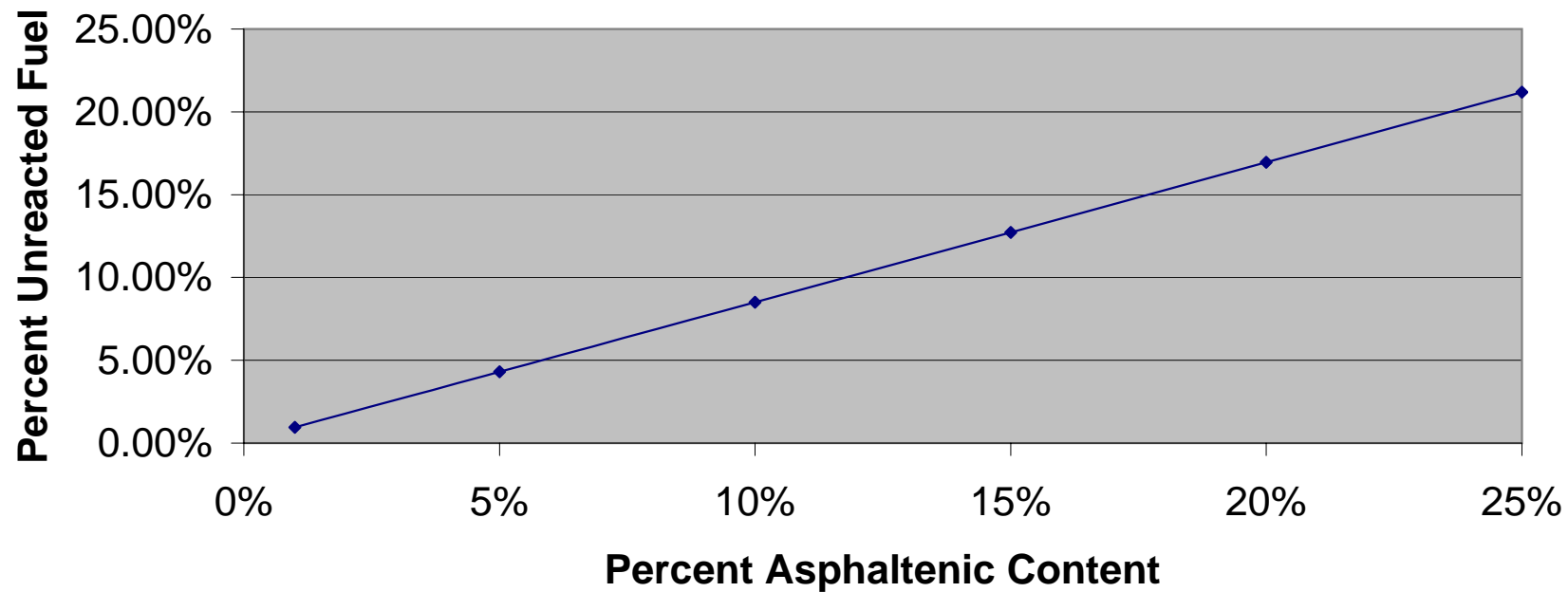


Figure 3.
Asphaltene Content and Sulfur Level

