THE PENNSYLVANIA STATE UNIVERSITY
SCHREYER HONORS COLLEGE

DEPARTMENT OF ENERGY AND MINERAL ENGINEERING

INVESTIGATION OF THE CETANE RESPONSE OF DIESEL BLENDED WITH BUTANOL

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ABSTRACT

Research into butanol as a possible fuel source has grown rapidly over the past couple of years. There is much excitement surrounding this possible new fuel due to several key benefits it holds over ethanol. However, butanol is still relatively unstudied as a standalone fuel or an additive.

This paper looks at the effects butanol has on the cetane number of diesel fuels. The four different isomers of butanol were blended with a stock diesel in concentrations up to 40% by volume. The fuel blends were then run through an Ignition Quality Tester (IQT™) to determine their Derived Cetane Number (DCN). The miscibility of the isomers of butanol with diesel was also studied.

The results show that all the isomers do depress the cetane number. However, not all the isomers performed the same. 1-Butanol and 2-butanol both performed very similarly, depressing the DCN 3-4 points at a 10% concentration, and depressing it a full 15 points at a 40% concentration. Iso-butanol, which performed the worst, reduced the DCN over 4 points at 10% concentration and nearly 18 points at the highest concentration. Somewhat surprisingly, tert-butanol performed the best. At the 10% concentration, the DCN was depressed less than 2 points, and at the 40% level, it was only depressed by 9 points. Furthermore, all of the butanol isomers were determined to be fully miscible in diesel up to at least a 40% concentration by volume.

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Chapter 1

Introduction

The world is slowly dieselizing – a phrase heard more and more often nowadays. As the demand for gasoline continues to increase, many parts of the world are looking towards other alternatives to try and meet this growing appetite. One of the alternatives that can make a large impact in the short run is diesel. The technology needed has been around for a long time and over the past several decades it has improved to a point where is can be appealing to consumers.

The demand for petroleum products has grown steadily from 21 million barrels per day in 1960 to more than 85 million barrels per day in 2008. A consumption timeline is shown in Figure 1-1 (U.S. Energy Information Administration 2010). This increased consumption, along with unrest in many of the key oil producing regions, has caused the price of petroleum products to go up, most notably gasoline. This has caused a look at alternative transportation fuels.

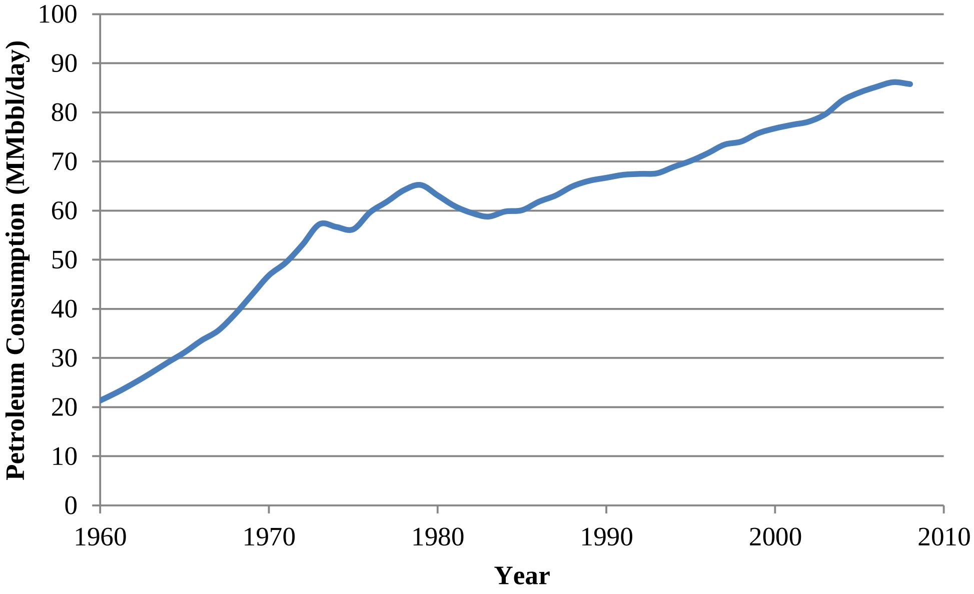

Figure 1-1: World petroleum consumption, 1960-2008

Diesel fuel, also called distillate fuel, is one alternative to gasoline. Using diesel as a transportation fuel has many advantages. First, most petrodiesels have a density that is higher than that of gasoline while having a similar energy content per unit mass. This means that diesel fuel has a higher energy content per volume than gasoline. Second, diesel engines are inherently more efficient than their gasoline counterparts. This is due to the high compression ratios used in diesel engines, which allow more work and power to be extracted from the combustion (Rakopoulos, et al. 2010, Al-Hasan and Al-Momany 2008). Finally, diesel engines have a lower carbon footprint than gasoline engines. While the amount of CO_2 produced per gallon is slightly higher for diesel engines, the much increased efficiency allows for an overall reduction per mile (Killick, Parnaby and Wrigley 1998).

While diesel does provide many benefits, there are also several drawbacks to using this fuel. First is the noise and vibration these types of engines create. However, recent advances in engine technology have all but eliminated this as a problem for modern diesel vehicles. Second, since diesel fuels typically contain much more sulfur which leads to SO_x formation. Again, this problem has all but been solved by requiring that all on road diesel sold in the U.S. contain less than 15 ppm sulfur (called Ultra Low Sulfur Diesel). This is an important advance because it allows the exhaust of diesel engines to be fitted with after treatment devices that would otherwise be poisoned by the sulfur. Also, since diesel is more viscous than gasoline and the engine uses compression ignition the cold temperature performance of the fuel suffers. However, this can be avoided by using additives that improve the cold weather properties of the fuel.

Another drawback of diesel is the production of particulate matter during combustion. This can be seen as the black cloud that exits the exhaust when a diesel powered vehicle accelerates. The formation of this particulate matter is caused by an insufficient local oxygen supply. The lack of oxygen prevents the fuel from fully combusting and instead converts the fuel to a carbon-rich soot. This soot is what forms the black cloud that cane be seen exiting the exhaust. The way to reduce this soot formation is to increase the amount of oxygen available during combustion (Xiao, Ladommatos and Zhao 2000).

One way to increase oxygen concentration is to run the engine under fuel-lean conditions. The main drawback here is that running in lean conditions results in a lower power output from the engine. Another way to increase the oxygen concentration is to add oxygen to the fuel itself. A good example of this is biodiesel, which is made up almost exclusively of fatty-acid methyl esters. These compounds, which contain oxygen, greatly reduce the soot formation (Chotwichien, Luengnaruemitchai and Jai 2009). Another way to get oxygen into a diesel fuel is to blend it with a compound containing oxygen. This blending compound can be biodiesel or it can be a compound unrelated to diesel, such as an alcohol.

There has been a large volume of research done on the effects of lowering the smoke point of diesel fuels by adding different oxygenate compounds. Some of the literature on this includes McCormick, Ross, and Graboski, 1997, and Xiao, Ladommatos, and Zhao, 2000. While these oxygenated compounds help to decrease the amount of soot formed, they can also have other effects on the performance of the fuel. For example, they can increase viscosity, decrease the flash point, or decrease the cetane number. Therefore, it is very important to study and understand all the effects a given additive has to the properties of a fuel.

Recently, there has been a push to use more environmentally friendly fuels. This push has been two-fold – use fuels derived from plant and other natural sources and use less fossil fuels. Since current scale of biofuel production in the U.S. is not nearly what it needs to be to begin replacing fossil fuels, one logical step to begin blending these fuels with conventional fuels. In the case of diesel, one can get the best of both worlds if this biofuel additive also happens to be an oxygen containing compound.

One example of a bio-based fuel additive is ethanol. The main source of ethanol in the U.S. is corn. Ethanol is a fine fuel for mixing with gasoline due to its high octane rating, but it does not mix well with diesel. This is because diesel is composed of long, straight chained alkanes which are highly non-polar, and ethanol is a short, rather polar molecule. In order to achieve adequate mixing, one often has to employ the use of stabilizers. However, if one uses butanol, which can also be made from bio-based sources, the mixing problem with diesel goes away (Chotwichien, Luengnaruemitchai and Jai 2009).

Butanol has several advantages over ethanol. First, it is longer and less polar making it more similar to both gasoline and diesel than ethanol is. Second, it tolerates water contamination much better than ethanol. Third, it is less corrosive to existing pipelines than ethanol is. Finally, it has a higher energy content than ethanol, meaning the penalty for adding it to a stock fuel is lower (DuPont and BP 2006).

While butanol appears to have many advantages over ethanol, it is still relatively unstudied as a fuel, especially when compared to ethanol. Most of the work that has been done involves blending butanol with gasoline, much the way ethanol is blended. There is also a volume of work showing how mixtures of gasoline-ethanol-butanol have better properties than just gasoline-ethanol mixtures. However, there is very little research into how butanol affects diesel. It is known that addition of butanol to diesel decreases the smokiness of the exhaust while simultaneously decreasing some key engine performance variables, such as break thermal efficiency and break power (Rakopoulos, et al. 2010). It is also known that butanol and diesel mixtures are fully miscible. However, the areas that still need to be researched are vast.

One area that has not been looked at is how butanol affects the cetane number of diesel. This is important to know because the cetane number gives a good overall indication of how well the diesel will perform. It is also important to know because there is a minimum cetane rating that all diesels must possess in order to be sold commercially. This project will look at the effect the different types of butanol have on the cetane number of a standard diesel fuel.

Butanol has four different isomers: 1-butanol, 2-butanol, iso-butanol and tert-butanol. In this project, all four will be blended with a standard diesel. The fuels will then be combusted to determine the Derived Cetane Number of the mixture. Previous work by Al-Hasan and Al-Momany, 2008, and Miller, Smith, and Workman, 1981, shows that butanol blends up to 40% have only small negative effects on engine performance. They also show that blends above 40% tend to drastically decrease the performance of the engine. Therefore, butanol blends up to 40% will be studied here.

This research is pertinent because as butanol becomes a bigger player in the fuels world, it will be important to know how it affects fuel blends, much the way ethanol has been studied. Currently there is also a push to make butanol from cellulosic material. Should this process become economically feasible, the explosion of butanol onto the fuels scene could happen very quickly.

Chapter 2

Methodology

The four different types of butanol, shown in Figure 3-1, were blended with a base diesel fuel. Blends of 10%, 20%, 30% and 40% by volume of each alcohol were produced for a total of 16 diesel/alcohol blends. The 1-butanol and 2-butanol fuel blends were produced in 500 mL quantities, while the iso-butanol and tert-butanol blends were produced in 250 mL quantities. All alcohol volumes are ± 0.5%.

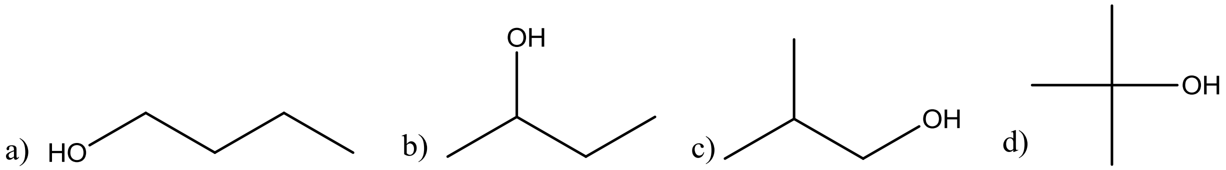

Figure 2-1: The four types of butanol – a) 1-Butanol, b) 2-Butanol, c) iso-Butanol, and d) tert-Butanol

In order to determine the cetane number of the alcohol/diesel blends, an Ignition Quality Tester (IQT™) produced by Advanced Engine Technology Ltd. The tests were run according to ASTM D 6890 – 09. The IQT™ automatically determines the Ignition Delay (ID) of the fuels. The ID (in milliseconds) can then be converted to the Derived Cetane Number (DCN) by using equation 1, which was also performed by the IQT™ software.

$$DCN = 4.460 + \frac{186.6}{ID} \tag{1}$$

The IQT™ measures the ID of a fuel by injecting a set quantity into a constant volume chamber, and then measuring the time between injection and ignition. The chamber is set at a pressure of 310 ± 1 psi. The ignition point is determined by the onset of a large pressure spike in the combustion chamber. The time of this pressure spike is then compared to the time of injection in order to get the ID.

Each run on the IQT™ consists of 15 preliminary cycles and 32 further cycles. Each cycle consists of injection, combustion, and the measurement of the ID. The final 32 cycles are recorded by software and the average is given. This average is then taken as the value for the run. For the test samples, two sets of three runs were completed for each. The sets for the individual fuels were carried out on separate days, and the three runs in each set were carried out sequentially. In all, six data points for each alcohol/diesel blend were obtained. The data collection took place over the course of three weeks.

Calibration for the IQT™ was carried out by using the base diesel fuel. This differs from the standard method of using n-heptane. However, in previous tests, the IQT™ was giving inconsistent results using the n-heptane calibration, so it was chosen to use the base fuel as the calibration. This was deemed acceptable for two reasons: 1) the DCN of the base fuel is known to be 45.0 and has been well documented on the IQT™ in previous experiments, and 2) the goal of these tests were to determine how much the alcohols depressed the cetane number of the base diesel, so the numbers obtained would be relative to that base anyway. Calibration was carried out until three consecutive runs of the base diesel yielded an average ID of 4.60 ± 0.01 ms. The ID was adjusted by controlling the external skin temperature of the combustion chamber. For all of the runs carried out, the skin temperature ranged between 578.0 °C and 580.0 °C.

Chapter 3

Results and Discussion

The base diesel used here has a Derived Cetane Number (DCN) of 45.0. This was used not only as the calibration standard for the IQT™, but also as the reference point for the blended fuels. The six runs for each butanol/diesel blend were averaged into a single data. The test results are summarized in Table 3-1.

Alcohol	**1-Butanol**		**2-Butanol**		**iso-Butanol**		**tert-Butanol**	
Percent by volume	**DCN**	**Std. Dev.**	**DCN**	**Std. Dev.**	**DCN**	**Std. Dev.**	**DCN**	**Std. Dev.**
10%	41.7	0.1	41.2	0.2	40.9	0.2	43.2	0.2
20%	38.2	0.1	38.0	0.2	37.2	0.3	41.4	0.1
30%	34.7	0.1	34.2	0.1	32.5	0.4	39.0	0.2
40%	30.6	0.1	29.8	0.2	27.4	0.2	35.9	0.2

Table 3-1: Average Derived Cetane Number (DCN) for the diesel/butanol blends. The base diesel, for reference, has a DCN of 45.0

Table 3-1 clearly shows a negative relationship between the amount of butanol in the blend and the resulting DCN. A 10% butanol concentration by volume depressed the DCN of the base diesel anywhere from 2 to 4 points, and a 40% concentration depresses the DCN anywhere from 9 to 15 points. This large spread indicates that the individual structures of the butanol molecules have a pronounced effect of the performance of the fuel. When looking at 1-butanol and 2-butanol, the DCNs at all of the concentrations are within 1 point of each other. Comparing 1-butanol to iso-butanol, there is a much bigger gap between the DCNs, sometimes as much as 3 points. Finally, comparing 1-butanol to tert-butanol shows the biggest difference of the three comparisons. Here, the DCN can vary as much as 5 points. From this data, it appears that the backbone has much more of an effect than the placement of the alcohol group.

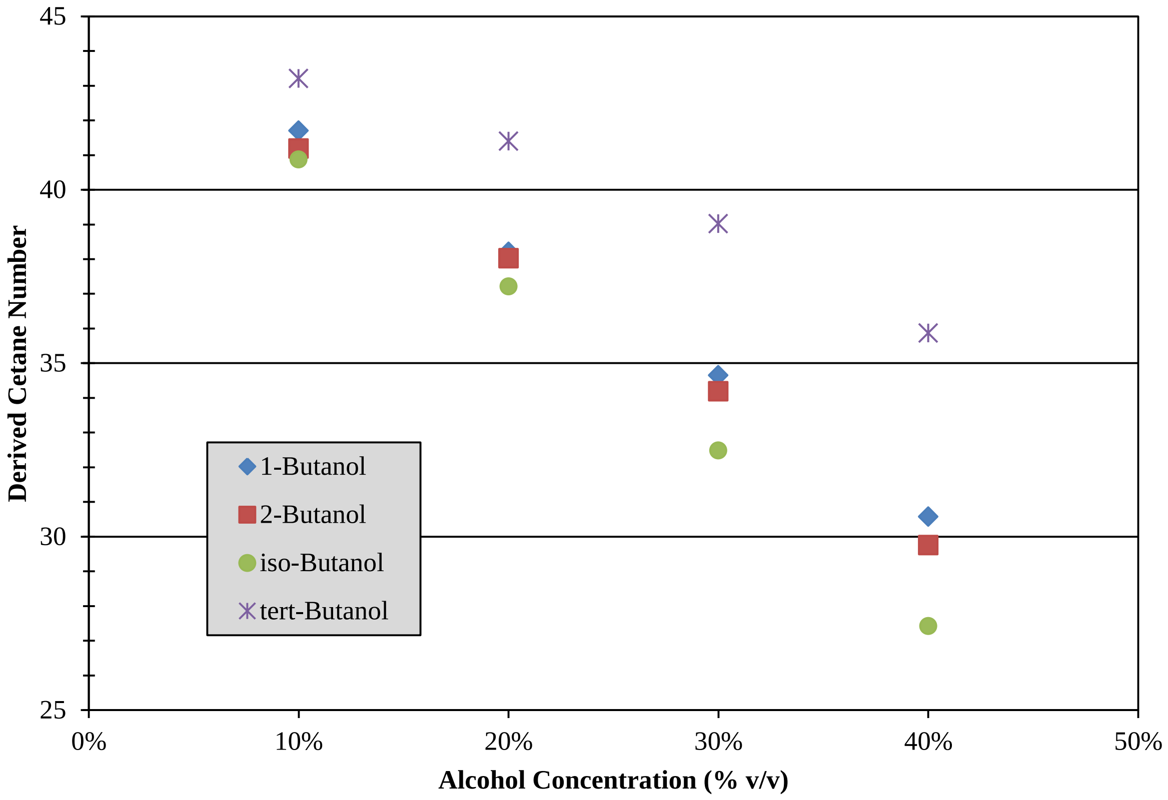

Figure 3-1: Derived cetane number of the alcohol/diesel blends as a function of alcohol concentration.

When this data is plotted, as in Figure 3-1, the discrepancy between the different butanol isomers becomes even more apparent. This figure shows that the tert-butanol clearly performed the best. This is a rather interesting result. Since diesel fuel is made up predominantly of long straight-chained alkanes, it was initially thought that 1-butanol would perform the best since it most closely resembles a straight chained alkane. On the other hand, tert-butanol was predicted to be the worst, since not only is it highly branched, but it also can be used to boost the octane number of gasoline, which means it should have the opposite effect on the cetane number. Even though this data suggests that tert-butanol has the least impact on the diesel fuel, not enough data exists to make a full judgment at this time. Future research should investigate how tert-butanol affects the other properties of diesel both inside and outside the engine, such as the cloud point, viscosity, and thermal efficiency.

Another point of interest was the percent the butanol depressed the cetane number of the diesel. A direct depression percentage calculation (amount reduced over original DCN) cannot be used in this case because the individual butanol isomers all have their own cetane rating which will act as a lower limit. However, the only isomer with a known cetane number is 1-butanol (CN25). None of the other butanol isomers have reported cetane numbers. Furthermore, straight butanol was not run through the IQT™ because the apparatus gives the best results with fuels that have moderately high cetane numbers (generally above 30), and because the machine used was calibrated for a relatively limited range of DCNs. Therefore, very little can be said about exactly how much, percentage wise, the butanol isomers depress the cetane number. This is of little concern since the goal of this experiment was not to develop a model to predict the mixing behavior, but rather to see the quantitative effects the different isomers of butanol have on the cetane number of diesel.

The final point studied here was the miscibility of the butanol with the diesel fuel. A small portion of all of the samples was set aside in a sealed jar and allowed to stand, untouched, for two weeks. None of the 16 samples experienced phase separation of the components. This is good news since it shows that no special care is needed to keep the butanol and diesel mixed with butanol concentrations up to at least 40% by volume.

Chapter 4

Conclusion

The results of this study showed that all the isomers of butanol depressed the Derived Cetane Number of a diesel fuel. 1-butanol and 2-butanol both performed about same, depressing the DCN 3-4 points at a 10% concentration, and depressing it a full 15 points at a 40% concentration. Iso-butanol, which performed the worst, depressed the DCN over 4 points at 10% concentration and nearly 18 points at the highest concentration. Tert-butanol, which in a surprising result, performed the best. At the lowest concentration studied (10%), the DCN was depressed less than 2 points, and at the 40% level, it only depressed the DCN 9 points. Also, all of the butanol isomers were determined to be fully miscible in diesel up to at least a 40% concentration by volume.

At small concentrations of butanol, the effect on the cetane number, as stated, is rather small. This means that the butanol can be used in diesel fuel with little to know further modification and still meet the current specifications. This added butanol can have many positive effects, especially on emission levels, while only minimally reducing the performance of the fuel and the engine. Development of butanol production as a fuel additive should be explored further, especially in terms of biobutanol production.

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Appendix A

IQT™ Data Collection

10%		20%		30%		40%	
ID	DCN	ID	DCN	ID	DCN	ID	DCN
5.021	41.62	5.532	38.19	6.169	34.71	7.180	30.45
4.978	41.95	5.531	38.20	6.179	34.66	7.145	30.57
5.018	41.64	5.502	38.38	6.219	34.46	7.153	30.55
5.028	41.57	5.548	38.09	6.166	34.72	7.132	30.63
5.004	41.75	5.544	38.12	6.212	34.50	7.133	30.62
5.013	41.68	5.520	38.26	6.138	34.86	7.136	30.61

Table A-1: 1-Butanol Raw Data

10%		20%		30%		40%	
ID	DCN	ID	DCN	ID	DCN	ID	DCN
5.116	40.94	5.571	37.95	6.307	34.04	7.296	30.01
5.085	41.16	5.604	37.76	6.282	34.17	7.404	29.69
5.079	41.20	5.598	37.79	6.310	34.03	7.263	30.11
5.053	41.39	5.557	38.04	6.244	34.35	7.471	29.50
5.087	41.14	5.533	38.18	6.277	34.19	7.427	29.63
5.067	41.29	5.498	38.40	6.244	34.35	7.444	29.58

Table A-2: 2-Butanol Raw Data

10%		20%		30%		40%	
ID	DCN	ID	DCN	ID	DCN	ID	DCN
5.165	40.59	5.669	37.68	6.587	32.39	8.265	27.45
5.134	40.81	5.672	37.36	6.735	31.85	8.210	27.58
5.091	41.11	5.691	37.25	6.658	32.13	8.148	27.73
5.143	40.74	5.720	37.08	6.594	32.76	8.154	27.34
5.103	41.03	5.748	36.92	6.531	33.03	8.185	27.26
5.113	40.95	5.739	36.97	6.601	32.73	8.225	27.15

Table A-3: iso-Butanol Raw Data

10%		20%		30%		40%	
ID	DCN	ID	DCN	ID	DCN	ID	DCN
4.855	42.90	5.061	41.33	5.439	38.76	5.935	35.90
4.829	43.10	5.061	41.37	5.392	39.07	5.916	36.00
4.833	43.07	5.056	41.23	5.36	39.27	6.000	35.56
4.812	43.24	5.025	41.59	5.392	39.07	5.920	35.98
4.796	43.37	5.052	41.39	5.416	38.92	5.962	35.76
4.770	43.58	5.039	41.49	5.401	39.01	5.921	35.98

Table A-4: tert-Butanol Raw Data

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    Softball Umpire: August 2007 – September 2009
Outward Bound – Sailing, March 2011