CARBON DEPOSIT FORMATION FROM THERMAL STRESSING OF PETROLEUM FUELS

Orhan Altin and Semih Eser

Department of Energy and Geo-Environmental Engineering and The Energy Institute
101 Hosier Building
The Pennsylvania State University
University Park, PA, 16802

Introduction
The thermal stability of fuels is of concern for the maintenance of all types of combustion engines. Thermal stability is measured in terms of the fuel’s tendency to form deposits on fuel lines and nozzles of jet engines as well as on intake valves, fuel injectors, and combustion chamber surfaces in gasoline and diesel engines. Fuel degradation can cause engine failure, engine malfunction, and affects engine performance. Poor stability of fuel can lead to increased maintenance costs, and maintenance problems, such as equipment vulnerability and decreased reliability which may result in profit losses.

This article covers thermal decomposition of diesel fuel, gasoline, and jet fuel, and their respective reactions on metal surfaces leading to the deposition of carbonaceous solids.

Petroleum Fuels
Petroleum fuels, such as gasoline, diesel, and jet fuel contain a complex mixture of hundreds of hydrocarbons. The hydrocarbons vary by class—paraffins, olefins, and aromatics, depending on the nature of chemical bonding between the carbon atoms in hydrocarbon molecules. These fuels also contain additives designed for specific purposes. The molecular composition of fuels determines their physical properties, engine performance, and thermal stability characteristics. In general, fuels are produced to meet the property limits dictated by the industrial specifications and regulations, not to achieve a specific distribution of hydrocarbons by class, or size. Figure 1 shows a carbon number distribution of typical gasoline, which is in the range of C4 to C12 with the average carbon number of C6.5. Gasoline also contains small amounts – less than 0.1 volume % – of heteroatom compounds with sulfur, nitrogen, or oxygen atoms (excluding added oxygenates) in their structures. Compared to gasoline, typical diesel fuel consists of a more complex mixture of thousands of individual compounds, most with carbon numbers between 10 and 22. Most of these compounds are members of the paraffins group (normal-, iso-, or cyclo-paraffins), or aromatic hydrocarbons boiling between approximately 150°C and 400°C. Originally diesel fuels were straight-run products obtained from crude distillation in a refinery. Today, where the demand for high-octane number gasolines and distillate fuels are high, diesel fuels may also contain distillates from cracking processes, such as light cycle oils (LCO) from Fluid Catalytic Cracking (FCC) unit.

Jet fuels (military and civilian turbine fuels, JP-5, JPTS, JP-7, JP-8, JP8+100, Jet-A, and Jet A-1) are mainly kerosene type having a carbon number distribution between about 8 and 16 carbon numbers, as seen in Figure 1. Kerosene fuels like JP-8 (military) or Jet A (civil) also contain a mixture of literally thousands of hydrocarbons. For JP-8, these hydrocarbons can be divided into three broad classes—aromatics (about 20%), n-paraffins and isoparaffins (60%), and cycloparaffins (napthenes, 20%). Typically, normal paraffins have the highest concentration among the hydrocarbons and cycloparaffins and aromatics consist mostly of methyl-substituted single-ring molecules. The concentration of various components can vary significantly from one batch to another, depending on the crude oil used and the process history of the fuels.

Problem of Thermal Stability
Thermal stability is typically described in terms of the fuel’s tendency to form deposits on fuel lines, valves, injectors, and combustion chamber surfaces in engines. These fuel system deposits can be created by two distinct free radical pathways: low temperature autoxidation—usually called fouling—and higher temperature pyrolysis, called coking or carbon deposition.

Autoxidation or oxidative stability differs from thermal stability by referring to the rate at which oxygen is consumed and oxidative products are formed. Autoxidation reactions occur during fuel storage and exposure to high temperature in fuel lines which results in a series of liquid oxidation reactions of alkyl radicals generating hydroperoxides and other oxidized products which are believed to be responsible for solid deposit formation (1-4).

At elevated temperatures (>350°C), carbon deposits usually form via two different routes: Decomposition of hydrocarbons to elemental carbon and hydrogen; or polymerization/condensation of hydrocarbon species to larger polynuclear aromatic hydrocarbons (PAHs) which then nucleate and grow to become carbonaceous deposit. Metal catalysis of carbon deposition often follows the decomposition route, whereas non-catalytic (or thermal) carbon deposition usually proceeds via the polymerization route.

The formation of catalytic or non-catalytic carbon deposit depends on the characteristics of the substrate surface. A non-catalytic surface may affect the heat/mass transfer in the system and act as an inert substrate to collect the carbon deposit the formation of which is thermally initiated in the fluid phase. In contrast, a catalytic surface could, in addition, interact with the reactive species and accelerate the deposit formation.

Carbon Deposit Formation on Metal Surfaces During Thermal Stressing
Gasoline Fuel. Almost all types of gasolines produce carbon deposits on engine components over time. The rate of deposit formation depends on the nature of metal surfaces in the fuel systems and gasoline additives used to inhibit solid deposition. Carbon deposits mainly build up on fuel injectors, intake valves and ports, and in the combustion chamber. Fuel injectors are designed accurately meter fuel to the engine and deliver it in a precise pattern of fine droplets. Since the fuel passages are small, injectors are highly sensitive to small amounts of deposits in the critical regions where the fuel is metered and atomized. These deposits can reduce the fuel flow and alter the spray pattern, degrading driveability, decreasing power and fuel economy and increasing emissions. Deposit formation can cause similar problems in carbureted engines because carburetors also use a number of small channels and orifices to meter the fuel.

Problems with solid deposition in the combustion chamber and or in the intake system can sometimes be underestimated during initial engine development. Often, these problems become apparent after long duration of engine running time. Deposit precursors in the fuel delivery, or combustion units are formed by thermal cracking, oxidation, and polymerization of the fuel, and these processes may be catalyzed by metal surfaces.

Numerous investigations have suggested some possibilities for reducing these problems in the future. For example, Aradi et al. (5) investigated the role of surface catalytic activity in injector deposit formation and observed that in the presence of stainless steel walls greater amount of insoluble materials formed on the surface than that on a glass insert. Guthrie (6), on the other hand, found that the surface temperature was the most important factor in the formation of
Jet Fuel. Recent advances in jet aircraft and engine technology have placed an ever-increasing heat load on the aircraft. Currently, jet fuels play two important roles in advanced aircraft, propellant and coolant. The need to cool hot parts of the engine has been evident ever since the invention of the internal combustion engine. As engine performance goals and flight speeds have increased, the need for more effective cooling has also increased. For example, the thermal stability limit of JP-8 fuel was established at a bulk temperature of 163°C and a wetted wall temperature of 204°C. Exposure to higher temperatures accelerates the fuels reactions that lead to gum and carbon deposit accumulation in: i) fuel filters, increasing the pressure drop across the filter and reducing fuel flow, ii) fuel injector nozzles, disrupting the spray pattern, which may lead to hot spots in the combustion chamber, iii) the main engine control, interfering with fuel flow and engine system control, and iv) heat exchangers, reducing heat transfer efficiency and fuel flow. These deposits may lead to increased maintenance and in extreme cases, to disastrous accidents. To resolve the problem, an Aircraft Thermal management Working Group of Wright Research and Development Center (WRDC) recommended the development of high thermally stability fuels, such as: (i) a high temperature thermally stable JP-8+100 fuel which provides a 50% improvement in the heat sink capability over conventional JP-8 fuel, and (ii) a new fuel JP-900 that has a 482°C thermal stability and could eliminate the need to recirculate fuel onboard an aircraft. To meet the evolving challenge of improving the cooling potential of jet fuel, while maintaining the current availability at minimal cost a joint government/industry/academia program developed an additive package for JP-8 fuel named as JP8+100 fuel. Hundreds of additives have been tested and a package has been formulated that contains a detergent/dispersant in addition to the standard antioxidant and metal deactivator additives. The additive package allows the bulk fuel temperature to increase from 163°C to 218°C without generating fuel system deposits (11).

Martenev and Spadaccini (12) suggested two basic coking processes: 1) A homogeneous oxidation reaction occurring in the fuel free stream forming coke particles which adhere to the fuel passage surface. 2) A heterogeneous catalytic reaction occurring at the fuel passage metal surface. If mechanism #1 dominates, a polished metal surface may prevent carbon from adhering. If, on the other hand, mechanism #2 dominates, an inert surface should reduce the coking rate. Metal surfaces could act as catalysts for dehydrogenation reactions that lead to the formation of carbon deposits. At elevated temperatures, stainless steel surfaces deposit large amounts of carbonaceous deposits from jet fuel decomposition. Carbon deposit precursors such as radicals and unsaturated hydrocarbons are formed in the gas phase and react with active centers on metal surfaces (13,14). An effective way of preventing deposition from pyrolysis of fuels was found to be the use of inert coatings such as Zirconia (15) and Silcosteel® (Restek Corp, State College, PA) (14). Coating of metal alloy surfaces prevents interaction between deposit precursors and active metal surfaces that lead eventually to deposition of solid carbon. Trace amounts of some sulfur compounds may also affect the rate of deposit formation and metal surface degradation. The sulphidation of metals at high temperatures has become a matter of increasing concern in industrial applications, particularly in energy conversion systems using fossil fuel. Because of high diffusivity and formation of eutectic melts with metals, sulfur reacts with metals to

form metal sulfides at relatively low temperatures, causing severe localized corrosion on heat-resistant alloys and superalloys. Taylor (16) examined the role of sulfur compounds in deposit formation from a JP-5 fuel. Addition of 300 ppm diphenyl sulfide and phenyl benzyl sulfide to JP-5 fuel enhanced the carbon deposit formation significantly. On the other hand, addition of benzothiophene and dibenzothiophene did not contribute to the formation of deposits. Figure 2 summarizes the carbon deposit formation mechanism on metal surfaces by combining hydrocarbon degradation on catalytic metal surface with sulfur–metal reaction resulting in amorphous and filamentous carbon deposition.

Conclusions
The long-term automotive and aircraft related technological benefits can be derived from fundamental understanding of fuel thermal stability issues such as, free radical autoxidation mechanism, establishing a global chemistry model, understanding of fuel-metal surface interactions, and developing additive packages to increase the thermal stability of gasoline, diesel, and jet fuels. Research and development efforts in these areas will help eliminate the operational problems associated with deposit formation on various components of fuel delivery and combustion systems in internal combustion engines.

References

Figure 1. Carbon number distribution of petroleum fuels.

Figure 2. Carbon deposition mechanism including sulfur-metal surface involvement.