



# King Fahd University of Petroleum and Minerals

Chemistry Department

CHEM 399

Summer Training

**Low Sulfur Diesel Characterization & CFPP**

**DONE BY**

**Mohannad Al-Khodaier**

**259861**

**31-Dec-2007**

## **Introduction:**

The development of the internal combustion engine began in the late eighteenth century. Slow but steady progress was made over the next hundred years. By 1892, Rudolf Diesel received a patent for a compression ignition reciprocating engine. But his original design, which used coal dust as the fuel, didn't work.

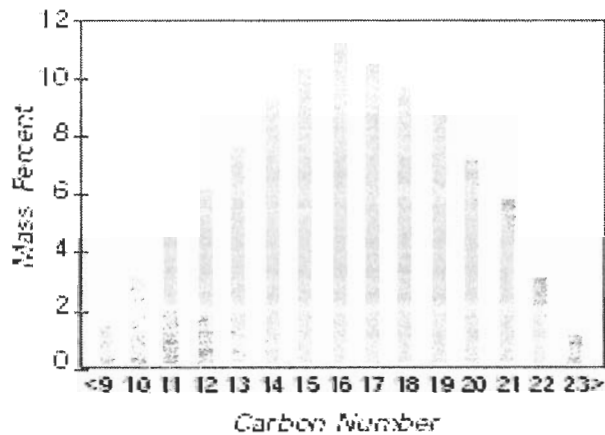
Diesel, recognizing that the liquid petroleum by-products might be better engine fuels than coal dust, began to experiment with one of them. This fuel change, coupled with some mechanical design changes, resulted in a successful prototype engine in 1895. Today, both the engine and the fuel still bear his name.

The first commercial diesels were large engines operating at low speeds. They were used to power ships, trains, and industrial plants. By the 1930s, diesels also were powering trucks and buses. An effort in the late 30s to extend the engine's use to passenger cars was interrupted by World War II. After the war, the automotive diesel became very popular in Europe, but hasn't enjoyed comparable success in the United States.

Today, diesel engines are used worldwide for transportation, manufacture, power generation, construction, and farming. The types of diesel engines are as varied as their use – from small, high speed, indirect-injection engines to low speed direct-injection behemoths with cylinders three feet in diameter. Their success is due to their efficiency, economy, and reliability.

## Diesel Composition:

Diesel fuel is a very complex mixture of thousands of individual compounds, most with carbon numbers between 10 and 22. Most of these compounds are members of the paraffinic, naphthenic, or aromatic class of hydrocarbons. These three classes of hydrocarbons have different chemical and physical properties. Different relative proportions of the three classes is one of the factors that make one diesel fuel different from another.



Typical Carbon Number Distribution in Diesel

## Diesel Specifications:

<b>TEST</b>	<b>GUARANTEE</b>	<b>METHOD</b>
Ash, wt %	Max 0.01	ASTM D-482
Carbon Residue, 10% Bottoms, wt %	Max 0.35	ASTM D-524
Sulfur, ppm wt.	Max 500	ASTM D-4294 or ASTM D-5453
Corrosion Cu strip, 3 hrs @ 50 °C (122°F)	Max # 3	ASTM D-130
Cetane Index	Min 45	ASTM D-976 or IP-218
Flash, P.M. Closed, °C (°F)	Min 55 (131) <b>Note (b)</b> Min 65 (150) <b>Note (c)</b>	ASTM D-93A
Gravity: Density, kg/m <sup>3</sup> at 15 °C	To be reported : <b>Note (b)</b> (Min-Max) (810 - 870) <b>Note (c)</b>	ASTM D-287 or ASTM D-4052 or ASTM D-1298
Viscosity:  cSt @ 40°C or SUS @ 104°F  cSt @ 40°C (104 F)	(Min-Max) 1.9 - 4.1 <b>Note (b)</b> 32.6 - 40.1  (Min-Max) 1.9 - 5.0 <b>Note (c)</b>	ASTM D-445 OR ASTM D-7042-04

<p style="text-align: center;"><u>Either (Note b)</u></p> <p>Cloud Point  Winter: Nov. - Feb.  Intermediate: Oct. &amp; Mar.  Summer: Apr. - Sep.</p> <p style="text-align: center;"><u>or</u></p> <p>Cold Filter Plugging Point  Winter: Nov. - Feb.  Intermediate: Oct. &amp; Mar.  Summer: Apr. - Sep.</p> <p style="text-align: center;"><u>And</u></p> <p>Difference between Cloud Point and CFPP, <b>(Note d)</b></p>	<p>Max +2 (36)  Max +6 (43)  Max +12 (54)</p> <p>Max -4 (25)  Max 0 (32)  Max +6 (43)</p> <p>Max 10 (18)</p>	<p>ASTM D-2500  or ISO 3015 or  ASTM D-5771, D-5772,  D-5773</p> <p>IP-309</p>
<p>Distillation (% Recovered)  85% Point °C (°F)  End Point</p>	<p>Max 350 (662)  To be reported</p>	<p>ASTM D-86</p>
<p>Water &amp; Sediment by  Centrifuge Vol %</p>	<p>Max 0.05</p>	<p>ASTM D-2709</p>

Notes:

- a) Domestic and Export specifications for low sulfur diesel are the same except where indicated in the notes.

- b) This requirement (test) is applicable only for domestic diesel (local supply).
- c) This requirement is applicable for Export diesel cargos ex-Saudi Aramco Facilities
- d) The 10 °C (18 °F) maximum margin specification applies only when the CFPP is being used as the primary method in conjunction with the injection of cloud point suppressant chemicals. The 10 °C (18 °F) maximum margin specification is calculated between the CFPP spec and the actual cloud point test.

## **Ash:**

This test method covers the determination of ash in the range 0.001–0.180 mass %, from distillate and residual fuels, gas turbine fuels, crude oils, lubricating oils, waxes, and other petroleum products, in which any ash-forming materials present are normally considered to be undesirable impurities or contaminants.

### *Method:*

The sample contained in a suitable vessel is ignited and allowed to burn until only ash and carbon remain. The carbonaceous residue is reduced to an ash by heating in a muffle furnace at 775°C, cooled and weighed.

## **Carbon Residue:**

This test method covers the determination of the amount of carbon residue left after evaporation and pyrolysis of an oil, and it is intended to provide some indication of relative coke-forming propensity. This test method is generally applicable to relatively nonvolatile petroleum products which partially decompose on distillation at atmospheric pressure. This test method also covers the determination of carbon residue on 10% (V/V) distillation residues. Petroleum products containing ash-forming constituents, will have an erroneously high carbon residue, depending upon the amount of ash formed.

### *Method:*

The sample, after being weighed into a special glass bulb having a capillary opening, is placed in a metal furnace maintained at approximately 550°C. The sample is thus quickly heated to the point at which all volatile matter is evaporated out of the bulb with or without decomposition while the heavier residue remaining in the bulb undergoes cracking and coking reactions. In the latter portion of the heating period, the coke or carbon residue is subject to further slow decomposition or slight oxidation due to the possibility of breathing

air into the bulb. After a specified heating period, the bulb is removed from the bath, cooled in a desiccator, and again weighed. The residue remaining is calculated as a percentage of the original sample, and reported as Ramsbottom carbon residue.

Provision is made for determining the proper operating characteristics of the furnace with a control bulb containing a thermocouple, which must give a specified time-temperature relationship.

### **Sulfur:**

This test method covers the measurement of sulfur in hydrocarbons, such as diesel, naphtha, kerosene, residuals, lubricating base oils, hydraulic oils, jet fuels, crude oils, gasoline (all unleaded), and other distillates. In addition, sulfur in other products, such as M-85 and M-100, may be analyzed using this technique. The applicable concentration range is 0.0150 to 5.00 mass % sulfur.

#### *Method:*

The sample is placed in the beam emitted from an X-ray source. The resultant excited characteristic X radiation is measured, and the accumulated count is compared with counts from previously prepared calibration standards that bracket the sample concentration range of interest to obtain the sulfur concentration in mass %.

### **Copper Corrosion:**

This test method covers the determination of the corrosiveness to copper of aviation gasoline, aviation turbine fuel, automotive gasoline, cleaners (Stoddard) solvent, kerosene, diesel fuel, distillate fuel oil, lubricating oil, and natural gasoline or other hydrocarbons having a vapor pressure no greater than 124 kPa (18 psi) at 37.8°C.

*Method:*

A polished copper strip is immersed in a specific volume of the sample being tested and heated under conditions of temperature and time that are specific to the class of material being tested. At the end of the heating period, the copper strip is removed, washed and the color and tarnish level assessed against the ASTM Copper Strip Corrosion Standard.

**Cetane Index:**

This test method covers the Calculated Cetane Index formula, which represents a means for directly *estimating* the ASTM cetane number of distillate fuels from API gravity and mid-boiling point. The index value, as computed from the formula, is termed the Calculated Cetane Index.

*Method:*

The Calculated Cetane Index is determined from the following equation:

$$\text{Calculated cetane index} = -420.34 + 0.016G^2 + 0.192G \\ \log M + 65.01(\log M)^2 - 0.0001809M^2$$

Or

$$\text{Calculated cetane index} = 454.74 - 1641.416D + 774.74D^2 - 0.554B + 97.803(\log B)^2$$

where:

$G$  = API gravity

$M$  = mid-boiling temperature, °F, corrected to standard barometric pressure

$D$  = density at 15°C, g/mL

$B$  = mid-boiling temperature, °C, corrected to standard barometric pressure.

**Flash Point:**

This test method cover the determination of the flash point of petroleum products in the temperature range from 40 to 360°C by a manual Pensky-Martens closed-cup apparatus or

an automated Pensky-Martens closed-cup apparatus.

*Method:*

A brass test cup of specified dimensions, filled to the inside mark with test specimen and fitted with a cover of specified dimensions, is heated and the specimen stirred at specified rates. An ignition source is directed into the test cup at regular intervals with simultaneous interruption of the stirring, until a flash is detected.

**Density:**

This test method covers the determination of the density or relative density of petroleum distillates and viscous oils that can be handled in a normal fashion as liquids at test temperatures between 15 and 35°C. Its application is restricted to liquids with vapor pressures below 600 mm Hg (80 kPa) and viscosities below about 15 000 cSt (mm<sup>2</sup>/s) at the temperature of test.

*Method:*

A small volume (approximately 0.7 mL) of liquid sample is introduced into an oscillating sample tube and the change in oscillating frequency caused by the change in the mass of the tube is used in conjunction with calibration data to determine the density of the sample.

**Viscosity:**

This test method specifies a procedure for the concurrent measurement of both the dynamic viscosity,  $\eta$ , and the density,  $\rho$ , of liquid petroleum products and crude oils, both transparent and opaque. The kinematic viscosity,  $\nu$ , can be obtained by dividing the dynamic viscosity,  $\eta$ , by the density,  $\rho$ , obtained at the same test temperature.

*Method:*

The test specimen is introduced into the measuring cells, which are at a closely controlled and known temperature. The measuring cells consist of a pair of rotating concentric cylinders and an oscillating U-tube. The dynamic viscosity is determined from the equilibrium rotational speed of the inner cylinder under the influence of the shear stress of the test specimen and an eddy current brake in conjunction with adjustment data. The density is determined by the oscillation frequency of the U-tube in conjunction with adjustment data. The kinematic viscosity is calculated by dividing the dynamic viscosity by the density.

**Distillation:**

This test method covers the atmospheric distillation of petroleum products using a laboratory batch distillation unit to determine quantitatively the boiling range characteristics of such products as light and middle distillates, automotive spark-ignition engine fuels, aviation gasolines, aviation turbine fuels, 1-D and 2-D regular and low sulfur diesel fuels, special petroleum spirits, naphthas, white spirits, kerosenes, and Grades 1 and 2 burner fuels. The test method is designed for the analysis of distillate fuels; it is not applicable to products containing appreciable quantities of residual material.

*Method:*

A 100-mL specimen of the sample is distilled under prescribed conditions. The distillation is performed in a laboratory batch distillation unit at ambient pressure under conditions that are designed to provide approximately one theoretical plate fractionation. Systematic observations of temperature readings and volumes of condensate are made, depending on the needs of the user of the data. The volume of the residue and the losses are also recorded.

## **Water & Sediment:**

This test method covers the determination of the volume of free water and sediment in middle distillate fuels having viscosities at 40°C (104°F) in the range of 1.0 to 4.1 mm<sup>2</sup>/s (1.0 to 4.1 cSt) and densities in the range of 770 to 900 kg/m<sup>3</sup>.

### *Method:*

A 100-mL sample of the undiluted fuel is centrifuged at a relative centrifugal force of 800 for 10 min at 21 to 32°C (70 to 90°F) in a centrifuge tube readable to 0.005 mL and measurable to 0.01 mL. After centrifugation, the volume of water and sediment which has settled into the tip of the centrifuge tube is read to the nearest 0.005 mL and reported as the volumetric percent water and sediment by centrifuge.

## **Cloud Point:**

This test method covers only petroleum products and biodiesel fuels that are transparent in layers 40 mm in thickness, and with a cloud point below 49°C.

### *Method:*

The specimen is cooled at a specified rate and examined periodically. The temperature at which a cloud is first observed at the bottom of the test jar is recorded as the cloud point.

## **Cold Filter Plugging Point:**

This test method covers the determination of the cold filter plugging point (CFPP) temperature of diesel and domestic heating fuels using either manual or automated apparatus. This was my project during summer training.

### *Method:*

A specimen of the sample is cooled under specified conditions and, at intervals of 1°C, is drawn into a pipet under a controlled vacuum through a standardized wire mesh filter. The

procedure is repeated, as the specimen continues to cool, for each 1°C below the first test temperature. Testing is continued until the amount of wax crystals that have separated out of solution is sufficient to stop or slow down the flow so that the time taken to fill the pipet exceeds 60 s or the fuel fails to return completely to the test jar before the fuel has cooled by a further 1°C. The indicated temperature at which the last filtration was commenced is recorded as the CFPP.

### **Field of Investigation:**

Blank low sulfur diesel from Yanbu refinery has a CFPP value of 2.0°C. This temperature is high, so we need to use an additive to decrease the CFPP temperature to domestic standard of -4.0°C. In addition, exported diesel to cold countries has to have a CFPP value of -12.0°C

### **Data:**

*Diesel + S1 additive*

	50 ppm	75 ppm	100 ppm	150 ppm	200 ppm
<b>CFPP (°C)</b>	-3	-4	-7	-11	-13

*Diesel + S2 additive*

	50 ppm	100 ppm	150 ppm	200 ppm
<b>CFPP (°C)</b>	-1	-2	-4	-6

*Diesel + O additive*

	50 ppm	100 ppm	200 ppm	400 ppm
CFPP (°C)	-3	-3	-3	-14

*Diesel + B additive*

	50 ppm	100 ppm	300 ppm	400 ppm
CFPP (°C)	-3	-3	-3	-4

**Data Analysis:**

From the above data we can clearly see that S1 is the best additive among the other ones. ARAMCO most probably will adopt S1 as the additive that will be added to the low sulfur diesel produced by Yanbu refinery.