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VORTEX TUBE EQUIPPED SYSTEM FOR REDUCING EMISSIONS OF HYDROCARBONS IN UNDERGROUND STORAGE TANKS

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Abstract. *The emission of hydrocarbon vapors into the atmosphere is one of the major sources of air pollution that is still under no regulation. Besides the environmental problems, the economic impact generated is an unavoidable issue! According to the US Environmental Protection Agency, there is an annual loss of approximately R$ 482 million caused by vaporization of various hydrocarbons and its emission to the atmosphere during small cars refueling. In addition to the environmental and economic factors, the most important of all the problems is human health. The continuous exposure to hydrocarbon vapors can cause various health hazards. For example, a long-term exposure to benzene, one of the hydrocarbons present in gasoline, may alter bone marrow, chromosomes, the immune system and the central nervous system, in addition to various types of cancer. Aiming to contribute to solve this problem, this paper presents a physical configuration of a new device equipped with Vortex Tube to remove, by liquefaction and/or solidification, hydrocarbon vapors from gas mixtures with air. A mathematical model evaluating the capability of this new device for hydrocarbon removal has also been developed and solved numerically when considering the current dependence of the vapor pressure of octane and benzene. The Vortex Tube potential for hydrocarbon (octane and benzene) removal was numerically evaluated between 6.2 – 8.0 grams of hydrocarbons vapors per kilogram of compressed air, when the pressure level at the Vortex Tube inlet was maintained in the range of 3-7 bars.*

Keywords: *gaseous emissions removal, benzene, octane, Vortex Tube*

1. INTRODUCTION

Most of the substances used in industries are not found in nature in its pure form and so, in many cases, a separation process is necessary to refine a certain component. Consequently, during the technological evolution several methods of separation of components from diverse natural mixtures were developed.

Hydrocarbons extraction processes deal with a more specific but not different issue. The lack of a rigorous legislation on the control of hydrocarbon vapor emissions may be one of the reasons for the relative scarcity of technologies for controlling such emissions. The available technologies have been adapted from those used previously in other separation processes. Therefore, it is not too much information provided by the scientific literature on such methods used for the separation of components from gaseous mixtures. The lack of adequate separation technologies drives companies in some European countries to incinerate hydrocarbon vapors, thereby preventing them from being released into the atmosphere, but causing damage to the environment through the emission of CO_2 and also wasting energy.

The characteristics of the Vortex Tube make this technology a possible option to control the emission of hydrocarbon vapors. The Vortex Tube is assembled of two tubes of different diameters and equipped with a flow control valve at the outlet of the larger diameter tube. Compressed air is tangentially injected into the larger tube's internal volume, generating a vortex into that separates the intake compressed gas into two low pressure air streams: a hot one, which leaves the device through the larger diameter tube, controlled by the valve, and a flow of cold air, which leaves the Vortex Tube by the smaller diameter tube. The ability of the Vortex Tube to generate air at low temperatures using only compressed air may be a good option to replace the complex refrigeration systems currently used in the separation of hydrocarbons by liquefaction.

For effective removal by liquefaction of hydrocarbon vapors from gaseous mixtures with air, the temperatures of such mixtures should be reduced below the temperatures of the specific dew points of the target hydrocarbons. A physical configuration of a device equipped with Vortex Tube to remove by liquefaction and / or solidification of hydrocarbon vapors from gaseous mixtures with air is presented in this paper. A mathematical model developed based on the equations of conservation of mass, energy and on the second law of thermodynamics is also presented to evaluate the main functional characteristics of such device.

Handling of flammable components, such as hydrocarbons, is an issue that requires special care with the flammability limits, which must be observed in order to avoid the risk of fire or explosion. The device presented minimizes the risks associated with flammability not only through the technical solution proposed for the control of hydrocarbon concentration in the mixture with air, but also because of the non-existence of moving parts in the Vortex Tube.

2. SYSTEM EQUIPPED WITH VORTEX TUBE TO CONTROL THE CONCENTRATION OF OCTANE OR BENZENE VAPORS IN AIR MIXTURES

2.1 Physical model

In order for hydrocarbon vapor to be physically removed from a mixture with air by a condensation process, it is necessary to reduce the temperature of the mixture below the saturation temperature of the hydrocarbon present. The characteristics of the Vortex Tube create the necessary conditions for such a phenomenon to occur.

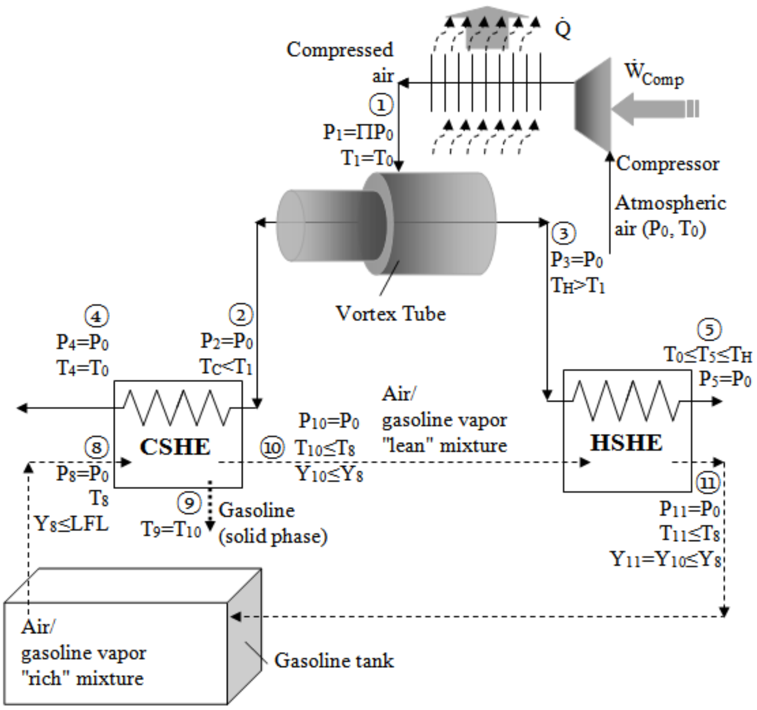

Figure 1 – System equipped with Vortex Tube to control contents of hydrocarbon vapors

When the air / hydrocarbon mixture is brought into contact with the cold air flow generated by the Vortex Tube, the mixture loses energy while undergoing a decrease in temperature. Fig. 1 presents the proposal of a device in which the mixture is forced to pass through a heat exchanger (CSHE control volume) that potentiates its thermal interaction with the cold air generated by the Vortex Tube. In this control volume the mixture is cooled until hydrocarbon is extracted in section 9 of the device. Before being returned to the tank, the lean mixture can be heated, decreasing the entropy generation in the process.

The objective of this work is to optimize the Vortex Tube in order to find the maximum hydrocarbon removal capacity of the air when it crosses the CSHE control volume. The control variable used to define the optimum operating point of the device is represented by the ratio of the mass flow rate of gas leaving the cold side of the pipe to the total gas mass flow rate admitted thereto ($\mu_c = \dot{m}_2 / \dot{m}_1$). In the proposed device, the Vortex Tube is fed with pressurized air at room temperature, such conditions are obtained through a compressor and chiller set, where the former is responsible for raising the air pressure and the second by lowering its temperature until it reaches room temperature.

Gasoline is composed of a combination of hundreds of hydrocarbons, among which octane is undoubtedly one of the most important.

In Fig. 2, the octane phase diagram and the physical behavior of the substance are presented throughout the process. Upon reaching the conditions of point B the mixture is brought to the CSHE heat exchanger where it is cooled at constant pressure. In order to avoid the flammability area of the diagram, point B is positioned at a vapor pressure 20% below its lower flammability limit. When the temperature of the mixture reaches point C, liquid octane begins to form on the walls of the heat exchanger, decreasing its concentration in the mixture. When the octane temperature and vapor pressure are the same as those at point D, the mixture will be heated at constant pressure through its thermal interaction with the hot air from the tube in the HSHE control volume.

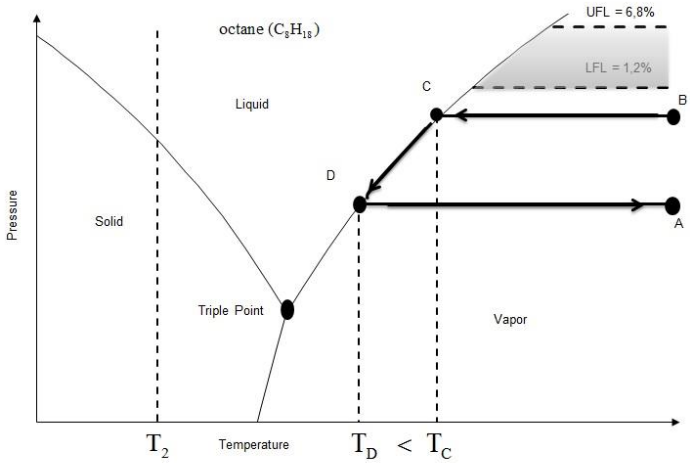

Figure 2 - octane extraction from the octane/air mixture

Benzene is another component that, besides being present in significant amounts in gasoline, is known to be carcinogenic and may pose a great threat to the health of those who have direct and frequent contact with fuels.

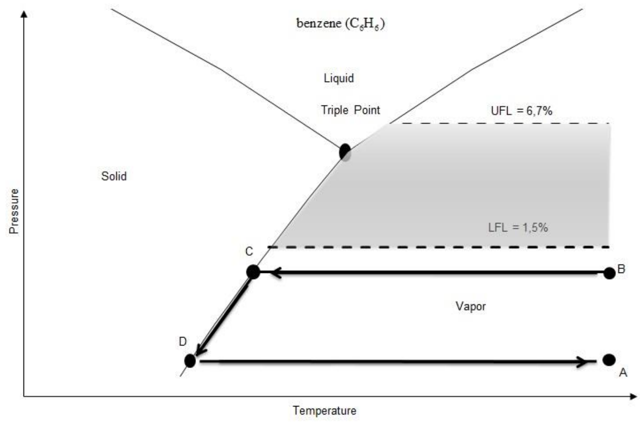

Figure 3 - benzene extraction of the benzene/air mixture

Despite going through a similar process, benzene exhibits a behavior different from octane. Since its triple point is at a vapor pressure greater than its lower flammability limit, in order to avoid flammability limits of benzene, hydrocarbon extraction must occur at a vapor pressure lower than its triple point, and as the mixture is cooled to constant pressure, benzene will reach the saturated solid curve of the diagram, showing the formation of solid benzene on the walls of the heat exchanger, an event known as desublimation.

2.2 Mathematical model

In order to size the amount of hydrocarbon removed by the device, a mathematical model was developed from the equations of conservation of mass, energy and the second law of thermodynamics applied to each of the control volumes of Fig. 1. In the control volume called "Vortex Tube", the application of these equations result in a function capable of calculating the temperatures in sections 2 and 3 of the system, depending on the operating regime of the Vortex Tube, μ_c .

By performing the energy balance for the CSHE control volume, it is possible to calculate the amount of hydrocarbon extracted in section 9 (Fig. 1), from the mass air flow admitted in the heat exchanger.

The model evaluates the temperature and the ratios between hydrocarbon vapors mass and dry air mass in the mixture in each of its sections. For this the following hypotheses are considered:

- Permanent operating regime.
- Instantaneous thermodynamic equilibrium between dry air and hydrocarbon vapor.
- All flows are considered to be isobaric.
- Heat losses are considered negligible.
- The Dalton model is used to calculate the properties of each of the components in the mixture of dry air and hydrocarbon vapor.

A numerical solution was developed to determine the fuel removal capacity of the blend and calculate the temperatures on the cold side and the hot side of the Vortex Tube.

2.3 Numerical method

The model is divided into two parts, the first one calculates the operating regime of the Vortex Tube ($\mu_c, T_c = T_2, T_H = T_3$), and then the analysis of the amount of fuel that is removed from the mixture is performed.

2.4 Operating system

Assuming permanent operation and disregarding the potential energy and kinetic energy variation of the gas passing through the Vortex Tube, the thermodynamic model is represented by the mass conservation, energy and the second law of thermodynamics:

$$\dot{m}_1 - \dot{m}_c - \dot{m}_H = 0 \quad (1)$$

$$\dot{m}_1 h_1 - \dot{m}_c h_c - \dot{m}_H h_H = 0 \quad (2)$$

$$\dot{m}_1 s_1 - \dot{m}_c s_c - \dot{m}_H s_H + \dot{S}_{ger} = 0 \quad (3)$$

Where, $\dot{m}_1$, $\dot{m}_2 = \dot{m}_c$ and $\dot{m}_3 = \dot{m}_H$ represent, respectively, the mass flow rate of compressed gas at the inlet of the Vortex Tube, the mass flow rate of cold gas and the mass flow rate of hot gas leaving the tube. h and s, in equations (2) and (3), represent the enthalpy and entropy of the compressed gas, and $\dot{S}_{ger} \geq 0$ is the generation of entropy in the process.

The relative efficiency η_{II}, or the utilization factor (BEJAN, 1997) of RHVT is chosen based on already published experimental results (FARZANEH-GORD and KARGARAN, 2010). As the whole process happens without the occurrence of chemical reactions, it is calculated considering only the physical exergy of the compressed gas.

$$\eta_{II} = \frac{\dot{E}_W}{\left(\dot{E}_W\right)_{rev}} = 1 - \frac{T_0 \dot{S}_{ger}}{\dot{m}_1 R T_1 \ln\left(P_1/P_2\right)} \quad (4)$$

Where $\dot{W}_{lost} = T_0 \dot{S}_{ger}$ represents the lost exergy rate, R is the constant of the compressed gas when it is assumed to be perfect gas, $T_0 = T_1$ are the room and compressed gas temperatures at the entrance of the Vortex Tube. P_1 and $P_2 = P_0$ represent the compressed air pressures at the inlet of the Vortex Tube and the air at the outlet of the cold side of the tube respectively.

Equation (1) is valid as long as the ratio between the mass flow of cold air and the total mass flow rate of the air entering the tube, μ_c, is used as a control variable, and considering that $\dot{m}_3/\dot{m}_1 = 1 - \mu_c$. In this way, after some algebraic manipulations and considering: $dH = C_P dT$, $ds = C_P\, dT/T - R_G\, dP/P$ and $\mu_c = \dot{m}_2/\dot{m}_1$, it is possible to write:

$$\mu_C \overline{T}_C + \left(1 - \mu_C\right) \overline{T}_H = 1 \quad (5)$$

$$\mu_C \ln \overline{T_C} + \left(1 - \mu_C\right) \ln \overline{T_H} = \frac{\left(1-k\right) \ln\left(\Pi\right) \eta_{II}}{k} \quad (6)$$

Where dimensionless temperatures $\overline{T}_c = \overline{T}_2$ and $\overline{T}_H = \overline{T}_3$ are calculated based on $\overline{T} = T/T_0$, k is the adiabatic exponent of the compressed gas and $\Pi = P_1/P_2 = P_1/P_3$. Dividing (5) by (6), making the necessary simplifications and replacing $X = \overline{T}_c/\overline{T}_H$ yields:

$$X - \frac{1}{\mu_C}\Pi^{\frac{k-1}{k}\eta_{II}} X^{\mu_C} + \frac{1-\mu_C}{\mu_C} = 0 \tag{7}$$

Dividing equation (5) by $\overline{T}_H$ and substituting $X = \overline{T}_c/\overline{T}_H$:

$$\overline{T}_H = \frac{1}{1-\mu_C + X\,\mu_C} \tag{8}$$

By solving equation (7) by the bisection method for 0 <X <1 it is possible to calculate the dimensionless temperatures $\overline{T}_c$ and $\overline{T}_H$, depending on the operating regime of the Vortex Tube (μ_c, η_{II}), the functional characteristics of the compressor used (Π) and the nature of the compressed gas (k). The numerical value of μ_c is determined by trial and error according to the temperature required on the cold side of the Vortex Tube so that the mixture is cooled below the dew point temperature of the hydrocarbon.

After calculating the air temperature in the hot and cold sections of the Vortex Tube, the mass, energy and second law of thermodynamics can be applied to the other control volumes of the system to calculate the amount of fuel that can be removed from the mixture.

Applying the energy balance in the CSHE control volume, it is possible to calculate the dimensionless mass flow rate of dry air $\overline{m}_a = \dot{m}_{a,8}/\dot{m}_1$ that can be processed when $T_2 = T_{c,opt}, T_4 = T_8 = T_0$.

$$\overline{m}_a = \frac{\mu_C c_P (T_0 - T_{C,opt})}{c_{Pa}(T_0 - T_{10}) + (\Omega_8 h_{octane,8} - \Omega_{10} h_{octane,10}) - (\Omega_8 - \Omega_{10}) h_{octane,9}} \tag{9}$$

Where c_p and $c_{pa} = 1.0035\, kJ/kgK$ are the specific heats at the constant pressure of the gas that expands in the Vortex Tube and the air, respectively. The mass flow rate of fuel is calculated in each state based on the definition $\Omega = \dot{m}_{octane}/\dot{m}_a = 3.936Y$, where $Y = V_{octane}/V_{air}$ the specific enthalpies of the fuel and compressed air are calculated through $h = C_p T$. The approximation of saturated vapor properties is used to calculate the specific enthalpies of fuel vapor (BEJAN, 1997).

2.5 Results

As seen in Eq. (7), the air temperature in sections 2 and 3 of the device depend, among other factors, on the operating regime of the Vortex Tube (μ_c) and the air pressure when admitted into the tube. With that, the calculation of the mixed mass flow rate admitted in the CSHE control volume and the amount of fuel extracted in section 9 of Fig. 8 were performed for compressors of 3, 5 and 7 bar. Isentropic efficiency of the compressor was kept constant and equal to 0.98.

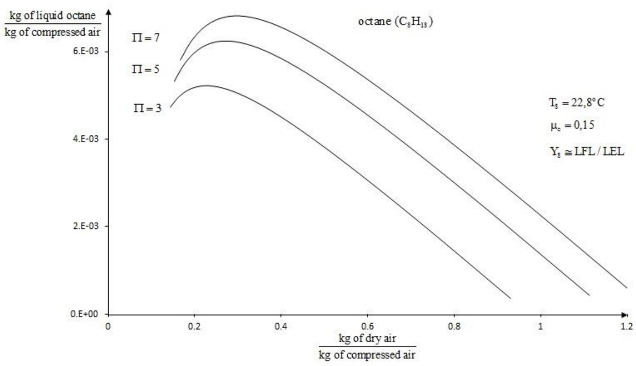

Figure 4 - Quantity of octane removed from the system in function of dry air flow rate admitted in section

It can be observed that the increase of the flow $\bar{m}_{a,8}$ causes in a decrease of the amount of octane extracted by the system. The increase of this mass flow leads to an increase in temperature in section 10 of the device, the more the temperature in section 10 approaches the saturation temperature of octane, fewer hydrocarbons is extracted.

As the octane removal capacity of the system increases with the temperature decrease in section 10, the difference in octane concentration present in state 8 and in state 10 $(\omega_8 - \omega_{10})$ also increases, the fact that the temperature increase in state 10 has adverse effects on the mixture flow rate admitted by the control volume CSHE $(\bar{m}_{a,8})$ and the difference between the quantity of octane in states 8 and 10 $(\omega_8 - \omega_{10})$, generates a point of maximum in the octane removal capacity chart of the system. This can be seen in Fig. 5.

When the tube is supplied with air at a pressure of 3 bar, the octane removal potential ranges from 0.35 (g liquid octane / kg compressed air) to 5.22 (g liquid octane / kg air). When the compressor supplies air at a pressure of 7 bar, it can achieve a capacity of up to 6.78 (g of liquid octane / kg of compressed air).

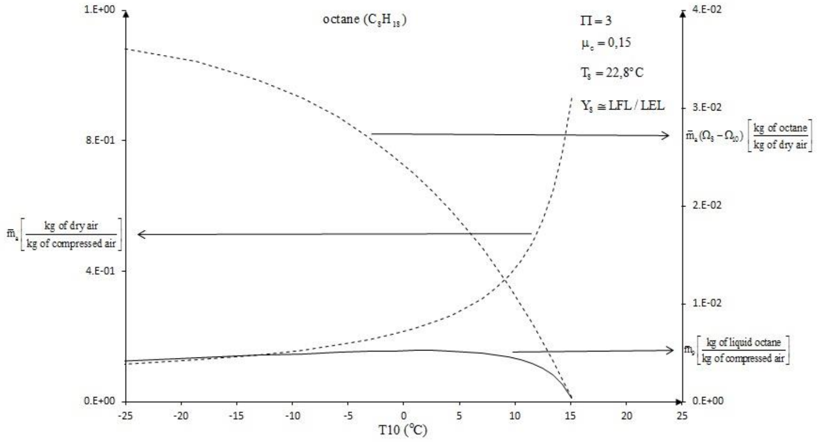

Figure 5 - Influence of temperature variation in state 10, of the dry air flow admitted at the CSHE and the difference in octane quantity in states 8 and 10 in system performance

On the other hand, benzene is cooled at constant pressure at a lower vapor pressure than its triple point, as a result of which vapor passes directly into the solid state, a process known as de-sublimation. To avoid a decrease in the efficiency of the heat exchanger as a result of the formation of a solid precipitate in its fins, a flow of hot air is directed to this heat exchanger to liquefy the solid benzene and to return it to the fuel tank. This hot air can come from either the chiller, positioned after the compressor, from the hot air generated by the tube itself, or even from an external heating system mounted parallel to the system.

In the same way as for the octane, the increase in mass flow in section 8 shows opposite behavior for the octane molar fraction difference between sections 8 and 10 $(\omega_8 - \omega_{10})$ and the temperature T_{10}. The combination of these factors also results in an optimal point of operation of the system, as can be seen in Fig. 7.

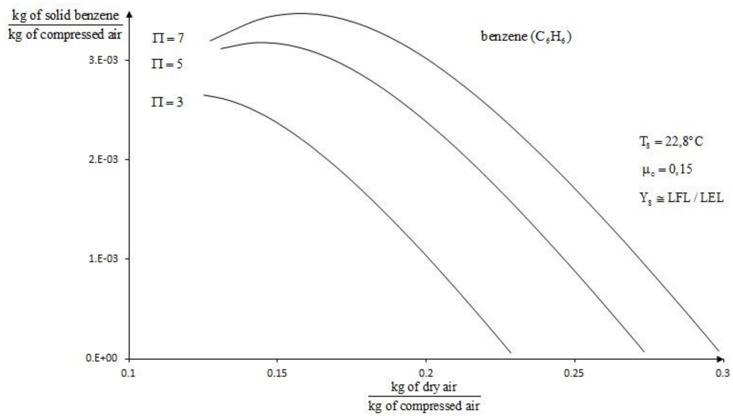

Figure 6 - Quantity of benzene removed from the system in function of the dry air flow rate admitted in section 8

In a system fed with air at 5 bar, the maximum extraction capacity is 3.17 (g of solid benzene / kg of compressed gas) and it happens for a mixture flow rate admitted in the CSHE of 0.14 (kg dry air / kg of compressed gas).

When the tube is supplied with air at a pressure of 3 bar the benzene withdrawal potential is 2.65 (g solid benzene / kg compressed gas) and when the tube is supplied with air at a pressure of 7 bar it achieves a removal capacity of up to 3.46 (g solid benzene / kg compressed air).

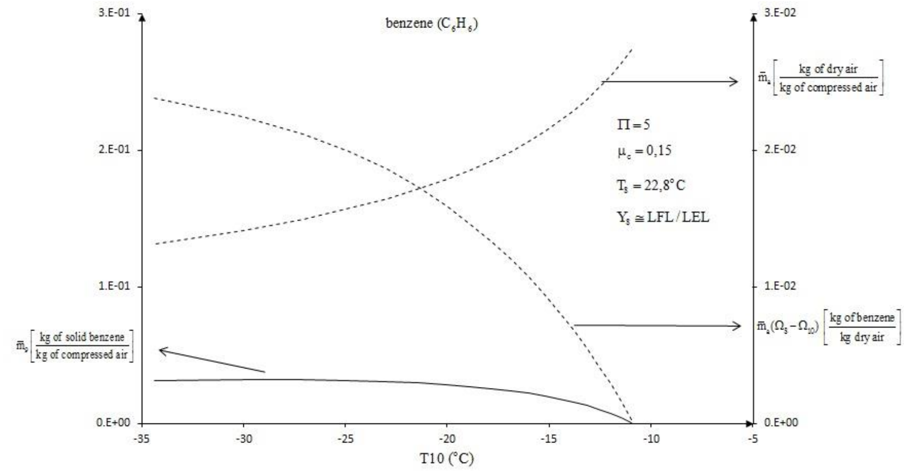

Figure 7 - Influence of temperature variation in state 10, of the dry air flow admitted at the CSHE and the difference in benzene quantity in states 8 and 10 in system`s performance

3. VORTEX TUBE SYSTEM FOR SIMULTANEOUS CONTROL OF CONCENTRATION OF OCTANE AND BENZENE VAPORS IN AIR MIXTURES

3.1 Physical model

Since gasoline is a complex mixture of several hydrocarbons, it is necessary to create a model involving the two hydrocarbons in a mixture with air in order to obtain a greater practical representativeness. The physical model of the device is the same as shown in Figure 1.

As can be seen in Figure 8, the saturation temperature of octane is greater than the saturation temperature of benzene, so octane removal begins before the temperature of the mixture reaches the saturated solid curve of benzene. The temperature of the mixture continues to be reduced until it reaches the vertical line formed by the points 10a, 9b and 9o (FIG. 8) which are the lean hydrocarbon mixture, benzene and octane temperatures at the Cool Side Heat Exchanger of the tube (CSHE) respectively. The temperature of the cold air generated by the tube, represented in the figure by the line Tc, is lower than the temperature of the mixture at the end of the removal process, which allows an even greater decrease of the temperature of the mixture if there is a decrease of the mass allowed in the CSHE. The reduction in temperature forces the expulsion of the hydrocarbon particles in order to maintain the thermodynamic equilibrium of the mixture, causing a decrease in the partial pressure of benzene and octane. The hypotheses assumed for the creation of the mathematical model are:

- Steady State operation.
- The Dalton model is used to calculate the properties of the dry air mixture components with benzene and octane vapors.
- The behavior of each of the components of the mixture is not influenced by the presence of the other components.
- All flows are considered to be at constant pressure.
- All control volumes are adiabatic and do not perform mechanical interactions with the environment.
- Variations of kinetic and potential energy at the macroscopic level are considered negligible.
- Instantaneous thermodynamic equilibrium between dry air and hydrocarbon vapors.
- Atmospheric air humidity is considered negligible.

After the start of the octane liquefaction its partial pressure in the mixture decreases causing an increase in the partial pressure of the air in the same proportion, keeping the total pressure of the mixture constant. Then the solidification of the benzene starts while the octane liquefaction still occurs, and consequently the partial pressure of the air increases at an even higher rate to maintain constant the total pressure of the mixture.

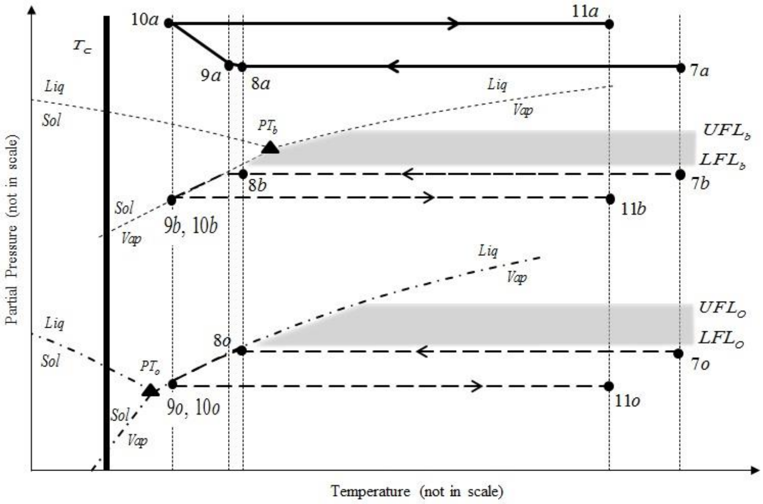

Figure 8 - Phase diagram of air / benzene / octane mixture

3.2 Mathematical model

As previously accomplished the mathematical model is constructed from the energy balance equations in each of the control volumes, in this case however, the mixture comprises dry air, octane and benzene simultaneously. After performing some algebraic manipulations in the energy balance for the CSHE control volume it is possible to find the equation that calculates the (dimensionless) dry air flow admitted in the CSHE:

$$\bar{m}_a = \frac{\mu_C c_p \left(T_4 - T_C\right)}{c_{pa}\left(T_8 - T_{10}\right) + \sum\limits_{j=ben,oct} \left(\Omega_{8j} h_{8j} - \Omega_{10j} h_{10j}\right) - \left(\Omega_{8j} - \Omega_{10j}\right) h_{9j}} \qquad (10)$$

3.3 Results

Plotting the curves of the amount of hydrocarbon removed by the system when extracting both hydrocarbons simultaneously on the same plot of the amount of octane or benzene removed when removed in a simple mixture with air, the influence of one component on the other can be clearly seen. The octane extraction process with simultaneous removal of benzene takes place at a lower flow rate of mixture than the flow rate of the point of maximum of the octane removal when in a simple mixture with air.

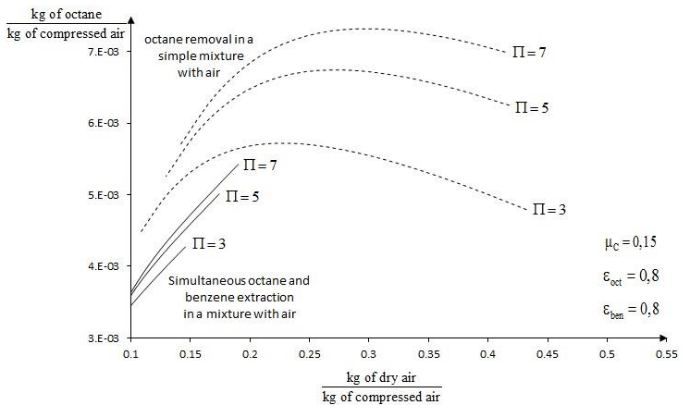

Figure 9 - Octane removal in a simple mixture with air and simultaneous removal of octane and benzene in a mixture with air

The same effect can be observed for benzene, although it is able to remove benzene with a lower mass of mixture admitted the CSHE, the amount of benzene removed decreases when octane is removed simultaneously.

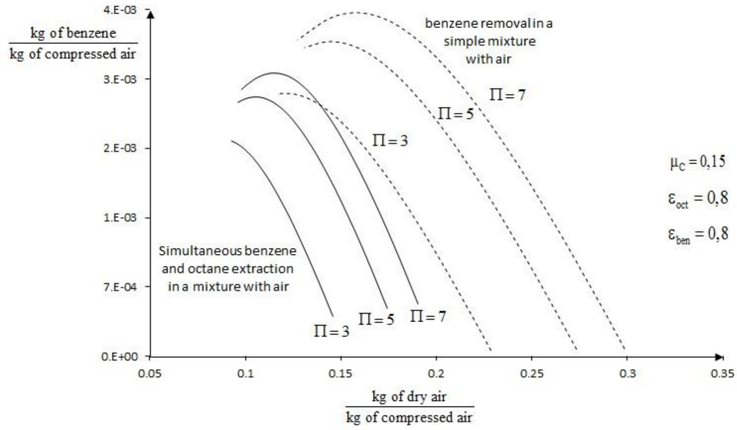

Figure 10 - Benzene removal in a simple mixture with air and simultaneous removal of benzene and octane in a mixture with air

4. CONCLUSIONS

The results obtained in this study demonstrate that the new equipment with Vortex Tube presented in the work represents a new technical and economically feasible solution for the thermo mechanical separation of the hydrocarbon vapors from mixtures with air through the liquefaction and / or solidification. In addition to the possibility of reusing the fuel at the end of the process, the new device presented has the ability to keep the mixture outside the risk zone even when the concentration is below the lower limit of flammability, combining a safe process with the efficient separation of the vapors of hydrocarbons.

The mathematical model was developed to initially calculate the specific mass flow (per kilogram of compressed air supplying the Vortex Tube) of octane or benzene removed when the hydrocarbons are in simple mixtures with dry air. The calculated numerical results indicate a potential for octane removal between 5.2-6.8 g octane / kg compressed air and 2.7-3.5 g benzene / kg compressed air when the Vortex Tube is fed with pressures within the range of 3 - 7 bar.

Taking into account the simultaneous presence of several chemical species in the actual composition of petroleum derived liquid fuel; calculations were carried out in a second stage to determine the specific mass flow of hydrocarbon vapors simultaneously removed by the same device when the mixture is composed of air, octane and benzene. Under these conditions the numerical results obtained indicate a potential for removal between 5.0 g of hydrocarbon / kg of compressed air (3.0 g octane and 2.0 g benzene) and 6.6 g hydrocarbon / kg air (3.9 g of octane and 2.7 of benzene) while maintaining the supply pressure of the Vortex Tube in the range of 3-7 bar.

In order to increase hydrocarbon removal capacity, the energy exchange between the mixture and the cold air of the Vortex tube should be potentiated, for that is suggested that the temperature of the mixture is reduced before being admitted in the heat exchanger on the cold side of the tube. To this end, the hydrocarbon rich mixture may be directed to a heat exchanger where it would be cooled down, losing energy to the lean hydrocarbon mixture that leaves the heat exchanger on the cold side of the tube at low temperature. The new control volume was considered into the mathematical model and the hydrocarbon removal potential (octane and benzene) increased to 6.2 - 8.0 g hydrocarbon / kg of compressed air when maintaining the same inlet pressure levels for the Vortex Tube (3 - 7 bar).

Considering the conventional COPEL (the Power supply company of the state of Paraná, Brazil) fare that is R$ 0.64543/kWh (Subgroup 3), the estimated operational cost for the new equipment with Vortex Tube presented in this work ranges from R$ 2.73 up to R$ 3.75 per kilogram of hydrocarbon removed for the specified pressure levels at the Vortex Tube inlet.

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