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TOWARDS A UNIFIED UNDERSTANDING OF ETHANOL IMPACT ON GUM FORMATION IN GASOLINE-ETHANOL BLENDS: COMPARISON OF EXPERIMENTAL RESULTS WITH LITERATURE

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Abstract. *During storage, gum is formed in gasoline by a slow oxidation of some unstable compounds, such as olefins. The excess of gum formation affects fuel combustion and durability, injection pattern and increases emission of pollutants. Therefore, it is extremely important to have a better understanding of the fuel behavior, in particular the impact of biofuels. Previous studies provided opposite interpretation of the impact of bioethanol in blends with gasoline. This work consists in an attempt to unify the data about gum formation in Brazilian gasoline-ethanol blends, investigating the influence of aging period, temperature and ethanol content on washed and unwashed gum formation. It seems that without aging or after storage at low temperature, ethanol has a dilution effect, while with aging at higher temperature, ethanol presented a catalytic impact, with a maximum activity around 20 % vol. Data from several works found in previous literature and experimental results of tests under progress were analyzed to validate this theory.*

Keywords: *Gum formation, gasoline-ethanol blend, storage, temperature.*

1. INTRODUCTION

Automotive gasoline is a complex mixture of olefinic, paraffinic, naphthenic, and aromatic hydrocarbons. It presents low concentration of oxygenates and traces of sulfur, nitrogen, and metals, therefore introducing instability to the product. During storage, some hydrocarbons react with each other and with absorbed atmospheric oxygen, forming a resinous, polymeric, and non-volatile material known as gum (Souza, 2005; Streva, 2011). ASTM D381 defines washed gum as an heptane-insoluble portion of the evaporation residue of motor gasoline, while unwashed gum would be the evaporation residue of motor gasoline consisting of existent gum and additive components. The oxidation process is product of the hydrocarbons instability: it starts from production and continues throughout transport and storage of the gasoline. Some factor contribute to accelerate the gum formation, such as an increase in temperature and storage time, and the presence of transition metal ions in solution. The formation of gum implies changes to the physicochemical characteristics of the whole blend, leading to an increase of fuel density, distillation temperatures, aromatic, oxygen concentration and decrease of the concentration of olefins. As gum content increases, the engine efficiency and durability decline due the incomplete combustion, and the amount of noxious substances in the exhaust gas increases. Not only that, the deposit of gum in the injection system and combustion chamber severely affects drivability, performance and contribute to exhaust gas emissions as the mix of air/fuel is non-optimal and combustion is turned more incomplete. (Pereira, 2005; Pradelle, 2015a).

Research and development of alternatives to automotive fossil gasoline have led to use ethanol as an alternative fuel and/or an additive for gasoline. Brazil, for example, commercializes its automotive gasoline with 27 % vol by volume of ethanol (Pradelle, 2016). However, few papers have studied gum formation in gasoline–ethanol blends and they had contradictory conclusions on the role performed by ethanol. This work consists in an attempt to unify the available data on literature in a unique understanding of contribution of the ethanol and validate the results through an investigation of the influence of aging period, temperature and ethanol content on washed and unwashed gum formation.

Some authors, such as D'Ornellas (2001), Pereira *et al.* (2005), Pradelle *et al.* (2015b and 2016) and Jeczmionek *et al.* (2016), have studied the gum formation process after storage, mainly in a Brazilian context. D'Ornellas (2001) found that, in most of the case, the presence of ethanol enhanced gum formation, for all storage periods (up to 168 days) and temperature (ambient [13 to 41 °C, with an average of 25 °C] and 43 °C). She also concluded that increasing the storage temperature enhanced the formation of gum. Pereira *et al.* (2005) concluded that, without aging, alcohol content had a dilution effect on the gasoline-derived gum present in the mixture. The author also stated that the addition of alcohol to gasoline is beneficial since it reduces the gum deposit in the engine, per liter of fuel consumed. Pradelle *et al.* (2015b) proposed a model based on a Doehlert design to study the impact of different variables in the gasoline - hydrous ethanol mixture, using regular and additivated gasoline. The results from their model stated that all studied variables (temperature, aging and ethanol content) were relevant in the washed gum formation, being the ethanol the most significant for the regular gasoline blend. Pradelle (2016) proposed another model based on a Doehlert design, studying the unwashed and washed gum on different gasoline - anhydrous ethanol blends. For regular gasoline blend, it was seen a catalytic effect at high temperatures, followed by partial evaporation of ethanol, and dilution effect for low temperature. It was concluded that temperature and aging are key factor on washed and unwashed gum formation. For additivated gasoline blends, aging and temperature were responsible for the formation of gum. Although, at low temperature, unwashed gum formation presented a different behavior, which increased slightly with increasing alcohol content, due to additive reactivity. For all blends, a dilution effect was observed at high ethanol content, as predicted by Pereira *et al.* (2005). Pradelle *et al.* (2017) proposed three new models based on a Doehlert design, trying to understand better the formation of unwashed and washed gum on gasoline – anhydrous ethanol blends, for regular and additivated blends. The same behavior was found as in Pradelle *et al.* (2016), but most reliable and robust models were found. Jeczmionek *et al.* (2016) studied the unwashed, existent and potential gum content for three different European gasoline (with 15, 20 and 25 % vol of ethanol, respectively), and concluded that for all of them, the gum content increased with storage time. They also observed that the washed gum content increased with ethanol content within the investigated range.

Table 1 gathers the main characteristics of the fuel properties and investigated experimental conditions from the previous works.

Table 1: Experimental data used in the former literature.

Reference	%EtOH (% vol)	Temperature (°C)	Aging (days)	%Aromatic (% vol)	%Olefin (% vol)	Washed gum (0 day)	Washed gum (mg/100 mL)	Unwashed gum (mg/100 mL)	Number of tests
D'Ornellas, 2001	13-25	25-43	56-168	NA	NA	NA	3.0-63.5	NI	24
Pereira, 2005	0-30	NA	0	30.7	29.1	40	30-40	NI	8
Pradelle, 2015b	21-94	20-40	0-150	22.0	25.3	<0.5	<0.5-5.9	NI	15
Pradelle, 2016	0-50	25-45	0-150	21.6	24.5	1.5	1.4-6.2	2.6-12.1	64
Jeczmionek, 2016	15-25	5-30	121	30.5	10.2	<0.5	<0.5-30.3	<0.5-40.3	7
Regular E0 gasoline – this study	0-80	20-40	75	23.4	27.2	3.5	1.9-7.6	5.4-11.8	70
Homologation E0 gasoline – this study	0-70	20-40	0-150	30.8	9.8	2.9	0.5-4.2	0.8-10.2	200

Legend: NA: Not available; NI: Not investigated;

Figure 1 displays the results taken from the cited previous works comparing values of washed gum content in samples with and without ethanol under similar storage conditions (temperature and aging period). It is important to mention that each point corresponds to different experimental conditions (ethanol content, temperature and aging period), but it illustrates well the effect of the alcohol on the mixture.

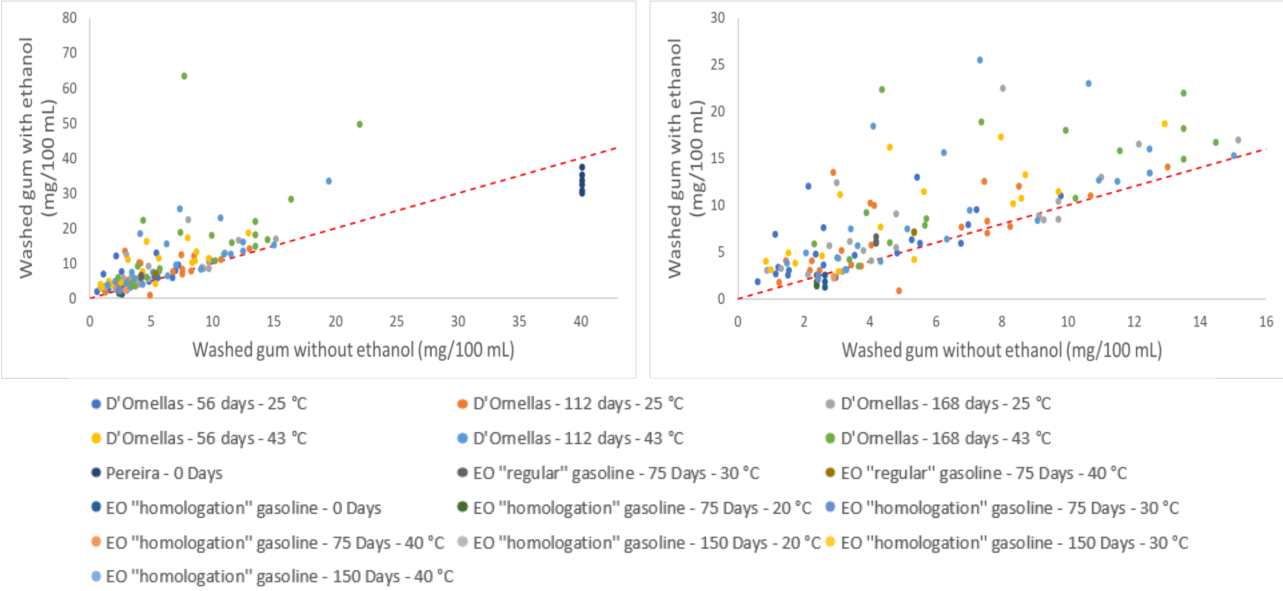


Figure 1: Comparison between washed gum content on samples with ethanol content: all data (left), zoom (right)

In most of the cases, it can be seen that the samples with some content of ethanol results in higher values of gum content, since those points are above the y = x curve. As it can be seen, with the increase of the temperature and storage time, the points tend to be above the y=x curve, evidencing the strong influence of both variables on gum formation. From this study, it can be seen that all points from "regular" E0 gasoline are above the curve, which would imply the existence of the catalytic effect. Some exceptions to this behavior can be observed, in particular the results from Pereira *et al.* (2005) and some blends with up to 10 mg/100 mL in free-alcohol blends (Figure 1 - right). Most of "Homologation" E0 gasoline data, are under of the curve. However, it is possible to see, at higher temperatures and also at higher storage time, that the data is above the y=x, implying the existence of the catalytic effect.

Figure 2 displays the normalized washed gum content in function of ethanol content in the blend for some data.

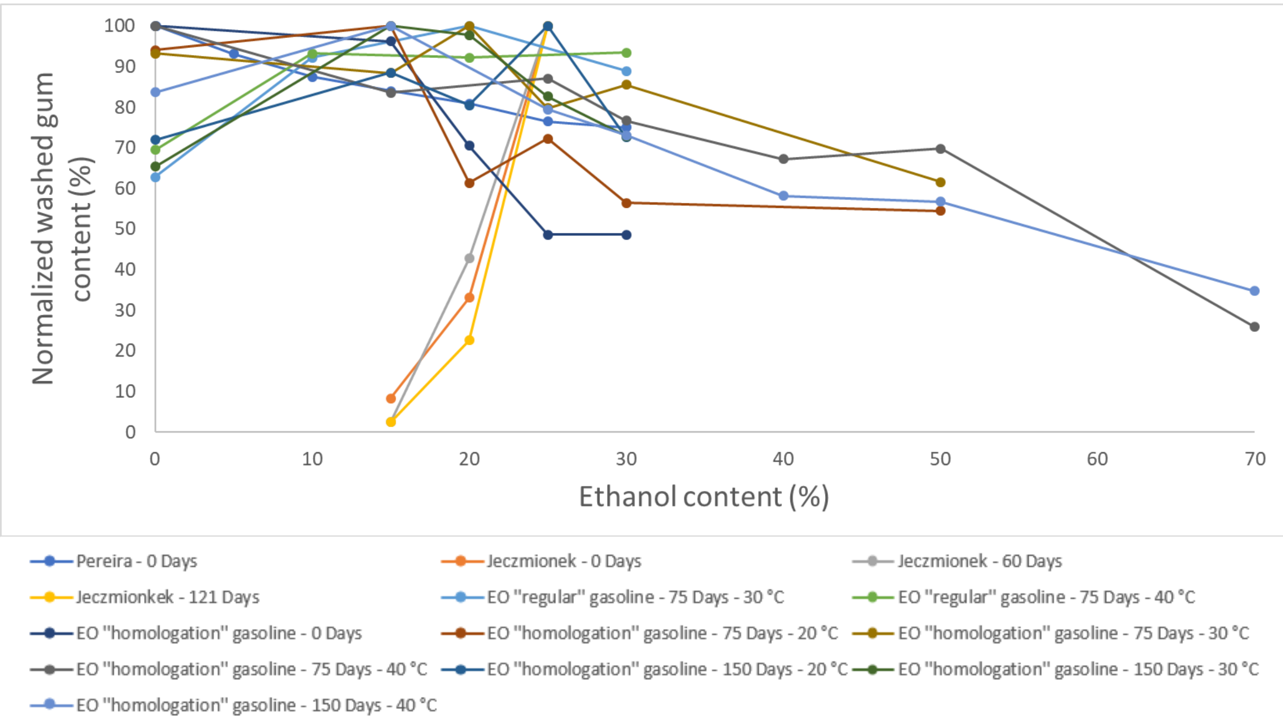


Figure 2: Normalized washed gum content in function of ethanol concentration in the mixture gasoline-ethanol.

Results from Jeczmionek *et al.* (2016) showed a clear catalytic impact of ethanol. However, these data must be studied more carefully because they are obtained in a European context. The relative variation of gum content was the highest among the studied blends. They evidenced the effect of aging in gum formation: in other words, from the results, it can be seen higher values of gum in samples, which have been stored for more days. Pereira *et al.* (2005) only varied the alcohol content and, as it can be seen from Fig.2, there is a clear dilution effect as stated by the author.

This work aims to analyze the behavior of ethanol-gasoline blend for unwashed and washed gums formation under different conditions, varying some parameters, such as temperature, ethanol concentration and aging in order to formulate a unified understanding of ethanol impact on gum formation in gasoline-ethanol blends.

2. MATERIAL

2.1 Fuels

In this study, two kinds of free-ethanol gasoline are investigated: a "regular" gasoline with a percentage of olefin around 25 % vol (Brazilian market average) and an "homologation" gasoline with a percentage of olefin around 9 % vol.

2.2 Experimental procedure

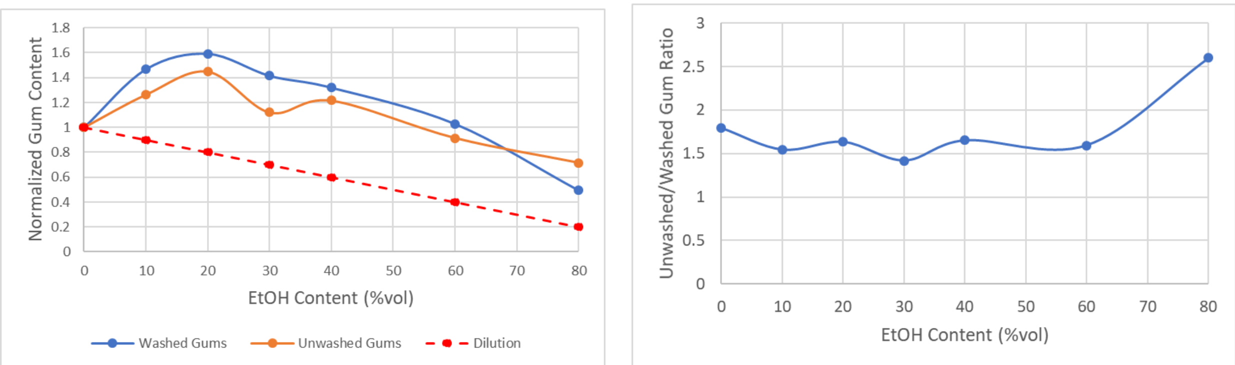
The experimental procedure is the same as in (Pradelle, 2017). A previous cleaning of the glassware was performed using alcohol-free gasoline and drying the transparent glass bottle of 250 mL in an environment without dust. 150 mL of fuel samples were added to the vessels. The samples also had different ethanol content ranging from 0 to 70 % vol. The recipients were closed with caps in order to avoid fuel evaporation and were immerged up to the bottle caps into a water bath. The samples were stored during 75 and 150 days at 20 °C, 30 °C and 40 °C. Several repetitions were made in order to investigate the repeatability of the experiment. Four results were taken for each condition, and one of them was disregarded in order to remove unrealistic values and reduce the mean square deviation. Unwashed and washed gums were measured according to ASTM D 381, which determine the existence of gum content of aviation fuel, motor gasolines or other volatile distillates under standardized condition.

3. RESULTS AND DISCUSSIONS

3.1 – Regular Gasoline

Data from regular gasoline mixed with ethanol was recorded after 75 days of storage, with two different operation temperatures of 30 and 40 °C. Moreover, the mixture was analyzed for different concentrations of ethanol, ranging from 0 to 80% in order to evaluate its influence on formation of washed and unwashed gum content. Results are shown as normalized gum contents, in which the reference is the washed and unwashed gum content, respectively, measured for free-ethanol blend after 75 days of aging.

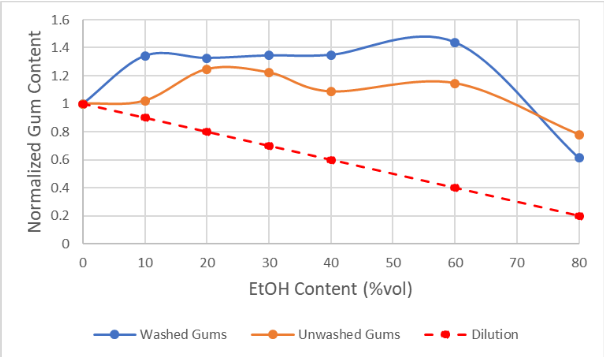
Fig. 3a displays the normalized content for both kind of gum at 30 °C. A catalytic effect is seen near 20% of ethanol concentration in the mixture, followed by a dilution until only ethanol is considered. The catalytic effect is seen as the growth of the difference between the gums contents and dilution law line in function of ethanol content, and the dilution effect is regarded as the behavior of both gum content lines following the same tendency of the dilution line. Fig. 3b displays the ratio between both kinds of gums in function of ethanol concentration. It can be seen that the ratio is almost constant until high concentration of ethanol.



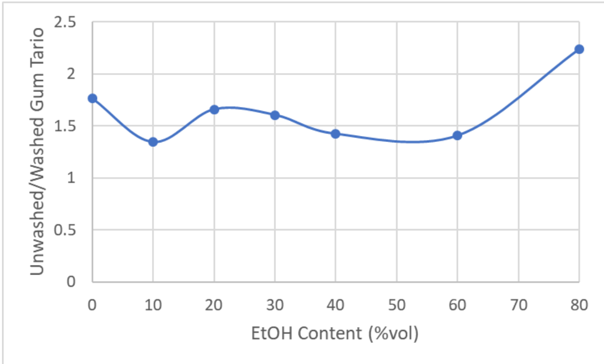
(a) (b)

Figure 3: Results for 30 °C using original gasoline and ethanol blend. Normalized gum content (left). Ratio of unwashed and washed gum content (right)

Fig 4a displays the normalized content for both types of gum content at 40 °C. A catalytic effect is also spotted as the prior case around 20% of ethanol concentration in the mixture. However, it seems that this value is almost constant, forming a plateau, until reach high values of ethanol of 60% where it starts to decrease. The maximum value for washed and unwashed gum contents increased with temperature, suggesting that this parameter plays a role in formation of gum. Fig 4b exhibits the ratio between the unwashed and washed gum content of the blend of regular gasoline and ethanol at 40 °C, and it seems that the behavior of the curve follows the same pattern found in Fig. 3b.



(a)



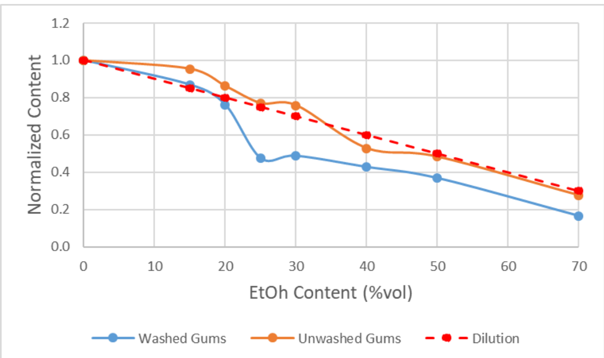
(b)

Figure 4: Results for 40 °C using original gasoline and ethanol blend. (a) Normalized gum content. (b) Ratio of unwashed and washed gum content.

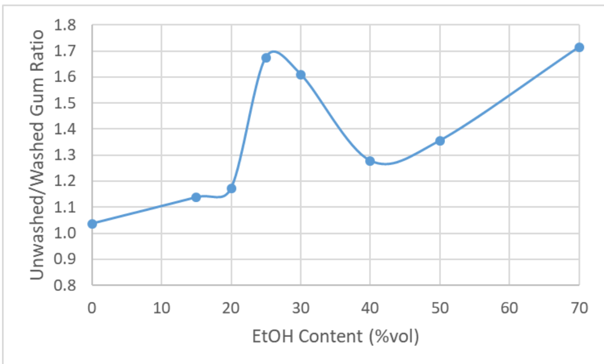
Based on results with regular gasoline, a complex role of ethanol was observed after an aging period of 75 days, at a temperature of 30 °C and 40 °C. The ethanol presented a catalytic role, with a maximum activity at 20 % vol of ethanol content at 30°C. It is also showed that for higher temperatures, the formation of gum is also higher, as predicted in the literature. These results differs from what it seen in Pereira *et al.* (2005), once the author states that alcohol content has no effect on gum formation, except for the dilution effect. This is probably due to the fact that the blends were tested just after pouring alcohol within gasoline and no aging effect of ethanol can be measured.

3.2– Homologation Gasoline

After 150 days of experiment, all the desired data was taken for investigation and the influence of the parameter was evaluated regarding unwashed and washed gum formation could be made for the mixture of homologation gasoline and ethanol mixture. An investigation of washed and unwashed gum formation is done for: (a) 0 day, (b) 75 days with three different temperatures (20, 30 and 40 °C), and (c) 150 days also with three different temperatures (20, 30 and 40 °C). Results are shown in Fig. 5 to 7 as normalized gum contents, in which the reference is the washed and unwashed gum content, respectively, measured for free-ethanol blend without aging.

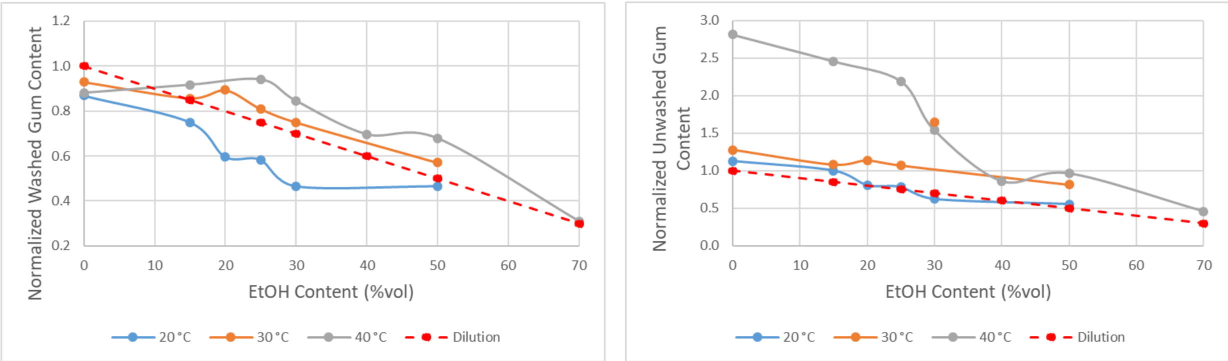


(a)



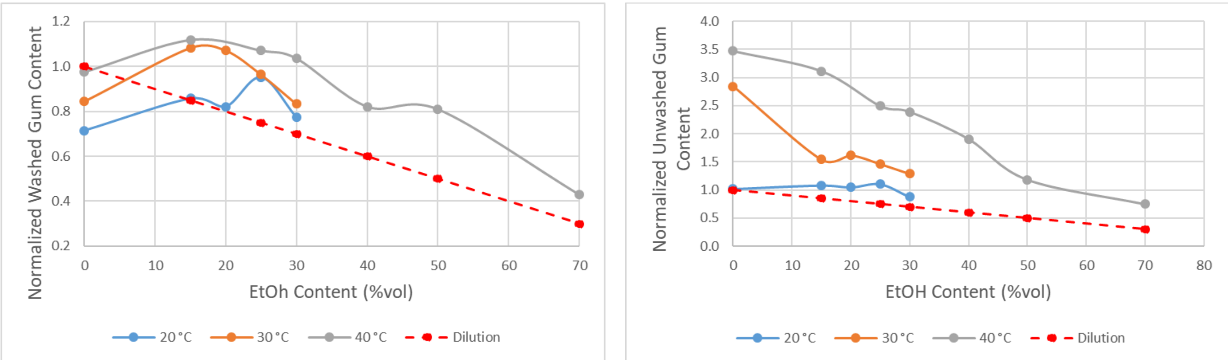
(b)

Figure 5: Results of the homologation gasoline and ethanol blend at 0 day. (a) Normalized gum content. (b) Ratio of unwashed and washed gum content.



(a) (b)

Figure 6: Normalized gum content for homologation gasoline and ethanol blend after 75 days. (a) Washed Gum. (b) Unwashed Gum.



(a) (b)

Figure 7: Normalized gum content for homologation gasoline and ethanol blend after 150 days. (a) Washed Gum. (b) Unwashed Gum.

3.2.1 – Without aging (0 day)

It can be seen from Fig. 5a that for the starting point of the experiment (0 days), there is a strong effect of dilution for both unwashed and washed gum content, as both curves follows the same behavior as the dilution curve. However, a light inhibition effect can be seen for the washed content due to its solubilization with heptane. Fig 5b suggests that the ratio between unwashed and washed gum grows with ethanol content. A local maximum was also observed for 25 % vol of ethanol in the blends. This can be explained by a change in the solubility of the gums that should be investigated.

3.2.2 – After storage of 75 days

A comprehensive analyzes can be done for 75 days of experiment, for all three temperatures. For unwashed gum content, the behavior of dilution is once again seen, with a inhibition effect for 40 °C for more than 30 % vol of ethanol. For washed gum content, the behavior is different at 40 °C as a catalytic effect is spotted at low concentrations of ethanol, around 15-25 % vol, while the other two temperature display a dilution effect at 30°C and an inhibition for 20 °C. Fig. 6a and 6b displays the normalized data for washed and unwashed gums content at all tested temperatures of operation respectively.

3.2.3 – After storage of 150 days

An analysis for 150 days of experiment is also made in order to have a better understanding of the effect of time storage in gum formation. For unwashed gum content, the dilution behavior seems to appear once again in gum formation. However, for washed gum the catalytic effect seems to be stronger when compared to 75 days case, and also appears for an ethanol concentration of 15-25 % vol for all three temperatures. Fig. 7a and 7b displays the normalized data for washed and unwashed gums content at all tested temperatures of operation respectively.

3.2.4 – Parameters influence

It is interesting to find out which of the parameters has a stronger influence in the formation washed gum. In order to do so, it was considered the difference between the value of gum formation and the dilution curve for all three different temperatures, as indicated in Eq. 1, where the subscripts indicate the difference between the experimental value of gum content and the concentration according the dilution low, respectively. The results are analyzed in function of the storage time and ethanol content in the mixture.

$$y_{dif} = y_{experimental} - y_{dilution} \tag{1}$$

From Fig.8 it can be seen the influence of all parameters on formation of washed gum. Storage time plays a huge role in formation of washed gum, as higher values of this difference are concentrated in 150 days rather than 75 days or 0 day. Ethanol content also has a large contribution in the formation of gum, as can be seen in Figs. 8a, 8b and 8c, especially at higher temperatures. It can be seen that indeed near 15-25 % vol of ethanol is found the higher values of washed gum, Temperature does not seem to have a strong impact on formation of washed gum, as it does not have a significant impact on the value of the difference from the dilution curve. This is due to the normalization process, but the absolute value of washed gum was strongly dependent on the temperature.

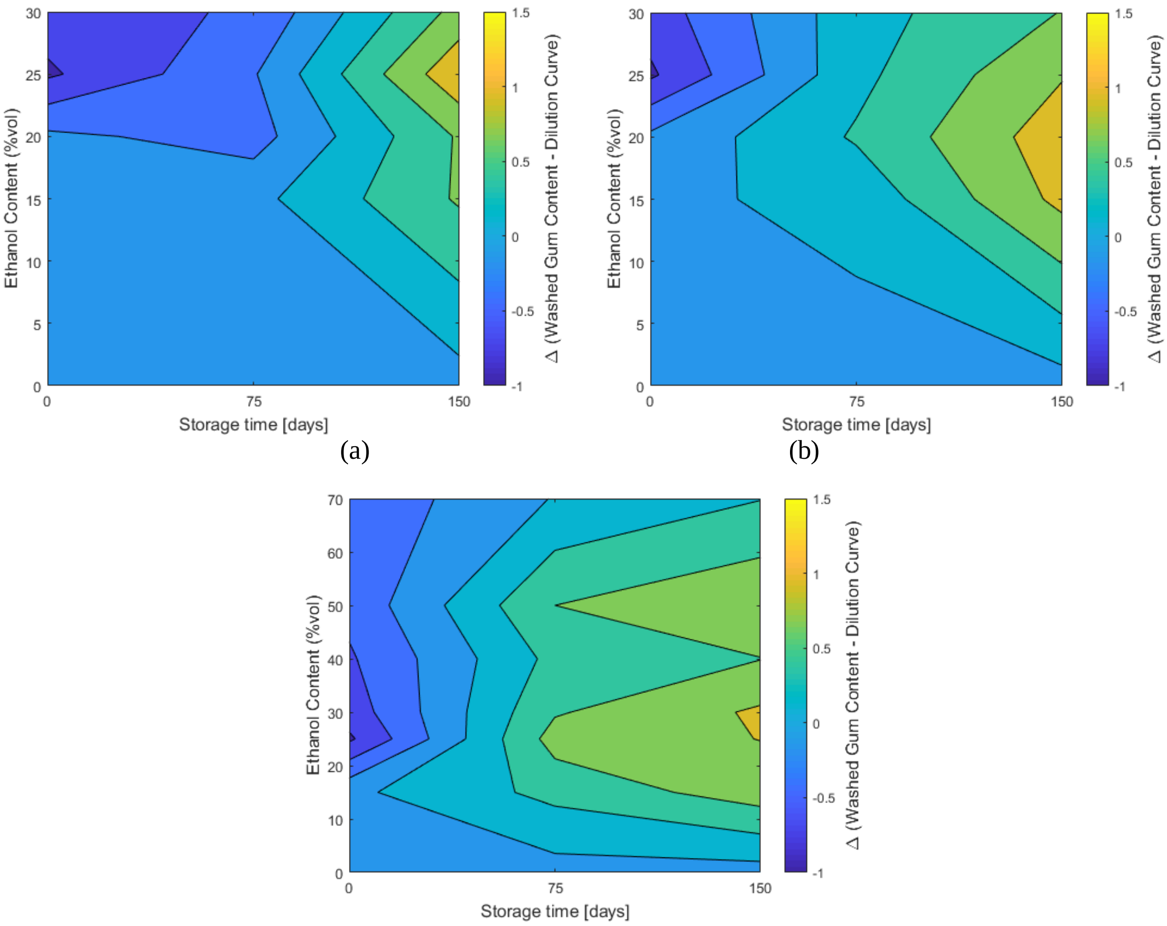


Figure 8: Isolines of washed gum formation in function of storage time and ethanol content. (a) at 20 °C. (b) at 30 °C. (c) at 40 °C.

Fig 9. displays the difference between the unwashed gum content with the dilution curve. Looking at the results from Figs. 9a, 9b and 9c, it can be said that the behavior of the unwashed gum formation is different from the previous case. It is difficult to conclude which of the parameters have a bigger impact in the difference between both curves, as the results from 20, 30 and 40 °C varies a lot from each other. However, it can be observed some regions with a strong inhibition effect (in dark blue). Such results should be strengthened in further investigations.

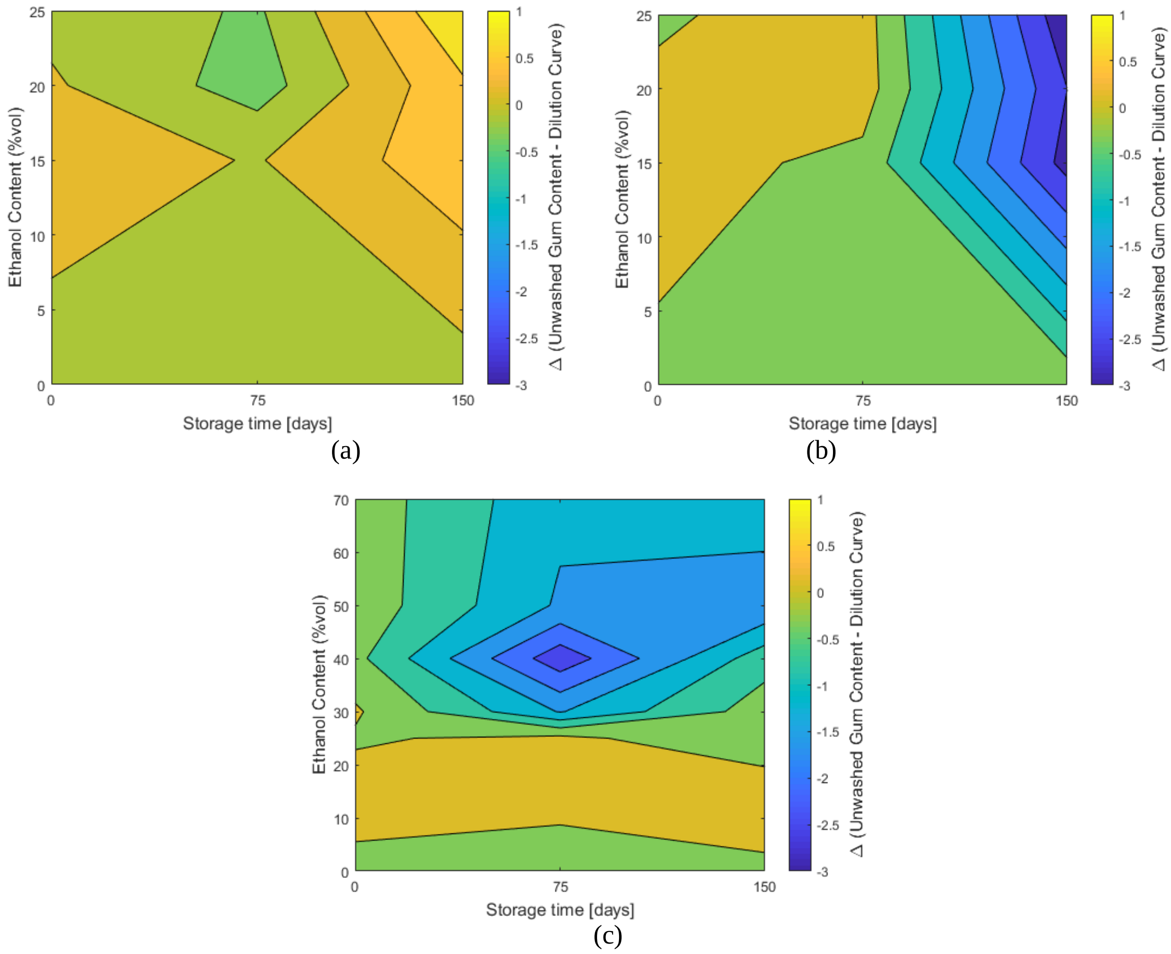


Figure 9: Isolines of unwashed gum formation in function of storage time and ethanol content. (a) at 20 °C. (b) at 30 °C. (c) at 40 °C

4. CONCLUSION

After an extensive experiment of taking record of washed and unwashed gum content from gasoline-ethanol mixture at different concentration of ethanol, temperatures and storage day, an evaluation of those parameters influence can be made. Prior to the results found in this study, it was already speculated a catalytic effect for washed gum formation at low concentration of ethanol considering the aging effect, especially at higher temperature of the mixture for both gasoline typed mixed with ethanol

Such catalytic effect was seen in the mixture of regular gasoline mixed with the ethanol. As the content ethanol grows, the catalytic effect appeared at low concentrations for 30 °C, while for 40 °C the effect extends to higher concentrations forming a “plateau” and are also more intense.

For the mixture of homologation gasoline with ethanol, it was found indeed the existence of such catalytic effect after 75 days for 40 °C, and for all temperatures after 150 days. The effect is more intense at 150 days. The maximum catalytic effect is found at concentration near 25 % vol of ethanol in the mixture for such cases.

Unwashed gum formation seems to present a dilution tendency as more ethanol is added to the mixture for all given test condition. However, it seems that aging and temperature increased the formation of unwashed gum content. All three parameters seems to have a strong influence on washed gum formation. Storage time and ethanol content seems to have a bigger impact as can be seen, and the catalytic effect can be seen as the difference between content and dilution line grows until reach the concentration of ethanol of 15-25 % vol. For unwashed gum content, it is hard to evaluate which of the parameters have a stronger effect in the formation of gum as all the results differs from each other showing any kind of tendency.

These qualitative results will be strengthened in a future work by the interpretation of these results in a design of experiments approach.

5. ACKNOWLEDGEMENTS

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