Hydro-Oxygenation of Gasoline (Petrol) & Diesel with Potassium Alum by Heat

Ammineni Shyam Sundhar, B.B.M, P.G.D.B.A,
Junior Assistant (Outsourcing),
Jawaharlal Nehru Technological University,
ANANTHAPURAMU-515002
ANDHRAPRADESH, INDIA
E-mail: a_shyamsundhar@yahoo.com

ABSTRACT

According to the Free radical theory of molecular transformation, under the conditions of heat the electron bond between carbon atoms in a hydrocarbon molecule can be broken, thus generating a hydrocarbon group with an unpaired electron. This negatively charged molecule, called a free radical, enters into reactions with other hydrocarbons, continually producing other free radicals via the transfer of negatively charged hydride ions (H^-). Thus a chain reaction is established that leads to a reduction in molecular size of the components of original material (Gasoline & Diesel). It is explained by carbonium ion theory. According to this theory, a catalyst (Potassium Alum) promotes the removal of a negatively charged hydride ion from Gasoline/Diesel or the addition of a positively charged proton (H^+) (from Potassium Alum $12(H_20)$ - H^+, OH^-) to Gasoline/Diesel. This results formation of a carbonium ion, weakening of carbon-carbon bonds in many of the hydrocarbon molecules into smaller compounds. As the Twelve Hydrated Aluminum Potassium Sulfate, $Kal(SO_4)_2.12(H_2O)$, is a compound that has water molecules trapped within the solid, upon heating (45^oC to 50^oC) the Potassium Alum, these water molecules will release hydrogen and oxygen $12(H_2O)$ to some or all. By keeping Potassium Alum (from 50gm to 250gm) in the fuel and by supplying heat to that fuel, it can release its $12(H_2O)$ to the concerned fuel it is kept. By this the Fuel is said Hydrogenated and Oxygenated. The increase in hydrogen, oxygen percentages is possible. This shows the Calorific value increase in the Fuels. By this, there is increase in horsepower, torque, and rotations per minute (rpm), complete combustion, more mileage; no pollution is possible with Alum. With heat to Potassium Alum, substitutes fuel additives; those are used to increase the Octane number in Gasoline and Cetane number in Diesel.

Key words: Potassium Alum, Crude Oil, Gasoline, Diesel, Fuel additives, Octane number, Cetane number, Calorific value

INTRODUCTION

Gasoline and Diesel are the primary sources of Transportation. The rapid reduction of petroleum fuels and their ever increasing costs have led to intensive search for more mileage from the fuel and alternative fuels. To improve the Quality, less the pollution, and to get the maximum mileage in both of these fuels, fuel additives are using. The fuel additives increasing the Fuel cost and emissions are not environment friendly. Incomplete combustion will only occur when there is not enough oxygen to allow the fuel to react completely to produce carbon dioxide and water. Potassium Alum, the low-cost material, twelve hydrated aluminum potassium sulfate, with no cost and no pollution does the same thing to the fuels as the fuel additives doing. Increase in the Fuels calorific value, torque, horsepower, increase in rpm (rotations per minute), and complete combustion by that the increase in mileage is possible. Potassium Alum is soluble in water, ethanol.

MATERIALS & MEASURES

1. Potassium Alum
2. Crude Oil
3. Gasoline
4. Diesel
5. Fuel Additives
6. Octane number
7. Cetane number
8. Calorific Value

1. Potassium Alum

Salt is a compound which is essentially made up of one acid radical and basic radical, Ex. Common salt and Blue vitriol. Salt is the end product of the chemical reaction between acid and alkali.
Ex: Hcl + NaOH = Nacl +H_2O
The water molecule makes the salts hydrous. A salt may even be composed of more than one basic radical along with other acid radical.
Ex. Alum (actually it is the double salt)

Potassium alum or alum-(K) is a naturally occurring sulfate mineral which typically occurs as encrustations on rocks in areas of weathering and oxidation of sulfide minerals and potassium-bearing minerals. Potassium Alum or Twelve hydrated

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aluminum potassium sulfate or potassium sulfate and aluminum sulfate double salt containing water of crystallization belongs to ∝- type double salt of alum class. In general, the crystallization of water present in Potassium Alum, at the temperature between 45^oC to 50^oC leading to loss of the H^+ and OH^- ions. It is soluble in Water and Ethanol. Alum is using in water purification in the past. It is the principle of Alum in water, ionization of the two metal ions
Kal(SO_4)2 = K ++Al3++2$SO_4$2, Al3+ is easy to hydrolysis, generate colloidal aluminum hydroxide Al(OH)3.
Al3++3H2o=Al(OH)3+3H+ (reversible), adsorption capacity of aluminum hydroxide gel is very strong, can absorb the impurities of the water suspension, and the formation of precipitation, so that the water clarification. So, the alum is a good purifying agent.
Molar Mass – 258.21 g/mol
Boiling Point – 200^o C
Density – 1.757g/cm^3
Melting Point – 92.5^o c
Solubility in Water is 14.00 g/100 mL (20 °C), 36.80 g/100 mL (50 °C)
Refractive Index (*n*D): 1.4564

2. <u>Crude Oil</u>

Crude Oil means all kinds of hydrocarbons in liquid form in their natural state or obtained by Natural Gas by condensation or extraction. It is a hydrocarbon mixture having simple to most complex structures such as resins, asphaltenes etc. Crude oil is formed by bacterial transformation of Organic matter (carbohydrates/proteins/from plant & animal origin) by decay in presence and/or absence of air into HC rich sediments by undergoing biological/physical and chemical alterations.
Crude oil is a veritable stew of these compounds, which range in heft and complexity from dainty methane (CH_4) (each molecule of which consists of one carbon atom and four hydrogen atoms) to sluggish penta-octacontane, or $C_{85}H_{172}$ (85 carbons, 172 hydrogens). In between methane and penta-octa-contane are a large number of compounds with individual properties and interesting names: propane, butane, pentane, heptane, decane, cyclohexane, benzene, toluene, and many others. Comparatively few of the hydrocarbons in crude oil end up in gasoline. Others go on to become kerosene, diesel fuel, heating oil, lubricants, solvents, plasticizers, polishes, waxes, graphite, asphalt, and many other products, including the fuel used to run oil refineries. Separating these compounds out of crude oil is first a matter of distillation.

3. Gasoline

Gasoline or Petrol, is a transparent, petroleum (crude oil) derived liquid that is used primarily as a fuel in internal combustion engines. It consists mostly of organic compounds obtained by the fractional distillation of petroleum, enhanced with a variety of additives. Some gasolines also contain ethanol as an alternative fuel.

4. Diesel

Diesel Fuel in general is any liquid fuel used in diesel engines. The most common is a specific fractional distillate of petroleum fuel oil. Petroleum-derived diesel is also called petro diesel. Ultra-low sulfur diesel (ULSD) is a standard for defining diesel fuel with substantially lowered sulfur contents. The word "diesel" is derived from the family name of German inventor Rudolf Diesel who in 1892 invented the diesel engine. Diesel engines are a type of internal combustion engine. Petroleum diesel, also called petro diesel, or fossil diesel is produced from the fractional distillation of crude oil between 200 °C (392 °F) and 350 °C (662 °F) at atmospheric pressure, resulting in a mixture of carbon chains that typically contain between 8 and 21 carbon atoms per molecule. Petroleum-derived diesel is composed of about 75% saturated hydrocarbons (primarily paraffins including *n*, *iso*, and cycloparaffins), and 25% aromatic hydrocarbons (including naphthalenes and alkylbenzenes). The average chemical formula for common diesel fuel is $C_{12}H_{23}$, ranging approximately from $C_{10}H_{20}$ to $C_{15}H_{28}$. The Higher Calorific value is 44,800 kJ/kg, Lower 43,400 kJ/kg.

5. Fuel Additives

Petroleum Crude Oils are complex mixtures of hydrocarbons, chemical compounds composed only of Carbon (C) (Calorific value-34,080 kJ/kg) and Hydrogen (H) (Calorific value High-1,41,400 kJ/kg, Lower-1,21,000 kJ/kg). The simplest of the Hydrocarbon molecules is Methane (CH_4), which has one carbon atom and four hydrogen atoms per molecule. The group containing hydrocarbons with boiling points between about 90° and about 220° is called straight-run gasoline. Straight-run gasoline has an octane rating of just 63 or so. To boost that number and enhance certain properties of gasoline, refiners blend in many additional components extracted from petroleum. Some of these are retrieved or created in complicated processes like naphtha reforming, catalytic cracking, hydro cracking, alkylation, and isomerization. In one way or another, these processes transform hydrocarbons that are of little or no use in gasoline into useful hydrocarbons. In a hydrocracker, for example, great big hydrocarbon molecules are split into smaller molecules, yielding several high-octane blending components known collectively as hydrocrackate.

In fuels, Oxygenate blending ads oxygen-bearing compounds such as Methyl Tertiary Butyl Ether (MTBE- CH_3CH_2OH), Ethyl Tertiary Butyl Ether (ETBE) with $CH_3CH_2OC(CH_3)_3$) and Ethanol ($CH_3OC(CH_3)_3$), TAME, Tertiary Amyl Methyl Ether ($(CH)_3CCH_2OCH_3$). The presence of these oxygenates reduces the amount of carbon monoxide and unburned fuel in the exhaust gas to reduce smog and other airborne pollutants. The resulting fuel is often known as reformulated gasoline (RFG) or oxygenated gasoline. MTBE use is being phased out and banned due to issues with contamination of ground water. Ethanol and, to a lesser extent, the ethanol-derived ETBE are common replacements for Oxygenate. Since most ethanol is derived from biomass, such as corn, sugar cane or grain, it is referred to as bioethanol. A common ethanol-gasoline mix of 10% ethanol mixed with gasoline is called gasohol or E10, and an ethanol-gasoline mix of 85% ethanol mixed with gasoline is called E85.

6. Octane Number

It is a measure of a fuel's resistance to pre-ignition, pinging, and detonation. There are three octane ratings for motor fuels; Research Octane Number (RON), Motor Octane Number (MON), and the average of the two (R+M/2). Spark ignition engines are designed to burn gasoline in a controlled process called deflagration. In some cases, however, the unburned mixture can autoignite, which causes rapid pressure rise which can damage the engine. This phenomenon is often referred to as engine knocking or end-gas knock. One way to reduce knock in spark ignition engines is to increase the gasoline's resistance to autoignition, which is expressed by its octane rating.

Octane rating is measured relative to a mixture of 2,2,4-trimethylpentane (an isomer of octane) and n-heptane. A higher octane rating allows a higher compression ratio or supercharger boost, and thus higher temperatures and pressures, which translate to higher power output.

7. Cetane Number

Cetane number is a measure of the ignition delay of a diesel fuel. The shorter the interval between the time the fuel is injected and the time it begins to burn, the higher is its cetane number. It is a measure of the ease with which the fuel can be ignited and is most significant in low temperature starting, warm up, idling and smooth, even combustion. Some hydrocarbons ignite more readily than others and are desirable because of this short ignition delay. The preferred hydrocarbons in order of their decreasing cetane number are normal paraffins, olefins, naphthenes, iso-paraffins and aromatics. This is the reverse order of their anti-knock quality. Cetane number is measured in a single cylinder test engine with a variable compression ratio. The reference fuels used are mixtures of

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cetane, which has a very short ignition delay, and alphamethyl naphthalene which has a long ignition delay. The percentage of cetane in the reference fuel is defined as the cetane number of the test fuel. The importance of cetane number is very evident as low cetane number usually causes an ignition delay in the engine. This delay causes starting difficulties and engine knock. Ignition delay also causes poor fuel economy, a loss of power and sometimes engine damage. A low cetane number fuel can also cause white smoke and odor at start-up on colder days. White exhaust smoke is made up of fuel vapors and aldehydes created by incomplete engine combustion. Diesel engines whose rated speeds are below 500 R.P.M. are classed as slow speed engines; from 500 to 1200 rpm as medium engines; and over 1200 rpm as high speed. Some refiners have used additives such as hexyl nitrate or amyl nitrate to increase cetane numbers.

8. Calorific Value

The calorific value or the heating value of a substance is the heat released during the combustion of a specified amount of it. It is a characteristic for each and every substance and is measured in units of energy per unit of the substance such as kcal/kg, kJ/kg, J/mol, MJ/kg. It is commonly determined by use of a Bomb calorimeter. It's actually a measure of the energy available from a fuel and the knowledge of this property is essential in assessing the commercial worth of the fuel and to provide the basis of contract between producer and user. If the calorific value of the substance is high/low, that means per gram of the substance on combustion produces high/low heat value and that ultimately determines fuel combustion rate in order to impart a fixed amount of heat.

METHOD

In general, Water dissociates according to the following reaction

$H2O = H^+ + OH^-$

In Potassium Alum, with heat, crystallization of water dissociates according to the following reaction

$12(H2O) = 12H^+ + 12OH^-$

Hydrolysis of alkanes with crystallized water at 45^oc to $48\,^oc$ is happening

For Gasoline

Ex: $2C_8H_{18} + 12H^+ + 12OH^-$ ----------------→ Hydro-oxygenated Gasoline + $Kal(So_4)_2$

For Diesel

Ex: $C_{12}H_{23} + 12H^+ + 12OH^-$ ----------------→ Hydro-oxygenated Diesel + $Kal(So_4)_2$

One liter Gasoline is taken in a plastic bottle and 50gm of Potassium Alum was purchased and kept in that plastic bottle without any further purification. The bottle cap is tightly fitted and cello tape is rounded to that cap. The bottle is kept in sunlight in a temperature of 45^{o}c to 48 ^{o}c per two hours. One liter Diesel is taken in a plastic bottle and 50gm of Potassium Alum is kept in that plastic bottle. The bottle cap is tightly fitted and cello tape is rounded to that cap. The bottle is kept in sunlight in a temperature of 45^{o}c to 48 ^{o}c per two hours.

DISCUSSION

In Gasoline or in Diesel or in Crude Oil or in whatever fuel or liquid which contains Carbon and Hydrogen, with keeping the Potassium alum (if not soluble), can be modified into useful burning fuel with little amount of heat to that Fuel. Crude oil is a mixture of hydrocarbons, molecules containing hydrogen and carbon molecules, with small amounts of other substances. Crude oil is comprised of different lengths of hydrocarbon chains, with some short chains and some very long chains. Depending on how much the oil is broken down, or refined, it may become any number of products. In general, the smaller the molecule, the lower the boiling point. Therefore, gas, with very small chains of one to five carbons, boils at a very low temperature. Gasoline with 6-10 carbons boils at a slightly higher temperature. The heaviest oils may contain up to 25 carbon atoms and not reach their boiling point until 761^o F (405^o C). Catalytic cracking is one the most important processes in Oil refining. This process uses a catalyst, high temperature and increased pressure to affect chemical changes in Petroleum. Catalysts such as Aluminum, Platinum, Processed Clay and acids are added to Petroleum to break down larger molecules so that it will possess the desired compounds of Gasoline.

Gasoline is primarily a mixture of Two Volatile liquids, Heptane and Isooctane. Pure heptane, a lighter fuel, burns so quickly that it produces a great amount of knocking in an engine. Pure isooctane evaporates slowly and produces virtually no knocking. The ratio of heptanes to isooctane is measured by the octane rating. The greater the percentage of isooctane, the less knocking and the higher the octane rating. For example, an octane rating of 87 is comparable to a mixture of 87% isooctane and 13% heptanes.

Potassium Alum substitutes this. As it contains the water molecules inside the solid, that means 12(H_2O), with heat, alum releases both the Hydrogen and the Oxygen to the concerned Fuel it is kept.

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