Evaluation of VOCs emissions from gasoline bulk terminals

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Abstract   The aim of this paper is to examine the effect of humidity, temperature and liquid gasoline composition on the flow and composition of hydrocarbon vapors released from the trucks or rail cars loading, in Romanian refineries. In order to estimate the flow and VOCs compositions, a PRO-VISION software package is used. The investigations were conducted for a temperature range between 0 and 40 °C and for four types of gasoline. The repartition coefficients between the liquid and vapor phases for the water and oxygenated compounds were investigated.

Keywords: gasoline, oxygenated compound, bulk terminals, repartition coefficients

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1. Introduction

The reduction of volatile organic compounds (VOCs) atmospheric emissions release from distributions activities is a requirement of environmental protection European Directive 96/61/EC. In this context, Romania assumed for 2010 a reduction of VOCs with 15%, toward 1990 level. The Romanian refineries facilities for gasoline vapors controls are non conventional processes, like pressure swing adsorption (PSA) on activated carbon or membrane separation techniques [1], and also combinations between conventional processes of physical absorption and non conventional separation techniques. For example, in the refinery presented in this study, the system collecting the vapors released when loading gasoline is continuously connected to an activated carbon pressure swing adsorption plant linked with an absorption process into naphtha gasoline.

The activated carbon absorption system is designed taking into account the hydrocarbons absorption capacity. However, the European and national legislation compels the refiners to obtain the oxygenated gasoline, so that, the vapors released when loading gasoline, should contain besides ethanol and ether (MTBE or ETBE), water vapors. Unfortunately, the presence of these components influences in a negative manner the adsorption of the hydrocarbons and shortens the life expectancy of the

activated carbon and good functioning of the plant. In order to suggest methods able to diminish these negative side effects it is necessary to know and analyze the composition of the vapors released when loading the various types of gasoline, in various temperature and weather conditions all throughout the year. It is impossible to perform an in situ chromatographic analysis of the vapors released when loading various types of gasoline. Alternatively, using a process simulation technique is the most efficient method in order to estimate and establish the composition of the vapors, in relation to the factors influencing it.

The aim of this paper is to examine the effect of humidity, temperature and liquid gasoline composition on the flow and composition of hydrocarbon vapors released from petrol trucks or rail tanks loading in Romanian refineries.

2. Computational simulation

In order to estimate the flow and VOCs compositions, a PRO-VISION version 8.1 software package is used [2]. The investigations were conducted for a temperature range between 0 and 40 °C and for four types of gasoline. The starting point in the computational simulation was a conventional
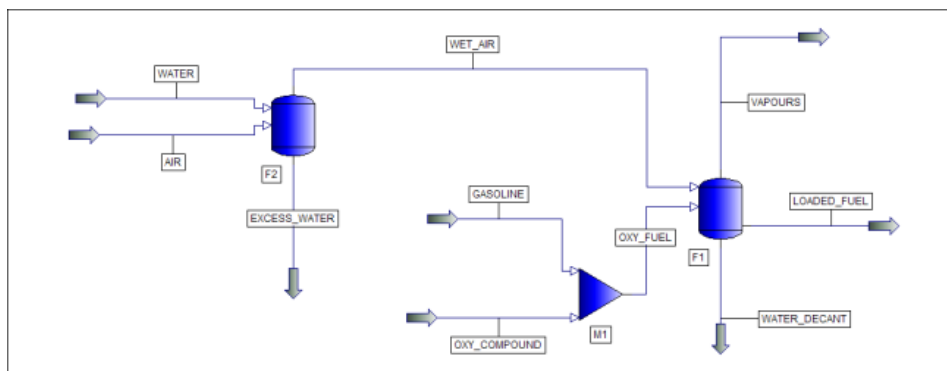

Fig.1. Diagram of the simulated process of loading gasoline into cisterns.

gasoline for which the components and composition was specified by chromatographic analysis. Next, from this standard gasoline, new type of gasoline were formulated: oxygenated with 4% vol. bio-ethanol, with 15% vol. MTBE, and finally, with 15% vol. ETBE. The trucks or rail tanks loading was simplified in simulation at an atmospheric equilibrium flash (F1) and the outlet composition of the vent stream is then computed using the UNIFAC-Lyngby thermodynamic equation [3, 4].

Taking into account that standard procedure requires that the loading degree should be max. 93% of the cistern's volume, calculations show the loading flow to be approximately $112 m^3/h$. In **Fig. 1.** a diagram of the process is presented. As a result of the F2 flash simulation (representing a liquid-vapor phase equilibrium) we have obtained the air's saturated (equilibrium) humidity recorded at different temperatures. It wasn't taken into account rainy weather conditions and seasons.

3. Results and Discussions

For each temperature and composition of the gasoline, we recorded the flow of released vapors, the water content and the gasoline flow, as seen in **Tables 1-4**.

The data recorded in Table 2 show a dramatic increase in the content of hydrocarbons and ethanol, increase that occurs for temperatures over 25°C.

This is explained by azeotropes formation between ethanol and light hydrocarbons.

Table 1. Simulation results for the loading process of standard gasoline

Temp. C	Total Hc., % vol	N2, % vol	O2, % vol	Water vapor, % vol	Vapor flow, m^3/h	Loaded gasoline flow, m^3/h
0	14.1	70.3	15.6	0.05	83.46	111.99
5	17.3	67.4	15.2	0.09	90.65	111.97
10	20.9	64.2	14.7	0.15	99.07	111.95
15	25.3	60.4	14.1	0.25	109.25	111.91
20	30.3	56.0	13.2	0.39	122.00	111.86
25	36.1	51.0	12.3	0.58	138.58	111.79
30	42.6	45.4	11.1	0.84	161.16	111.69
35	50.1	39.1	9.7	1.17	193.66	111.55
40	58.4	32.0	8.0	1.55	243.91	111.32

Table 2. Simulation results for the loading process of 4% vol. ethanol oxygenated gasoline

Temp.,C	Total Hc., % vol	N2, % vol	O2, % vol	Water vapor, % vol	Ethanol in vapor phase. % vol	Vapor flow. m^3/h	Loaded gasoline flow, m^3/h
0	13.8	70.5	14.9	0.0044	0.79	62.5	112.0
5	16.9	67.4	14.6	0.0088	1.10	71.9	112.0
10	20.6	63.8	14.1	0.0170	1.50	82.6	111.9
15	24.8	59.6	13.5	0.0320	2.03	95.1	111.9
20	29.7	54.9	12.7	0.0582	2.70	110.7	111.9
25	35.3	49.4	11.7	0.1028	3.55	130.9	111.8
30	41.7	43.1	10.4	0.1762	4.62	158.9	111.7
35	48.9	36.1	8.9	0.2918	5.93	200.8	111.5
40	56.3	28.2	7.5	0.4625	7.54	270.7	111.2

For this reason, a supplementary thermodynamic study has been performed, study

which confirmed that i-pentane, l-pentene and n-pentane form with ethanol, minimum boiling temperature azeotropes.

Table 3. Simulation results for the loading process of 15% vol. MTBE oxygenated gasoline

Temp., C	Total Hc., %vol	N2, %vol	O2, %vol	Water vapor, %vol	MTBE in vap phase, %vol	Vapor flow, m³/h	Loaded gasoline flow, m³/h
0	12.5	70.3	15.5	0.0062	1.7	81.5	110.2
5	15.3	67.4	15.1	0.0115	2.2	87.9	111.9
10	19.0	64.1	14.6	0.0210	2.3	96.8	111.9
15	22.3	60.2	13.9	0.0371	3.5	107.4	111.9
20	26.6	55.7	13.1	0.0640	4.4	120.7	111.8
25	31.7	50.6	12.1	0.1075	5.4	137.9	111.8
30	37.4	44.9	10.9	0.1760	6.7	161.6	111.7
35	43.8	38.4	9.5	0.2807	8.1	196.1	111.5
40	50.9	31.1	7.8	0.4330	9.8	250.7	111.3

Table 4. Simulation results for the loading process of 15% vol. ETBE oxygenated gasoline

Temp., C	Total Hc., %vol	N2, %vol	O2, %vol	Water vapor, %vol	ETBE in vap. phase, %vol	Vapor flow, m³/h	Loaded gasoline flow, m³/h
0	12.4	71.3	15.7	0.0108	0.622	80.4	112.0
5	15.2	68.6	15.4	0.0200	0.820	87.2	111.9
10	18.4	65.5	14.9	0.0360	1.068	95.1	111.9
15	22.2	62.0	14.4	0.0630	1.376	104.3	111.9
20	26.5	57.9	13.6	0.1070	1.756	115.9	111.9
25	31.6	53.3	12.7	0.1770	2.218	130.6	111.8
30	37.3	47.9	11.6	0.2846	2.778	150.2	111.7
35	43.8	41.9	10.3	0.4447	3.448	177.5	111.6
40	51.0	35.3	8.8	0.6715	4.247	218.4	111.5

From Tables 1-4 we may conclude that: as temperature increases, the concentration of hydrocarbons, water and oxygenated compounds in vapors increases at the level of polluted air. The highest content of water in the released vapors results when loading standard gasoline. This is normal, taking into account that in the case of oxygenated gasoline the highest degree of air humidity is absorbed in the liquid phase. It has been shown in different studies [5], that oxygenated gasoline with bio-ethanol has a higher degree of tolerance to water (their level of water retention is more elevated) compared to the oxygenated gasoline with ethers. When analyzing gasolines with the same ether content, the differences in water content result from the structure of the ethers and from the strength of the hydrogen bonds. In the liquid phase, ETBE retains less water that MTBE. Thus, in the vapor phase, results more water (Table 3-4). The previous analysis, related to the liquid water phase (the gasoline loaded for transport) and in the vapor phase (polluted air with organic compounds) can be easily correlated to the water repartition between liquid and vapor phases. Taking into account the temperature and the type of gasoline loaded for transport, the water repartition coefficient between liquid and vapor phases has been calculated (**Fig. 2**).
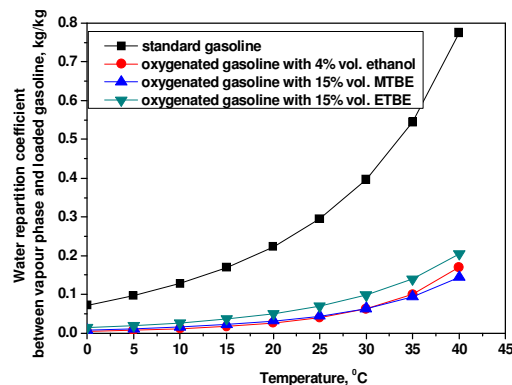

Fig. 2. Variation of the water repartition coefficient in relation to the temperature and type of loaded gasoline.

From Table 1-4 we can conclude that the highest content of oxygenated compound recorded in vapors results when loading gasoline with MTBE. This was expected, because MTBE has the lowest normal boiling point (55.2°C) from all studied oxygenated compound (ethanol 78.32°, ETBE 72.8°C). Their vapor pressures are inversely proportional to their boiling points. The vapor pressures of the oxygenated compounds have a great influence on the volatility of the gasoline they substitute. In order to continue the list previously mentioned, the next oxygenated compound should be ETBE, if they are to analyze its concentration in the vapor phase. However, the vapor phase resulted from loading gasoline substituted with 4% volume ethanol, contains slightly more of the previously

mentioned substance that the vapor phase resulted from loading gasoline that show 15% volume ETBE. The explanation is that some hydrocarbons (i-pentane, l- pentene and n- pentane) form minimum boiling point azeotropes (maximum vapor pressure), in the presence of ethanol. So, these azeotropes mixtures lead to an increase in the ethanol and hydrocarbons content in vapor phase. This behavior of gasoline with ethanol, compared to gasoline with ethers is even better illustrated with the help of the repartition coefficient of the oxygenated compound at the level of the two phases (**Fig. 3**).
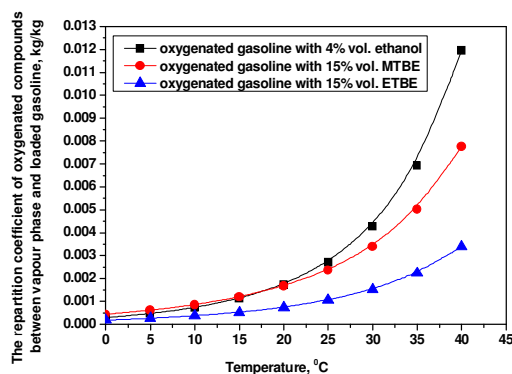

Fig. 3. Variation of the repartition coefficient of oxygenated compounds in relation to the temperature and type of loaded gasoline.

Regarding the content of hydrocarbons in the polluted air, we can say that the hydrocarbons which show normal boiling points in the studied temperature range will release a higher quantity of vapors. As we have shown above, in the case of hydrocarbons-ethanol, azeotrope mixtures that have boiling temperature between 15°C and 40°C, the quantity of hydrocarbon and ethanol vapors released is higher than the quantity of vapor resulted in the case of hydrocarbons- ethers non-azeotrope mixtures (**Fig. 4**).
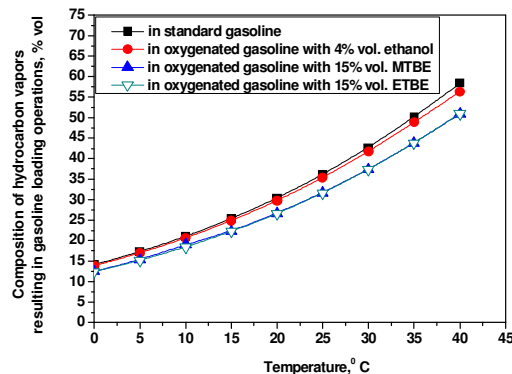

Fig. 4. Variation of vapor hydrocarbons composition, with temperature.

At the end of this study, we can show the vapor flow variation in relation to temperature and chemical composition of the loaded gasoline (**Fig. 5**).

Figure 5 shows that the vapor flow increased with temperature. The vapor flows (and composition) are influenced greatly by the type of oxygenated compound found in the loaded gasoline. The highest vapor flow recorded at the temperature of 40°C, is obtained in the case of oxygenated gasoline with 4% volume ethanol. In a decreasing sequence, the vapor flow resulted from loading gasoline with MTBE, is justified by the high volatility of MTBE, compound which has the tendency to be highly released in the vapor phase.
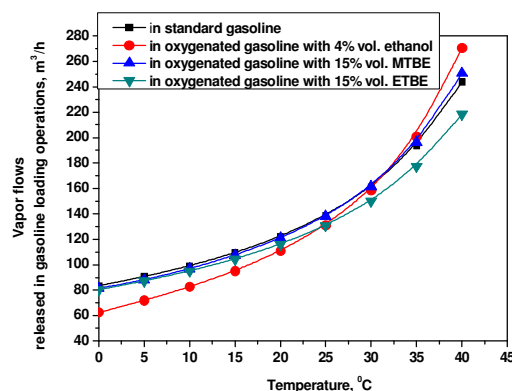

Fig. 5. Variation of vapor flows released in gasoline loading operations, with temperature.

4. Conclusions

The study presented in this paper shows that the flow and composition of the vapors released when loading petrol tanks depends on a multitude of factors. The study also shows that in the vapor phase, besides hydrocarbons a water flow resulted from the air inside the tank. At 40 °C, the vapor water flow has a value of approximately 3 kg/h in the case of non-oxygenated gasoline, a value of 1.18 kg/h for gasoline with ETBE, a value of 1.0 kg/h for gasoline with ethanol, and in the case of gasoline with MTBE, reaches value of 0.78 kg/h (Tables 1-4).

The water and the other vapors released when loading gasoline, will reach the vapor recovery system (membrane separation technique or physical absorption coupled with adsorption on activated carbon), water is a substance that is highly unwanted there. For this reason, it is necessary it's separation before entering the recovery system.

5. References

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