

# In-Line, Continuous Monitoring of Fuel Dilution in Motor Oils by Fourier Transform Infrared (FTIR) Spectroscopy

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## Abstract

Fuel dilution is an important consideration in engine oil performance and ultimately one of the key reasons oil changes are required. The current accepted method for determining fuel dilution in motor oils is by gas chromatography (GC). Although workable, it is not practical from the standpoint of obtaining timely, real time fuel dilution data.

An in-line Fourier Transform Infrared (FTIR) monitoring system has been designed and utilized to continuously monitor fuel dilution in an engine test-bed. This analytical system samples oil, which contains a dissolved heat-stable spectral marker, directly from the engine sump and continually passes it through a specialized temperature controlled IR transmission flow cell, which is mounted on a movable track. Through software control, this cell is programmed to travel in and out of an IR beam taking background and sample spectra at predetermined intervals. The progressive decrease in the IR absorption of the marker that results from dilution of the oil by fuel is continuously monitored to track fuel dilution.

This novel FTIR system and analytical approach were validated by analyzing samples taken from the circulating oil and correlating the FTIR results with GC data. The two methods tracked each other very well. In conjunction with other test-bed monitoring parameters gathered, the fuel dilution data provided in real time by the FTIR monitoring system can be of great assistance in optimizing one of the key variables limiting engine oil performance and allows for the rapid assessment of fuel dilution performance of test-bed engines.

## Introduction

Every liquid-fueled engine will have a certain amount of raw fuel in its normal blow-by. If solid contamination is not present, the raw fuel is evaporated by the internal heat of the engine. However, fuel dilution does occur within a healthy engine when there is a sufficient amount of solid contamination for the fuel molecules to adhere to. The determination of fuel dilution in engine oil samples is of prime importance because the presence of fuel in the crankcase reduces oil viscosity and weakens detergency. Excessive amounts of fuel contamination can also diminish the oil's lubrication properties, resulting in engine failure. Although some fuel dilution is expected, amounts in excess of 3% in two-cycle engines and 4% in four-cycle engines must be considered abnormal<sup>1</sup> and may indicate mechanical problems resulting from defects in injectors, fuel pumps, gaskets or seals.

Contamination or dilution of the lubricating oil of biodiesel-fueled vehicles has frequently been a concern of engine manufacturers. The mechanism for the dilution is essentially the same as for dilution with the heavier fractions of diesel fuel. Low-volatility fuel components, which for biodiesel are essentially the entire fuel, are slow to vaporize after injection into the cylinder<sup>2</sup>. Some of these low-volatility compounds will be deposited on the cylinder wall and can then be swept down into the crankcase by the normal scraping action of the piston's oil control rings. The two key questions for lubricating oil contamination are whether the amount of dilution by a biodiesel fuel is significant and then whether the

presence of the biodiesel, itself an excellent lubricant, causes any deterioration in the lubricant's performance.

All major engine manufacturers use test beds to gather a whole range of data on-line and in real-time, which is used to assess engine performance, emissions and other variables and on which design changes can be predicated. To address the above questions, engine manufacturers would require a quick, accurate, and cost-effective method to determine fuel dilution in biodiesel-fueled engines. The implementation of such a method on engine test beds would also allow for rapid assessment of the impact of engine design changes on fuel dilution. At present, there are no methods available that meet all the above criteria but, conceptually, FTIR spectroscopy can do so. Within this context, we propose to develop an in-line FTIR system capable of real-time monitoring fuel dilution in biodiesel-fueled engines. The present study takes several steps toward this goal.

## Background

Biofuels in some form or other are here to stay, and thus it is important to take the time to understand the pros and cons of using such fuels and the cautions that apply. Biofuels consist of two basic categories: (a) bio-ethanol (produced primarily from corn in the U.S.) blended with gasoline and (b) biodiesel [fatty acid methyl esters made by chemically processing vegetable or animal fats] blended into low-sulfur diesel. It is of interest to note that current research is looking at algae as a potential source of both categories of biofuel. Their oil is being extracted to make a biodiesel biofuel, leaving a green dry flake that can be converted to bio-ethanol. Harvested daily, algae have the potential to produce 57,000 liters of biodiesel per acre compared to just 230 liters per acre from a soybean crop.

The focus of the present study is biodiesel. Rudolf Diesel demonstrated the first engine to run on peanut oil at the World Exhibition in Paris in 1900. In 1912 he said: "The use of vegetable oil may seem insignificant today. But such oils may become, in the course of time, as important as the petroleum and coal tar products of the present time." Approximately one century later, both these statements remain valid, with minor modifications. Although the term "biodiesel" can convey the impression of running engines on vegetable oils (which Diesel in fact did), this view is inaccurate on two grounds. First, the viscosity of such oils is too high for them to be effectively atomized by most diesel injector systems. Thus, biodiesel generally consists of fatty acid methyl esters (FAMES) produced by transesterification of triacylglycerols (fatty acid tri-esters of glycerol)—the predominant chemical constituents of fats and oils of plant, animal or marine origin—with methanol. These smaller molecules have a viscosity similar to that of diesel fuel. Second, although pure FAMES (designated as B100) can be used directly as a fuel, the physicochemical properties of B100 deviate appreciably from those of petro-diesel. Therefore, the final step in biodiesel production generally involves blending of the FAME products with conventional diesel fuel in defined proportions, usually up to B20 (designating a 20% biodiesel/petro-diesel fuel blend), with B1, B2, and B5 blends being the most common biodiesel fuels.

For the environmentalist, the primary benefit of biofuels in general is the recycling of carbon dioxide, potentially resulting in 80% reduction in net carbon dioxide, according to some sources, but this is just one of the environmental benefits of biodiesel. Diesel engines are by design lean-burn engines, but when run on biodiesel, which contains oxygen within the chemical structure of the FAMES, they are even more lean-burn. That means reduced hydrocarbon, carbon monoxide and particulate emissions. Also, B100 (pure FAMES) does not contain any aromatics or sulphur, so local air quality benefits. Biodiesel auto-ignites easily as its cetane number (the measure of ignition quality) is inherently higher than that of petroleum-derived diesel. Because of the fatty nature of the fuel, it also has good inherent lubricity and, in blends with petroleum-derived diesel, compensates for the removal of sulphur and oxygen-containing compounds during processing, and provides anti-wear protection for pump and injector components.

These advantages of biodiesel are of course accompanied by several drawbacks. Environmentalists extol the use of biodiesel because it is non-toxic and biodegradable. So fuel retailers and motorists can be proud that they will be giving a home to all sorts of micro-organisms that will happily feed on this fuel. The corrosive nature of biodiesel can stem from impurities remaining after processing but also from the fact that biodiesel is hygroscopic, and so absorbs water. Under the right (or wrong) conditions, absorbed water can convert some of the FAMES to fatty acids plus methanol, and the acids formed can then react with metals. Furthermore, the poorer oxidative stability and lower volatility of biodiesel as compared to diesel refined by crude stock have a large number of implications in relation to engine performance. These include filter plugging issues, deposit formation, and potentially higher crankcase accumulations of fuel in biodiesel-fueled engines.

In the following, we will first consider the problems associated with fuel dilution and then describe the methods conventionally used to quantitatively detect fuel dilution in crankcase lubricants.

### Fuel Dilution

Frequent starts of an engine, excessive idling and cold running conditions can lead to moderate fuel dilution problems. Severe dilution (>2%) is associated with leakage, fuel injector problems and impaired combustion efficiency. These are symptomatic of serious conditions that cannot be corrected by an oil change. According to one reference, 0.36 percent of total fuel consumption ends up in the crankcase. Problems associated with fuel dilution include:

- Diesel fuel dilution in cold operating conditions can cause waxing. During start-up, this can result in low oil pressure and starvation conditions.
- Diesel fuel carries unsaturated aromatic molecules into the motor oil. These act as pro-oxidants and can result in a premature loss of base number (loss of corrosion protection) and oxidative thickening of the motor oil, causing deposits and mild starvation.
- Fuel dilution can drop the viscosity of motor oil. This collapses critical oil film thicknesses, resulting in premature combustion zone wear (piston, rings and liner) and crankcase bearing wear.
- Fuel dilution from defective injectors commonly causes wash-down of oil on cylinder liners, which accelerates ring, piston and cylinder wear. It also causes high blow-by conditions and increased oil consumption (reverse blow-by).
- Severe fuel dilution dilutes the concentration of oil additives, hence reducing their effectiveness.

### Quantitative Detection of Fuel Dilution

Fuel dilution in crankcase lubricants is almost impossible to quantify by conventional wet chemistry tests<sup>3</sup> because gasoline and diesel fuel are chemically very similar to the oil itself. Accordingly, fuel dilution is usually detected in the laboratory by three methods: viscosity, flash point and gas chromatography.

Fuel dilution is usually detectable by a drop in the viscosity of the oil from the original or new oil viscosity. Table 1 is a chart used to predict an approximate percent diesel fuel dilution of lubricating oil based on

0	60	80	100	120	140	160	180	200	220	240	260	280	300	320	340	0
1	58	77	96	114	133	152	170	189	207	226	244	263	281	300	318	1
2	56	74	91	109	126	144	161	179	196	213	230	247	264	281	298	2
3	54	71	87	104	120	137	153	169	185	201	216	232	248	264	279	3
4	52	68	83	99	114	130	145	160	174	189	204	218	233	247	262	4
5	50	65	80	94	109	123	137	151	165	178	192	205	219	232	245	5
6	48	62	76	90	104	117	130	143	156	168	181	193	206	218	230	6
7	46	60	73	86	99	111	123	135	147	159	171	182	194	205	216	7
8	45	58	70	82	94	106	117	128	139	150	161	172	182	193	203	8
9	43	55	67	78	90	100	111	121	132	142	152	162	172	181	191	9
10	42	53	64	75	85	95	105	115	125	134	143	153	162	170	179	10
11	40	51	61	72	81	91	100	109	118	127	135	144	152	161	169	11
12	39	49	59	68	78	86	95	104	112	120	128	136	144	151	159	12
13	37	47	56	65	74	82	90	98	106	114	121	128	135	142	149	13
14	36	45	54	63	71	78	86	93	101	108	114	121	128	134	141	14
15	35	44	52	60	67	75	82	89	95	102	108	115	121	127	133	15

Table 1. Fuel Dilution Prediction Chart<sup>5</sup>

fuel oil viscosity of 3cSt at 40°C. To use the chart, one picks the column headed by the viscosity nearest that of the new oil at 40°C. In that column, one finds the viscosity nearest that of the used oil sample also at 40°C. Then looking across in the same horizontal line, in the outside columns (headed "fuel oil dilution") one reads off the predicted percentage of fuel dilution<sup>4</sup>.

One must be aware, however, of several important limitations of this method. First of all, the decrease in viscosity due to fuel dilution can be offset by other factors that increase viscosity such as fuel soot levels and oil oxidation. Also, shearing of the viscosity index improver in multi-weight oils can add to viscosity drop.

Flash point of the oil is a better way to quantify percentages of fuel contamination. This test measures the temperature at which the oil will ignite when an open flame is applied to it. Since diesel fuel typically flashes at approximately 54°C and engine oil flashes at approximately 215°C, the amount of fuel can be estimated by the decrease in used oil flash as compared to new. One caution advised when using this method to determine percent fuel dilution is that excessive antifreeze contamination will also reduce flash point. Therefore, if antifreeze contamination is a possibility or indicated, flash point assessment cannot be relied upon to accurately measure fuel percentages.

The most accurate and accepted method to date for a quantitative measurement of fuel dilution is gas chromatography (GC), which basically separates the fuel by boiling point. Two GC methods for the evaluation of fuel in used engine oil samples (ASTM D3524 for fuel contamination and ASTM D3525 for gasoline contamination) are among the few ASTM (American Society for Testing and Materials) tests specifically designated for used oil analysis. In both cases, calibration mixtures of known dilution factors are used to calibrate the GC instrument, prior to running the test sample. Measurement of the percentage of fuel contamination by GC is accurate to within ~0.1% and is normally repeatable to the nearest 0.05%. However, GC analysis can be problematic, especially when in-service lubricant samples, which are inherently dirty, are injected onto the column, and this time-consuming technique is far from conducive to real-time monitoring of fuel dilution on an engine test bed.

Finally, it may be noted that fuel dilution is among the parameters that

may be measured when FTIR spectroscopy is employed in condition monitoring of in-service lubricants, as per ASTM Practice E2412. However, it must be made clear that condition monitoring is a trending procedure and, as such, does not provide quantitative data per se but rather generates relative values that are used to monitor changes in various condition monitoring parameters (oxidation, nitration, soot, moisture, and fuel dilution among others) as a function of time. Thus, while condition monitoring can be helpful in assessing oil quality, it does not provide definitive analytical results as would, say, a Karl Fischer analysis for moisture in a lubricant. Accordingly, the methodology developed for the quantitative detection of fuel dilution by FTIR spectroscopy in the present study is based on an approach that is completely distinct from that employed in condition monitoring.

### FTIR Approach to Fuel Dilution

FTIR spectroscopy is a spectroscopic technique that responds to the various functional groups present in organic molecules and in effect provides a spectral fingerprint that may be used to identify chemical compounds and to quantify them, even when they are present in complex mixtures. In the field of lubricant analysis, FTIR spectroscopy has seldom been used in this manner but is instead widely employed by commercial laboratories in qualitative condition monitoring of in-service lubricants, in the manner just described. Over the past few years, FTIR spectroscopy has evolved in our laboratory from a qualitative to a quantitative methodology for lubricant analysis specifically in relation to the determination of acid number (AN), base number (BN) and moisture. Nevertheless, the concept of replacing GC-based diesel-fuel dilution measurements by FTIR spectroscopy remains problematic because diesel fuel is spectrally similar to the base lubricant. The only basis for differentiating between diesel fuel and lubricant is the slightly higher aromatic content of the fuel, and this is the principle employed in the tracking of fuel dilution as a condition monitoring parameter. However, the aromatic content can be quite variable between fuel sources, and the fuel contaminant is likely to be undefined, thereby making FTIR quantification of fuel dilution on the basis of aromatic content inherently unreliable.

On the other hand, there is a way in which fuel dilution can accurately be measured by FTIR spectroscopy – when a chemical marker can be dissolved into the oil to serve as a spectroscopic indicator of the extent of dilution of the oil contributed by fuel contamination. Clearly, this is not an approach that can be used for on-the-road vehicles but it is workable when the engine is being run in a test facility. A large diesel manufacturer has worked on developing an at-line FTIR method based on this concept.

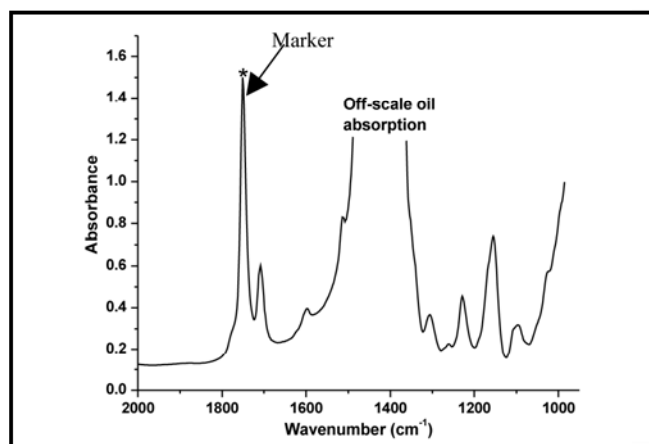


Figure 1. FTIR spectrum of a lubricating oil containing a modified ester as a spectral marker.

The spectral marker utilized was a modified ester, which was custom blended into a commercial crankcase lubricant formulation. The ester functional group has a strong IR absorption at 1750  $\text{cm}^{-1}$  (marked with an asterisk in Figure 1) that is readily measurable in the FTIR spectrum of the lubricant. Crankcase lubricant samples were taken at specific time intervals while the engine was running and were subjected to both GC and FTIR analysis. By tracking the progressive reduction in the intensity of the marker absorption as a function of time and relating it to the GC analysis, it was demonstrated that this decrease was directly proportional to the fuel dilution as measured by GC<sup>6</sup>.

The above approach has important implications for the quantitative detection of fuel dilution in biodiesel-fueled engines. Like the modified ester whose spectrum is shown in Figure 1, the FAMES in biodiesel have an intense IR absorption also at  $\sim 1750 \text{ cm}^{-1}$  due to their ester groups.

Accordingly, measurement of the intensity of this absorption in the spectrum of a crankcase lubricant provides a means of quantifying fuel dilution. Under these circumstances, the ester absorption will increase rather than decrease as fuel dilution increases, since the “spectral marker” is inherently present in the fuel as opposed to being blended into the oil. Despite this difference, the two approaches are analogous, and thus the performance of the latter was considered to provide a good basis for evaluation of the potential extension of this methodology to biodiesel.

Thermal-Lube implemented this approach on one of its COAT<sup>®</sup> System<sup>7</sup> spectrometers (Figure 2) to detect and quantify fuel dilution in a diesel-fueled test engine in real time.

The whole system was connected to the test engine through a



Figure 2. In-Line CFDA<sup>®</sup> (COAT) System

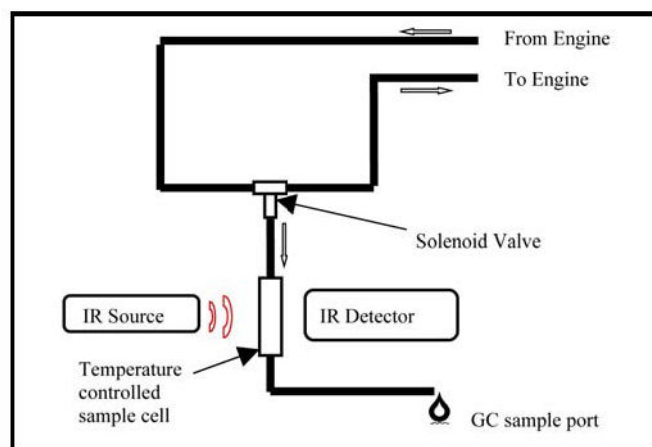


Figure 3. Kidney Loop Diagram

'kidney-loop' (Figure 3). This required a modification to the COAT® system flow-through transmission cell, installation of a temperature controller, and mounting of the entire cell assembly on a programmable movable platform stage to collect a background spectrum prior to each analysis. Accurate temperature control was considered paramount since slight temperature variations inside the cell affects the density of the lubricant and can thereby generate erroneous results. The UMPIRE™ software<sup>9</sup> under which the COAT® System operates was modified to allow the system to be run in a continuous-flow mode, with spectral data being collected at 2-minute intervals throughout an engine test run. A bypass valve was also installed to manually collect samples at selected intervals for comparative analysis by GC.

### Performance

The COAT® FTIR fuel dilution monitoring system was calibrated with standards prepared by gravimetric addition of fuel to a commercial crankcase oil containing the modified ester spectral marker. Figure 4 presents a standard curve obtained by plotting the intensity of the IR absorption of the spectral marker as a function of percent fuel dilution over the range of 0.1-6.5%. Linear regression of the data plotted in Figure 4 yielded a calibration equation for the prediction of percent fuel dilution, with  $R = -0.9988$  and an SD of 0.11%.

Figure 5 shows the tracking of fuel dilution by the COAT® FTIR fuel dilution monitoring system during an engine test run, together with the results obtained by subsequent FTIR analysis in the laboratory as well as GC analysis.

Both sets of FTIR data have been processed through calibration equations derived in the manner described above, whereby decreases

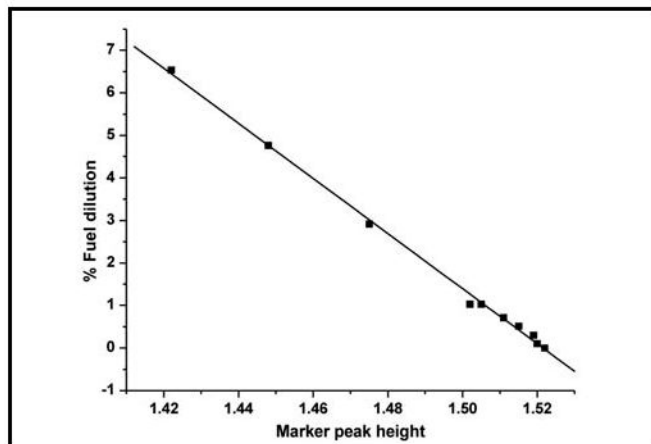


Figure 4. Marker standard curve

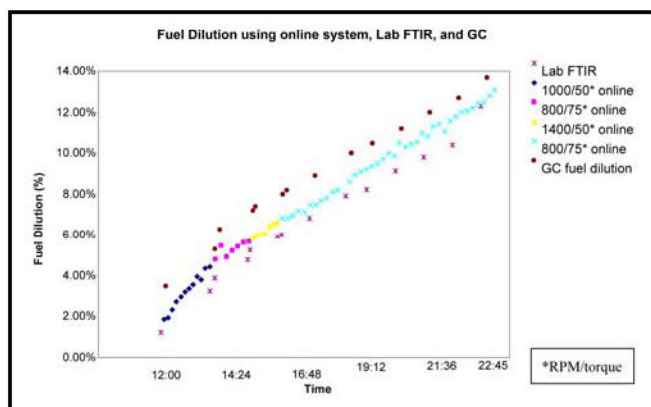


Figure 5. Fuel dilution tracking

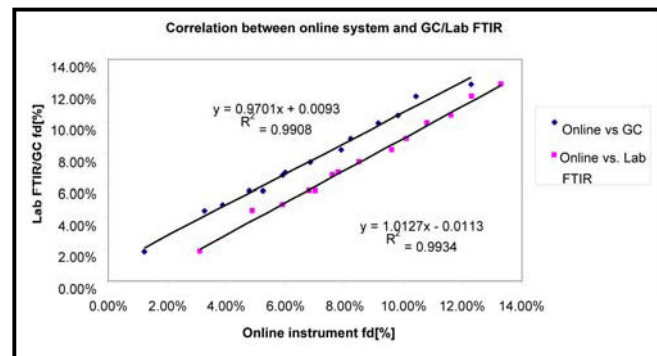


Figure 6. Correlation of on-line FTIR data with lab FTIR & GC data.

in the marker absorption have been converted into the corresponding percentage of fuel dilution. Figure 6 illustrates the excellent correspondence between the COAT® data and both the laboratory FTIR and GC data, as indicated by correlation coefficients of  $>0.99$  as well as the negligibly small intercepts of the linear regression equations presented on the figure.

### Discussion and Conclusion

The benefits of FTIR on-line analysis are obviously apparent in terms of being able to turn around test bed data in real time. This also provides the ability to quickly change operating conditions or even fuel/lubricant formulations and monitor their effects while adjusting engine parameters. At present, this novel marker-based methodology is limited to conventional diesel engines burning hydrocarbon refined diesel fuel. Now with increased interest to optimize engine performance operating with biodiesel fuels, this concept may still be used in effect; however, in this case, fuel dilution would be detected by the associated increase in the  $1750\text{ cm}^{-1}$  band, rather than its decrease. In this case, one could formulate an oil with low ester content or alternatively use a phenyl based ester and use the phenyl absorption band dilution to monitor fuel dilution. At this point in time, FTIR on-line detection of fuel dilution has been proven to be a viable procedure in rather specific circumstances, replacing costly GC analysis and providing real-time fuel dilution data conducive to in-house engine optimization. The move to assessing fuel dilution in the real world is still far off; however, this new tool does provide a useful step forward in optimizing engine performance in relation to fuel dilution issues.

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7 Continuous Oil Analysis and Treatment System – Patented and registered by Thermal-Lube Inc. All rights reserved.

8 Continuous Fuel Dilution Analyzer – Patent applied for by Thermal-Lube Inc.

9 Universal Method Platform for Infra-Red Evaluation- Registered Trade Mark of Thermal-Lube Inc. All rights reserved.