

# An adsorption-precipitation model for the formation of injector external deposits in internal combustion engines

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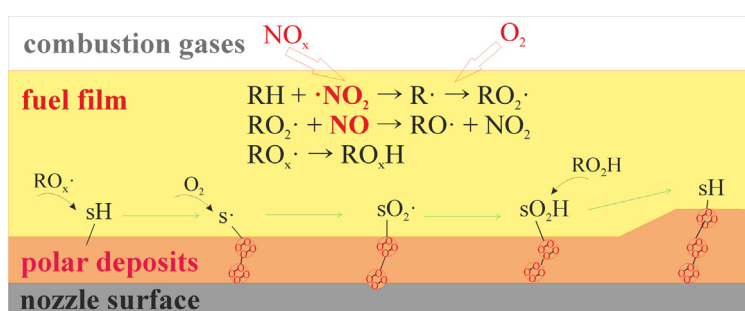
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## HIGHLIGHTS

- Kinetic model for gasoline injector deposit formation in engines is developed.
- Injector leakage causes accumulation of fuel near the nozzle post-injection.
- The leaked fuel degrades under the action of NO<sub>x</sub> and O<sub>2</sub> in the quench layer.
- Radical chain oxidation takes place involving a branching reaction with NO.
- The pressure drop during the power stroke causes the leaked droplet to boil.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

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## ABSTRACT

The occurrence of deposits on fuel injectors used in gasoline direct injection engines can lead to fuel preparation and combustion events which lie outside of the intended engine design envelope. The fundamental mechanism for deposit formation is not well understood. The present work describes the development of a computational model and its application to a direct injection gasoline engine in order to describe the formation of injector deposits and quantify their effect on injector operation. The formation of fuel-derived deposits at the injector tip and inside the nozzle channel is investigated. After the end of an injection event, a fuel drop may leak out of the nozzle and wet the injector tip. The model postulates that the combination of high temperature and the presence of NO<sub>x</sub> produced by the combustion leads to the initiation of a reaction between the leaked fuel and the oxygen dissolved in it. Subsequently, the oxidation products attach at the injector surface as a polar proto-deposit phase. The rate of deposit formation is predicted for two limiting mechanisms: adsorption and precipitation. The effects of the thermal conditions within the engine and of the fuel composition are investigated. Branched alkanes show worse deposit formation tendency than n-alkanes. The model was also used to predict the impact of injector nozzle deposit thickness on the rate of fuel delivery and on the temperature of the injector surface.

## 1. Introduction

Modern engines use injectors that must insert a fuel jet of very high

velocity into the hot gases in the cylinder with good precision in terms of amount of fuel added, timing of the injection event and the spray shape. The accurate timing of the injection in gasoline and some diesel

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engines depends on the efficient sealing of the fuel pathway, realized by the injector needle seating onto the entrance of the nozzle channels. This seal is never perfect, and under the action of the high injection pressure ( $\Delta p \sim 10\text{--}40$  MPa for gasoline; cf. the S6 supplement for a list of symbols), fuel droplets leak out of the nozzle after the end of the intended injection event, wetting the nozzle channel and the injector tip surfaces [1–3]. The leakage appears in at least two stages:

- (i) The non-steady end-of-injection fuel dribble immediately after injection, due to needle bouncing and capillary forces acting on the jet when it breaks off the nozzle. In this case, a significant amount of fuel may remain attached at the injector tip, wetting the surface [2,4].
- (ii) A slower steady leakage (*static fuel dribble*) [3] due to Poiseuille flow through the imperfect seal acts during the whole engine cycle, and leads to accumulation of fuel at the injector surface when the cylinder pressure is high enough [1] to prevent vaporization of the fuel.

The leaked fuel remains exposed to heat and combustion gases for certain period, and, before evaporating completely, the liquid degrades. The degradation products remain at the injector surface, eventually developing into carbonaceous deposits.

Injector deposits have existed since the invention of the fuel injector, but they became a significant problem only with the recent advances in the injector technology, both in diesel [5,6] and gasoline [7–9] engines. The combined requirements for high precision and small nozzle radii ( $R_n \sim 50$   $\mu\text{m}$ ) mean that a very small amount of *nozzle channel deposits* can result in a serious dysfunction of the injector. For example, even a deposit layer as thin as 1  $\mu\text{m}$  can cause a reduction in geometric flow area of 4%. The *nozzle tip deposits* cause distortion of the optimum spray pattern [5,8,10,11], may heat up to high temperatures, and tend to soak with fuel due to their porosity [3,12]. The *needle ball and seat deposits* [8] can spoil the seal, leading to increased leakage rate.

The studies of the injector deposits meet with serious difficulties. The first obstacle is that the *deposition process is very slow*. The accumulation of an observable amount of deposit requires many hours of engine operation [1]. For this reason, many studies and standardized tests of fuels and machinery are accelerated in some way, e.g.: the fuel is artificially additized with a fouling agent that produces deposits [13–15]; fuel formulations with high levels of olefins and sulfur are often utilized (like the “plugging” fuel of Bacho et al. [16]); sometimes the degradation is investigated at increased partial pressure of  $\text{O}_2$  [17]. The second obstacle is that, once formed, the *deposits experience complicated evolution* [18]. This causes uncertainty in the literature regarding their composition – the deposit that is initially formed has little to do with the deposit one finds after 30 h of engine operation with concomitant exposure to high temperature, combustion gases, lubricant mist, and corrosion products. A third obstacle is that the field deposits are often caused by problems specific to a particular fuel or engine.

Given the above, it is likely that there is no single general mechanism of formation of injector deposits. Yet, there are several general features of the deposit formation that seem to be valid not only at the injector surface but anywhere in the engine:

- (i) the engine deposits are formed in a *liquid hydrocarbon* phase, and the existence of fuel (or lubricant) in the liquid state is a requirement for them to occur [1,19–22].
- (ii) The deposits are a polydisperse mixture of polar oxidized hydrocarbons (HCs) with dispersed organic and inorganic salts [5,8,23–25].
- (iii) The deposit growth process occurs at a hydrophilic surface in contact with a hydrophobic fluid. For the injector, this is the interface of *polar deposit|liquid fuel*. With brand new injectors, it could be the metal oxide|liquid fuel or the metal oxide|lubricant interface instead.

Generally, every component of the injector that is in contact with hot liquid fuel inevitably experiences deposit formation. Fuel degradation is observed in the common rail supplying the individual injectors and its filters [26]. The *internal injector deposits* found on the needle and the pressure control valve [27] are a serious problem in diesel engines. They are similar in nature to the soapy deposits found on the fuel filter – we do not consider this type of fouling in the present work. Instead we are mainly interested in the *external injector deposits* [5–8], which are common with direct injection spark ignition (DISI) gasoline engines, where they accumulate at the injector tip, inside the nozzle channel<sup>1</sup> and even deeper inside the nozzle, on the needle ball and its seating area [8,28]. Diesel fuels normally would not cause deposits inside the nozzle channel [5]. Most of the deposited material at the injector tip is fuel-derived, bearing chemical similarities with fuel gum [28], but blended with lubricant elements with a concentration of the latter increasing with distance from the nozzle hole [8,17]. The chemistry of the fuel affects the injector deposits very significantly, especially when polar blends are used. Thus, for gasoline, an ethanol blend results in lower deposit propensity [8,29]; conversely, the relatively polar biodiesel components found in market diesel blends lead to more deposits. Unlike mineral diesel, biodiesel forms deposits inside the nozzle channels of the injector [5].

The initial nascent deposit, or proto-deposit, could be a viscous liquid (e.g., [18]) containing products of the low-temperature oxidative degradation of the fuel (such as alkylhydroperoxides, aldehydes, ketones, alcohols, ethers and acids, found in the tip deposits – e.g., [6]). Certain aromatic species native to the fuel are also found in the deposit [6,30]. As the deposit evolves and ages, it loses the organic oxygen – for example, the fresh deposit at the diesel injector tip contains 20 w% oxygen [5], while the aged carbonaceous material located further away from the nozzle is of decreased oxygen content ( $\sim 10$  w%). The deposit evolution leads also to increased aromatic content, porosity, and advanced polymerization. Lubricant- and corrosion-derived material stick to the deposit, eventually forming together with the organics the familiar reinforced composite material that can be so hard to remove.

The precursors of the external gasoline injector deposits, according to Ref. [8], are polar compounds present in the fuel, peroxides, and ash (resulting from combustion of the lubricant). It has been claimed that two main chemical routes contribute to the formation and the evolution of the injector deposits – low-temperature autoxidation [8,17,31] and high-temperature pyrolysis [8,17], with subsequent isomerization and polymerization of the fuel [17]. Indeed, there is a strong correlation between the outcome of various standardized liquid phase oxidation bench tests and rate of deposit formation [24]. Indicators in use that exploit this correlation include: the induction time for the onset of the intensive consumption of oxygen for gasoline in a closed reactor at 100 °C and 1 atm  $\text{O}_2$ ; the mass of the oxidation products formed at 110 °C over a 6 h period in air [24]; the peroxide number [16]. On the other hand, the formation of polyaromatic hydrocarbons occurs at around 350 °C [8] and is probably a secondary process. The metallic substrate may influence these processes by acting as a catalyst [8]. A separate process that contributes to the injector fouling is the deposition of lubricant-derived salts (ash), which we will not consider here.

Venkataraman and Eser [6] reported interesting data on the microstructure of the *injector tip deposits*. The material contains clusters of spherical particles forming densely packed aggregates, with large voids

<sup>1</sup> There is confusion in the literature over the terminology used for nozzle channel deposits: many researchers call both the orifice and the tip deposits “external injector deposits”; others prefer to use “external” for tip deposits only, as opposed to the “internal” channel deposits. We utilize the former terminology, as it offers a better contrast to the internal deposits on the needle and control valve found in diesel injectors. More specifically, in this work, “external” indicates possibility for contact with combustion gases, and “internal” means that there is no such possibility.

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