

Experimental Study of Isoamilenes Separation from C₅ Fraction through Extractive Distillation with Monopropilenglicol

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Abstract

For the improvement of saturated hydrocarbons from unsaturated hydrocarbons separation, from the C₅ fraction, experimental determinations of the liquid-vapors equilibrium have been made, for the saturated i-C₅ and n-C₅ hydrocarbons –isoamilenes in the presence of a new solvent. The results of the experiments are presented under the form of y-x system equilibrium diagrams without solvent.

Key words: liquid – vapor equilibrium, equilibrium diagrams, isoamilenes, solvent.

Introduction

It is well-known that, in fractioning, the relative volatility represents a measure of the separation procedure cost of a binary component when $\alpha' < 1,05$, because, in this field, the trays necessary and the reflux ratio reach a very high level, thing which leads to an exaggerated increase of the investment and operating expenses. That is why, in cases of this sort, scientists have tried to increase the relative volatility, so that the separation process should occur easier and with lower costs.

One of the possibilities of increasing the relative volatility level is that which represents the basis of the extractive fractioning process, which means, adding a lesser volatile substance to the mixture that needs to be separated, a substance named solvent, dissolvent or extractive distillation agent, in the presence of which non-ideal behavior is created, or modifies the existing non-ideal behavior, thing which finally leads to the increase of the relative volatility level.

In the case of liquid phase non-ideal behavior binary mixtures, the relative volatility α' can be defined with the help of the relation (1).

$$\alpha' = \frac{P_1}{P_2} \cdot \frac{\gamma_1}{\gamma_2} \quad (1)$$

Where: $\frac{P_1}{P_2}$ and $\frac{\gamma_1}{\gamma_2}$ represent the vapor pressures ratio, respectively the ratio of the activity coefficients of the two components among which the separation process takes place.

In order to increase the relative volatility α' , the solvent must act differently as compared to the other two components of the mixture. This feature, of the solvent's behaving differently, in the sense of a faster increase rate of γ_1 compared to γ_2 , is named, selectivity. So, the essential characteristic of the solvent in favor of an easy separation is selectivity, feature that needs to be as high as possible throughout the entire concentration domain of the mixture.

In the case further presented, I have analyzed a pentanic fraction which has been considered a hypothetical binary, the alkanes being the more volatile component, and the lesser volatile component being the alkenes. In view of optimizing this process of separation, experiments have been performed regarding the influence of the monopropilenglicol solvent $C_3H_8O_2$ (MPG) on the relative volatility of the isoamilenes – C_5 saturated hydrocarbons hypothetical binary.

Experimental details

These experimental determinations have been performed in 2 stages.

1. The liquid – vapor equilibrium data has been determined for the pentanic fraction, without the solvent.
2. The liquid – vapor equilibrium data has been determined for the same pentanic fraction, but this time, in the presence of MPG.

1. Experimental determinations without solvent

The experimental data has been recorded with the help of an OTHMER type apparatus, built and adapted for the parameters of the extractive distillation and which is presented in figure 1.

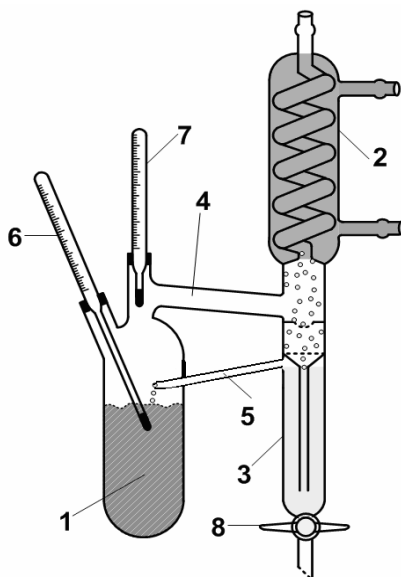


Fig. 1. The “OTHMER type” equilibrium apparatus which deals with the recirculation of condensed vapors.

Apparatus description and work mode

The equilibrium device shown in figure 1, is formed of a distillation vessel (1), an ascendant condenser (2), an accumulation tank, destined for the distilled product, the connectors (4) and (5), two thermometers, (6) and (7) for measuring the liquid and vapor temperature, a faucet (8) necessary for testing samples from the accumulation tank.

Because the accumulation tank is linked with the atmosphere through the vertical condenser, the equilibrium determinations are calculated at atmosphere pressure.

In order to obtain a $x - y$ equilibrium point, we must pass through the following stages:

- a mixture quantity is introduced in the distillation apparatus
- the faucet and the thermometers are connected to the apparatus
- the cooling water is turned on
- the heating system of the distillation tank is connected to the electric network with the help of an autotransformer.

On account of that heat application, the liquid from the distillation tank is brought to the boiling point, the generated vapors being totally condensed in the ascendant condenser, the product being added to the accumulation tank. When the accumulation tank is filled with liquid, the recirculation of the condensed product in the distillation vessel and after approximately an hour of circulation, a stationary functioning regime is reached. This stage of the process is characterized through a constancy in time of the two temperatures indicated by the thermometers (6) and (7).

Reaching a stationary status does not necessarily mean that the thermodynamic equilibrium point has been touched. At the point of thermodynamic equilibrium, the vapor and liquid temperatures are identical, in the two phases there are no temperature or concentration gradients.

Because the heat application is an irreversible pronounced process, a temperature gradient in the two phases inside the distilling vessel must be maintained at all times. This is the reason why the thermometers (6) and (7) show different temperatures.

In view of decreasing the temperature gradient from within the distillation vessel and in this manner, reaching a stationary regime closer to the thermodynamic equilibrium status, the distillation tank is insulated against the environment with a metal sheet casing.

After a recirculation regime that lasts approximately 2 hours, 2-3 cm³ condensed product samples have been taken (vapor phase test) and from the residual liquid (liquid phase) for the chromatographic analysis of the fractions.

When graphically representing the $y - x$ equilibrium curve, the mixture was considered to be binary, the saturated hydrocarbons being the more relative component, whereas the unsaturated hydrocarbons being the lesser volatile component.

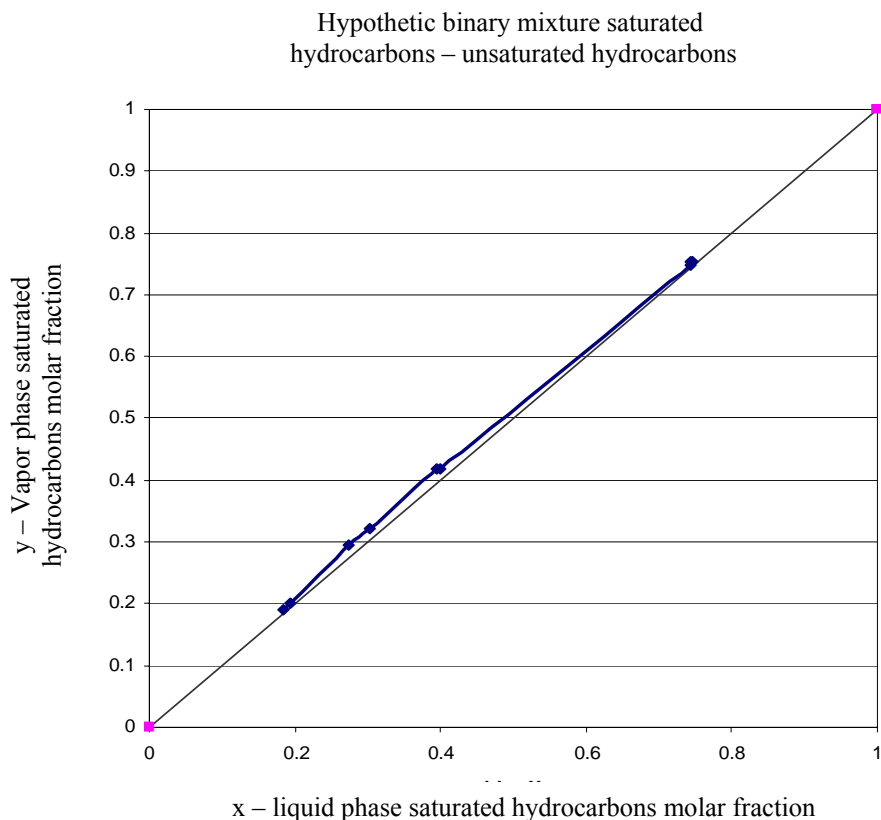


Fig. 2. The x-y curve of the isoamilenes – C₅ saturated hydrocarbons hypothetical binary mixture, where y and x represent the molar fractions of the more volatile component in vapor, respectively in liquid.

As it can be easily observed the curve, is situated very close to the diagonal, α_m being 1,04, fact which denotes that a separation, given these conditions, is practically impossible.

2. Experimental determinations in the presence of solvent.

Initially, in order to eliminate possible errors regarding the quality of the solvent, this has been purified in a Fisher type fractioning column, after which, its boiling point was determined and it coincided with the one described in the literature, the difference being 0,4⁰C.

This new solvent, has been used in two different concentrations in mixture with the pentanic fraction, expressing the concentrations at the equilibrium x' and y' being made "on base without solvent".

In the case of the experimental determinations in the presence of a solvent, there has been used the same type of OTHMER apparatus as the one shown in figure 1. In order to avoid the solvent's leaking inside the collecting vessel, this has been filled with C₅ fraction, before the start of the experiment. In this manner, the solvent's concentration from within the distillation vessel, is determined from the beginning of the experiment and has remained constant during the whole time. For this type of experiment, only condense phase samples have been taken, the determination of the residual liquid's composition being made through the operation of subtraction, because the composition of the whole mixture was known in the moment of its introducing in the apparatus.

When graphically representing the y – x equilibrium curves, the mixture was considered to be a saturated hydrocarbons – unsaturated hydrocarbons, hypothetical binary mixture on base "without

solvent”, the saturated hydrocarbons being the more volatile component, whereas the unsaturated hydrocarbons being the lesser volatile component.

In the following stages, from the experimental results, there has been a solvent with a 85% concentration and 95%, and there have been obtained the following y – x equilibrium curves, presented in figure 3.

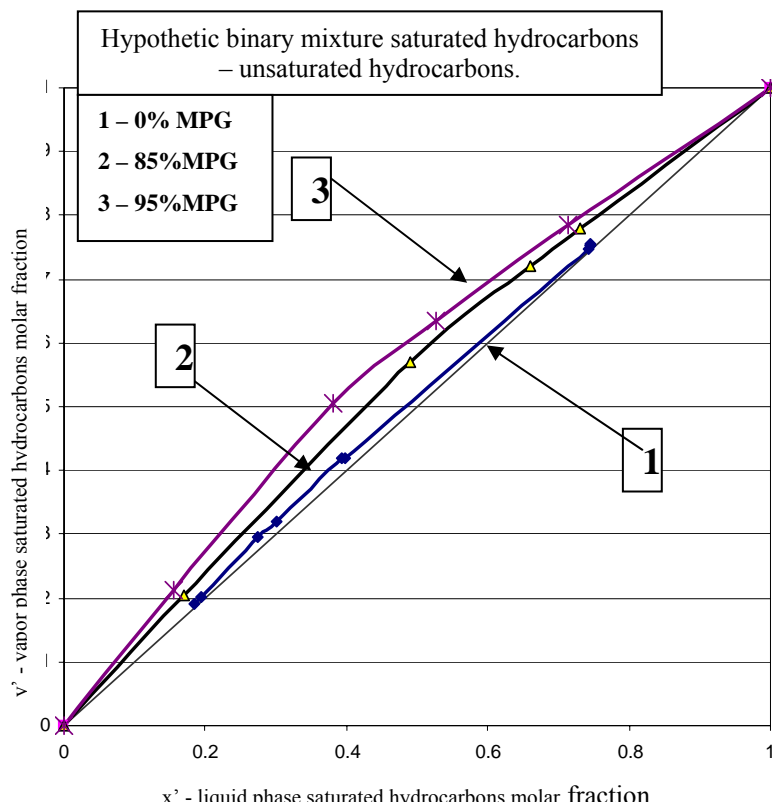


Fig.3. The influence of the solvent’s (MPG) concentration on the liquid - vapor equilibrium curve, in the y’ and x’ coordinates, of the isoamilenes – C₅ saturated hydrocarbons hypothetical binary mixture, where y’ and x’ represent the molar fractions of the more volatile component in vapor, respectively in liquid, after the total removal of the solvent, respectively, the concentrations of the phases at the point of equilibrium, on base “without solvent”.

Results and discussions

From the analysis of these curves, the conclusion resides in a higher value of the concentration of the vapor phase saturated hydrocarbons as compared to their liquid phase, for the experiment performed in the presence of the solvent.

For the hypothetical binary, saturated hydrocarbons – unsaturated hydrocarbons in the presence of a 85% concentration and 95% mass MPG solvent, the α'_m average relative volatility, was calculated with the help of the relation (2).

$$\alpha'_m = \frac{\frac{y'_m}{1 - y'_m}}{\frac{x'_m}{1 - x'_m}} \tag{2}$$

where:

- y_m' - the molar fraction of the more volatile component in gaseous phase;
- x_m' - the molar fraction of the more volatile component in liquid phase;
- α_m' the volatility of the component with a boiling point lower, as compared to the component with a higher boiling point for $x_m'=0,5$ in the presence of the solvent.

Table 1. The average relative volatility α_m' for the unsaturated hydrocarbons - saturated hydrocarbons hypothetical binary mixture in the presence of a 85% concentration and 95% mass MPG.

Unsaturated hydrocarbons – saturated hydrocarbons hypothetical binary mixture dissolvent	
solvent	α_m' pentru $x = 0,5$
MPG 0%mass	1,04
MPG 85%masss	1,44
MPG 95% masss	1,78

For equilibrium curve number 2 from figure 3 $x_m'=0.5$ and $y_m'=0.5902$, the average relative volatility being $\alpha_m'=1.44$ in the case of 85% mass solvent in the mixture, and for equilibrium curve number 3 from figure 3, $x_m' = 0.5$, and $y_m' = 0.6403$, $\alpha_m' = 1.78$ for 95% mass solvent in the mixture.

The quantitative observation regarding the influence on the separation of isoamilenes from C_5 saturated hydrocarbons is made through the minimum reflux ratio (R_{min}) and through the minimum number of trays (N_{min}).

Regarding R_{min} it can be calculated with the help of the following relation

$$R_{min} = \frac{x_d - y_f}{y_f - x_f} \quad (3)$$

where:

- x_d – represents the C_5 saturated hydrocarbons molar fraction in the highest purity product.
- x_f - the C_5 saturated hydrocarbons molar fraction in liquid phase of the feed flux
- y_f - the C_5 saturated hydrocarbons molar fraction in vapor phase of the feed flux (at equilibrium with the liquid phase which is of the x_f concentration)

The y_f concentration value is calculated with the help of the relation (4)

where α_m' represents the average relative volatility of the isoamilenes – C_5 hydrocarbons binary (on base without solvent), value that is calculated with the help of the relation (2).

Regarding the (N_{min}) minimum number of trays, it can be calculated with the help of Fenske's relation:

$$N_{min} = \frac{\lg \frac{x_d}{1-x_d} - \lg \frac{x_b}{1-x_b}}{\lg \alpha_m} - 1 \quad (5)$$

where x_b – represents the C_5 saturated hydrocarbons molar fraction in the product at the base of the fractioning column. Using these relations, the (N_{min} , R_{min}) minimum parameters for the multiple variants taking into account the α_m' average relative volatility, has been calculated. The results are presented in table 2.

Taking into account the x_f , feed flux composition, values for x_d , x_b , have been imposed, thus observing the variation of the R_{min} and N_{min} parameters in the case of isoamilenes – C₅ saturated hydrocarbons hypothetical binary and in the presence of the (MPG) solvent. The obtained values are presented in table 2.

Table 2. The variation of R_{min} and N_{min} parameters in the case of separating the unsaturated hydrocarbons – saturated hydrocarbons hypothetical binary, without and in the presence of the solvent, for fixed values of the x_f , x_d , x_b parameters.

Solvent %	α	x_d	x_f	x_b	y_f	R_{min}	N_{min}
Without solvent	1.04	0.90	0.53	0.10	0.54	36.92	111.04
	1.04	0.90	0.53	0.20	0.54	36.92	90.21
	1.04	0.90	0.53	0.30	0.54	36.92	76.63
MPG 85%	1.44	0.90	0.53	0.10	0.62	3.16	11.05
	1.44	0.90	0.53	0.20	0.62	3.16	8.83
	1.44	0.90	0.53	0.30	0.62	3.16	7.35
MPG 95%	1.78	0.90	0.53	0.10	0.67	1.85	6.62
	1.78	0.90	0.53	0.20	0.67	1.85	5.21
	1.78	0.90	0.53	0.30	0.67	1.85	4.28

The obtained results show that N_{min} and R_{min} decrease approximately 11 times in the case “without solvent” as compared to its use at a 85% mass solvent.

In the case of using a 95% mass solvent concentration as compared to the situation “without solvent”, the results show that N_{min} decreased approximately 17 times and R_{min} decreased approximately 21 times.

In the case of increasing the solvent’s concentration from 90% mass to 95% mass, N_{min} decreases 2 times and R_{min} decreases approximately 1,8 times. For a better observation of R_{min} and N_{min} variations, I have provided the graphic from figure 4.

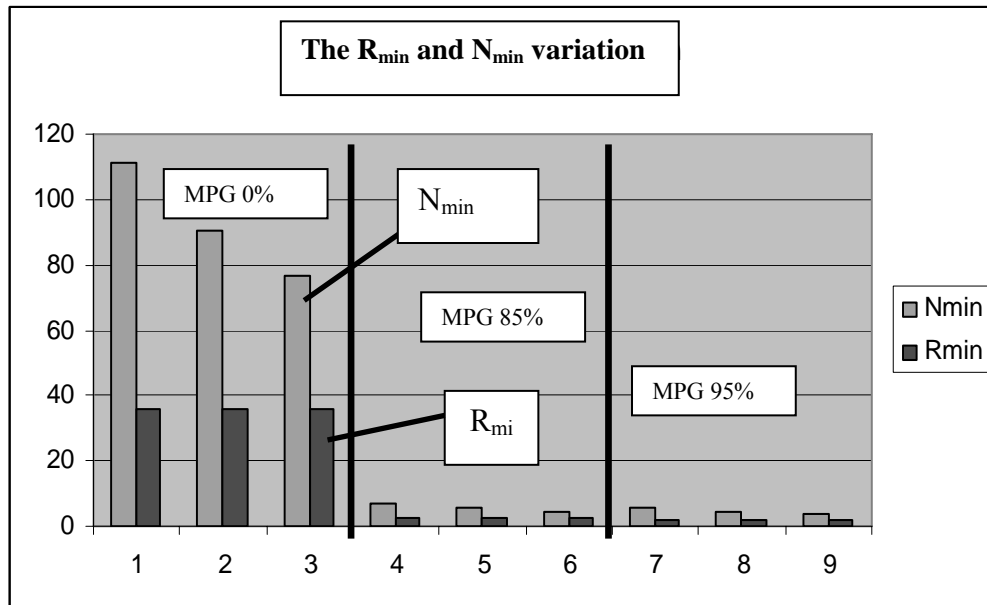


Fig. 4. The R_{min} and N_{min} variation in the case “without solvent”, parts 1,2,3; in the presence of a 85% mass solvent, parts 4,5,6; in the presence of a 95% mass solvent, parts 7,8,9.

Conclusions

For the experimental determinations of the previously considered binary equilibrium points, the “OTHMER type equilibrium apparatus that deals with condensed vapors recirculation”, presented in figure 1, has been used, apparatus built and calibrated in the laboratory to suit the conditions for extractive distillation.

In the case of $y - x$ equilibrium curves determined in the presence of a MPG, we can observe a substantial α' relative volatility increase, of the hypothetic hydrocarbon, respectively on base “without solvent”, for the 85% mass MPG in the system, comparing with the system without solvent the α' relative volatility is rising from 1,04 to 1,44 and for 95% mass solvent up to 1,78, which means a better separation .

The R_{\min} and N_{\min} calculated values clearly prove the substantial improvement of the separation process of saturated hydrocarbons from isoamilenes in the presence of the monopropilenglicol, the R_{\min} is smaller in presence of MPG in the system this parameter decrease from 36 for the experiments without solvent to 3,16 for MPG 85% mass in to the mixture and to 1.85 for 95% mass MPG, for the same concentrations of feed, top, and base products. Also for the same concentrations of the products N_{\min} is decreasing form 111 to 4,28 in the presence of 95% mass MPG in the system

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Studiul experimental al separării izoamilenelor din fracția C_5 prin fractionare extractivă cu monopropilenglicol

Rezumat

Pentru îmbunătățirea separării hidrocarburilor saturate de hidrocarburile nesaturate din fracția pentanică C_5 , s-au efectuat determinări experimentale de echilibru lichid vapori pentru sistemul hidrocarburi saturate iC_5 și nC_5 – izoamilene în prezență de un nou solvent. Rezultatele experimentale sunt prezentate sub forma diagramelor de echilibru în sistem $y-x$ pe bază fără solvent