Certainties and challenges in modeling unwashed and washed gums formation in Brazilian gasoline–ethanol blends

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ABSTRACT

During the gasoline storage, gums are formed by a slow oxidation of some unstable compounds, such as olefins. The high molecular mass oxidation products can become insoluble and form deposits. Its excess affects the injection pattern, the fuel combustion, the durability of the fuel line parts and increases the pollutant emissions. Consequently, a robust knowledge is required to assess better the behavior of the fuel, in particular the impact of biofuels. This article discussed the certainties and challenges in modeling gum formation in blends of Brazilian gasoline with anhydrous ethanol. The impact of experimental and mathematical procedures on the robustness of the model was investigated. They make possible to assess quantitatively the impact of aging period, temperature, ethanol and additive contents in the formation of unwashed and washed gums. The results confirmed the promotion of the process with the increase of the temperature and aging period and showed the complex role of ethanol, strongly dependent on the values of the other factors. Moreover, the comparison with former literature showed that the models from this study were more robust and the dependence with chemical matrix of gasoline and ethanol quality was reduced. Recommendations were given to overcome the remaining challenges.

1. Introduction

Gasoline is a flammable mixture of thousands of liquid hydrocarbons commonly used in Otto cycle (or spark ignition) engines. These compounds have, in average, a carbon chain between C_4 and C_{12}, distilled in the range 30–220 °C and can be separated into four main families: olefins, paraffins, naphthenes, and aromatics. Some hydrocarbons with heteroelements (mainly oxygen, nitrogen and sulfur) in low concentrations and traces of metal are also present. The chemical matrix of the fuel determines their physicochemical properties and their oxidation stability. Indeed, some unstable compounds, in particular olefins, can be slowly oxidized at room temperature with absorbed oxygen. The products of this oxidation reaction, named gums, are high-molar-mass (200–500 g/mol) compounds and they can form insoluble products that deposit on the surface of the fuel line (Pereira and Pasa, 2005; Streva et al., 2011; Teixeira et al., 2007; Zanier, 1998). Characterizations showed that these resins are highly substituted aromatic compounds. Moieties involving heteroatoms, such as oxygen, nitrogen and sulfur, were also detected (Ackermann, 1969; Kawahara, 1965; Schwartz et al., 1964). However, the strong impact of sulfur observed in the 1960s was significantly reduced in the current gasoline since sulfur content drastically decreased (Pereira and Pasa, 2005).

Nomenclature

ANOVA	Analysis of variance
ANP	Brazilian National Agency of Petroleum, Natural Gas and Biofuels (in portuguese, *Agência Nacional de Petróleo, Gás Natural e Biocombustíveis*)
ASTM	American Society for Testing and Materials
b_0	Constant term in the mathematical models
b_i	Coefficient associated to the linear contribution of factor i in the mathematical models
b_{ii}	Coefficient of the quadratic contribution of factor i in the mathematical models
b_{ij}	Coefficient of the interaction (or rectangular) term between the factors i and j ($i \neq j$) in the mathematical models
i or j	Identification of the factor ($i=1$: anhydrous ethanol content (in % (v/v)); $i=2$: aging period (in days); $i=3$: temperature (in °C))
E0	Identification of samples from Pradelle et al. (2016)
E21	Identification of samples from this study
GC	Gas chromatography
GFAAS	Graphite furnace atomic absorption spectrometry
k	Number of factors (or variables)
NBR	Brazilian standards (in portuguese, *Norma Brasileira*)
N_o	Number of repetitions performed in the center of the experimental region
X_i	Reduced (or normalized) independent variable i; Ranges between -1 and $+1$
x_i	Real independent variable i
x_i^0	Value of the real factor i when $X_i=0$ (center of the experimental region)
x_i^{max}	Maximum value of the real variable i
x_i^{min}	Minimum value of the real variable i
x_1'	Added hydrous ethanol content (in % (v/v)) in Pradelle et al. (2016)
R	Coefficient of determination of the mathematical models; Ranges between 0 and 1
Y	Parameter to be modeled (or experimental response): unwashed or washed gum content (in mg/100 mL)
Δx_i	Half of the interval between the limit values of the real variables i
ε	Residue
σ_{res}	Residual standard deviation

This oxidation process also modifies the physicochemical properties of the fuel, since higher specific gravity and distillation temperatures, greater contents of oxygen and aromatics, and lower concentration of olefins are observed. The accumulation of deposits in large quantity can lead to the improper work of the parts and reduce their durability because of wear. Consequently, the air/fuel mixture can be nonoptimal and the exhaust emissions of pollutants due to incomplete combustion, like CO, NO_x and unburned hydrocarbons, increases. Deposition in injectors' nozzle, admission valves, and combustion chambers also influences the drivability (higher occurrence of engine choking and hesitation) and the engine performance (power loss, reduced acceleration and increased fuel consumption, due to incomplete recovery of the

chemical energy of the fuel). In case of excessive accumulation, detonation can even occur, gums can clog the filters and block the engine components (Pereira and Pasa, 2005; Streva et al., 2011; Teixeira et al., 2007; Zanier, 1998). In North American, European and Brazilian legislations, the ability of gasoline samples to resist to oxidative processes is assessed through the washed gum content and the induction period. Brazilian standard for gasoline currently defines the maximum washed gum content as 5.0 mg per 100 mL of fuel and the minimum value for induction period at 100 °C as 360 min (ANP, 2013).

Due to the variability of the conditions, two mechanisms are commonly described in literature to explain gum formation, both involving free-radical species. The mechanism of autoxidation occurs at ambient temperature to oxidatively polymerize the olefins through a peroxyl radical mechanism. The general scheme is given by the Eqs. (1)–(6):

$$RH \rightarrow R^\bullet + H^\bullet \tag{1}$$

$$R^\bullet + O_2 \rightarrow ROO^\bullet \tag{2}$$

$$ROO^\bullet + RH \rightarrow ROOH + R^\bullet \tag{3}$$

$$R^\bullet + R^\bullet \rightarrow R-R \tag{4}$$

$$ROO^\bullet + R^\bullet \rightarrow ROOR \tag{5}$$

$$ROO^\bullet + ROO^\bullet \rightarrow Products \tag{6}$$

During the initiation step, a free radical $R^\bullet$ from an unsaturated compound RH (for instance, an olefin) is produced (Eq. (1)). Then, this species oxidizes into a free peroxyl radical $ROO^\bullet$ that therefore reacts with other olefin to produce an hydroperoxide ROOH (Eqs. (2) and (3)). The propagation reactions are repeated until the chain reaction is broken by one of the termination reaction (Eqs. (4), (5), or (6)). The formation of high molar mass species with long carbon chain results of these three reactions (A'reff, 2011; De la Puente and Sedran, 2004; Heneghan and Zabarnick, 1994; Pradelle et al., 2015a; Roan and Boehman, 2004).

At the high temperatures met in engines, a second oxidation mechanism, known as thermal oxidative degradation, involves a peroxyl radical chain chemistry where unhindered phenols oxidized into quinones. This last family of compounds undergoes further oxidative coupling reactions that increase the molar mass of the products. An important literature has been published for jet fuels and diesel oil on this issue (Batts and Fathoni, 1991; Beaver et al., 2005; Hardy and Wechter, 1994; Hazlett, 1991).

These oxidation reactions are strongly related to the composition of the gasoline (which is deeply influenced by the origin of the crude oil and the refinement processes), aging period, and temperature. Literature showed that the stability of hydrocarbons decreases in the order of paraffins, naphthenes, isoparaffins, aromatics, monoolefins (in particular, cyclic and branched olefins), aromatic olefins and diolefins, especially conjugated compounds (De la Puente and Sedran, 2004; Gilbert, 2004; Nagpal et al., 1994, 1995a, 1995b; Pereira and Pasa, 2006, 2007; Pradelle et al., 2015a; Rahimi et al., 1998; Teixeira et al., 2007). The oxidation rate is proportional to the concentration of atmospheric oxygen absorbed by the fuel (Schwartz et al., 1968a, 1968b; Shatalov and Seregin, 2009; Stavinoha et al., 1990). Traces of ions from transition metal strongly catalyze gum formation, since they facilitate the for-