Production of Anhydrous Ethanol Using Azeotropic Distillation with Petroleum Cuts or Gasoline Pool

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It is now a fact that biofuels have a certain future, whether it is about "biodiesel" or "bioethanol". EU intends to impose continuous increase of biofuels proportion in commercial products. Ethanol can be used "per se" in commercial gasoline (in different proportions) or can be used instead of methanol in etherification reaction. In both cases it is necessary to use anhydrous ethanol. There are several drying processes: azeotropic distillation, extractive distillation, pressure swing distillation, and adsorption. Present work proposes azeotropic distillation using like entrainer petroleum cuts or commercial gasoline pool. Finally, anhydrous ethanol contains hydrocarbons in several proportions and can be used like commercial gasoline component. The main advantage of this process is that the separation alcohol-hydrocarbons is not so tight, resulting important reducing of the energy consumption in process. There is used a rigorous thermodynamic model as the results are very trusted.

Keywords: biofuels, azeotropic distillation, extractive distillation

The use of the biofuels is clearly necessary and it is commanded by the global concerns regarding the effect of the carbon dioxide on the environment. Even if the opinions are parted between the biofules supporters and those who do not consider it a long term solution, the statal and european regulations command the continual increase of biofuels proportion. Therefore, the european regulations [1] impose a minimum level of 2% biocarburants reported to the whole amount of gasoline and Diesel fuels (2005), a following increase of the percentage being scheduled to reach the value of 5.75% in 2010. The indicated values are considered taking the energy content into account. For example, a percentage of 5.75 for gasoline means 8.75% of ethanol weight or 14% of ethyl tert- butyl (ETBE). The cost of biofules is generally higher than the one of the correspondent fosile fuels, but the applied tax exception policy can modify this report. Austria, France, Germany, Italy, Spain, Sweden and Great Britain have 0 taxes for the biofuels.

The effect of adding ethanol or ethers into the gasoline is shown by the oxygen content, by the volatility and the octane value.

The european regulations command a maximum ethanol content of 5% volume, 5% volume ethers, 2.7 % oxygen weight and a maximm of 18% volume of olefines. World-Wide Fuel Charter [2] brings pressure to bear on the producers by wanting to decrease the olefines content to 10% volume.

The balance between the ethanol and the ethers content is the subject of the optimal correlation between the cost and the oxygen content. The maximum ethanol content of 5% volume means an oxygen content of 1.77% weight, while a maximum content of 15% volume ethers means 2.26% weight oxygen. As far as the costs are concerned, optimal value means the maximum allowed by the oxygen, which is 15% volume ETBE and 1% volume ethanol.

The volatility of the ethanol is higher than the one of the ethers (ETBE or TAEE). The Reid vapor pressure of the ethanol is of 18 psia, that of the ETBE is of 4.0 psia and the one of the TAEE is of 1 psia. Therefore, the ethanol addition substantially increases the vapor pressure of the gasilene, forcing the producers to decrease the light components content. Even though the ethanol's octanic number is higher (115) than the one of the ethers (ETBE – 110 and TAEE – 100), the ether content leads to higher increases of the octanic number for the gasoline. Thereby, 5% volume ethanol increase the octanic number of the gasoline with 1.5 points, 15 % ETBE with 3.8 points and 15% ETBE with 2.3%. It can be clearly observed that these increases compensate the losses on account of the decrease of the sulphur content.

In the above mentioned context, the ethanol plays a very important role, that will certainly increase in the future. This is why the ethanol anhidrization is both scientifically and technologically important.

The ethanol anhidrization using azeotropic processes

The ethanol is nowadays produced by hydrating the ethylene and by fermentation processes of the biomass (cereals, agricultural, forest or other organic waste). The ethanol price depends on the cost of the biomass production and on the fermentation cost. The first component depends on the conversion – fermentation stage and on its recovery from the fermentation product. No matter what the ethanol source is, the result is a diluted solution. The ethanol separation also depends on the final purpose of its use and on the actual impurities. Disregarding impurities other than water, the most difficult problem of this separation is the fact that the ethanol and water create a low boiling point azeotrope. Its composition changes once the pressure changes, the ethanol content increases once the pressure decreases, and the azeotrope disappears at 11.5 kPa.

The ethanol anhidrization can be completed by a series of procedures such as: the azeotropic distillation, the extractive distillation, the azeotropic – extractive distillation, by pressure swing distillation and adsorption [3].

The so called azeotropic processes (the azeotropic distillation, the extractive distillation, the azeotropic – extractive distillation, are far from being the most frequently used anhidrization processes.

The azeotropic distillation uses a third component that, along with one of the components from the innitial binary creates a binary azeotrop. Since most of the time a low boiling temperature azeotrope is created, the third component is called an entrainer. A special case is the one

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Table 1
RULES FOR ENTRAINER SELECTION

A. Mixtures with a minumum-boiling azeotrope
1. Low boiler (lower than the original azeotrope).
2. Medium boiler that forms a minimum-boiling azeotrope with the low boiling species.
3. High boiler that forms minimum-boiling azeotropes with both species. At least one of the new minimm-boiling azeotropes has a lower boiling point than the original azeotrope.
Mixtures with a maximum-boiling azeotrope:
1. Low boiler (higher than the original azeotrope).
2. Medium boiler that forms a minimum-boiling azeotrope with the high boiling species.
3. High boiler that forms maximum-boiling azeotropes with both species. At least one of the new maximum-boiling azeotropes has a higher boiling temperature than the original azeotrope.

when a ternary azeotrope is formed, this case being the actual purpose of this article. The main condition for a good entrainer is to increase the volatility of a component more than the other one's. The use of an entrainer that forms a heteroazeotrop leads to simplifed technological solutions by using two columns that have common condenser and reflux drum.

The extractive distillation uses a third relative nonvolatile component (solvent) that increases the relative volatility of one component in the detriment of the other, when the solvent is present in relatively high concentrations in the liquid phase. In the case of the water-ethanol mixture, the solvent may increase the volatility of the ethanol (in this case the ethanol is obtained on the top, the water remaining at the base with the solvent) or the one of the water (when the water is obtained at the top and the ethanol is obtained as a basic product along with the solvent). Following the azeotropic distillation, the solvent recovery/regeneration happens by separating it from the mixture component-solvent that leaves the first column.

Another process could be a combination between the azeotropic distillation and the extractive one (AZEX), which uses a mixture of two components one of which plays the role of the entrainer, and the other one is the solvent. Sometimes the same component may play both roles.

Black [4] presented the first complete study based on modeling and simulation of the process which compares different anhydrization processes based on operation costs. In the literature there are a impressive number of papers [5, 6, 7] about azeotropic processes. The use of simulation software [8, 9] and of rigurous thermodynamic models [10] help the studies in the fields.

Choosing the entrainer

The main problem of the azeotropic distillation is choosing the entrainer. The old procedure has been replaced by the use of the termodynamical methods, the use of residue curve maps (RCM), the distillation limits and the regions in the ternary diagrams [5, 11]. The RCM describe the composition of the liquid phase in a simple distillation process that takes place either in a baloon, or in a distillation process that takes place in a packed column. The distillation limits are curves that separate the distillation regions. The distillation region is that area of the ternary diagram where all the residue curves have the same starting point and the same arrival point. The main restriction is that the curve that represents the distillation column cannot have the ends in different regions. By overtaking these restrictions the sinthesys of the azeotropic mixtures separation train is completed.

Stichlmair and Herguijuela [6] have presented some rules for choosing the entrainer based on the operating lines that cross or not the distillation limits. These rules are presented in the table 1[6].

The technological evolution has turned the past few years' researches and the accomplishments to the area of the use of some entrainers that form ternary azeotrops and two liquid phase.

The regards that can be made using the ternary diagrames cannot be completed without a detailed simulation of those certain processes. There are modern tooles, simulation software [8, 9], that allow the extremely accurate process simulation.

This paper proposes a new class of entrainers. The use of different petroleum cuts and even that of gasoline pool seems an interesting and attractive technological solution as far as the entrainer and the costs are concerned.

Thermodynamics analyses of vapor-liquid-liquid equilibrium for the systems presented in the study

Not every study of these systems can be trusted if rigorous termodynamical models are not used. On the other hand, it is impossible to consider all the components presented in petroleum cuts or in gasoline pool for the calculations. Fortunately, the thermodynamic packages from the simulation programmes [8, 9] cover most of the components that can be taken into account considerring their content in those certain fractions. It is completely barren to consider substances that are present in low proportions because their influence is not significant.

Prausnitz and Renon have proposed an activity coefficients calculation model [5], NRTL model (Non-Random Two Liquids).

Some of the NRTL model's performances are:

- the 3 to 8 parameters allow the rather exact representation of the activity coefficients for binary mixtures and their variation on a large domain of temperature;
- allows the calculation of the liquid–liquid equilibrium in binary, ternary and multicomponent mixtures;
- the calculation of the activity coefficients in liquid-liquid multicomponent systems is done starting from ternary equilibrium data;
- allows the calculation of activity coefficients in multicomponent systems starting from the liquid-liquid equilibrium data of all the binaries in the considered system.

Table 2

AZEOTROPES IN THE SYSTEMS ETHANOL - WATER - BENZENE

Temp. °C	Classification	Type	No. Comp.	Composition, molar fraction		
				ETHANOL	WATER	2-MB
69.35	Saddle	Heterogeneous	2	0	0.299	0.701
64.02	Unstable Node	Heterogeneous	3	0.281	0.1914	0.5276
78.15	Saddle	Homogeneous	2	0.8952	0.1048	0
67.71	Saddle	Homogeneous	2	0.4452	0	0.5548
Temp. °C	Classification	Type	No. Comp.	Composition, weight fraction		
				ETHANOL	WATER	2-MB
69.35	Saddle	Heterogeneous	2	0	0.0896	0.9104
64.02	Unstable Node	Heterogeneous	3	0.2247	0.0599	0.7154
78.15	Saddle	Homogeneous	2	0.9562	0.0438	0
67.71	Saddle	Homogeneous	2	0.3213	0	0.6787

For this paper, the termodynamic ALCOHOL PACKAGE from the PRO/II software [8] has been chosen. This model is specialized in the alcohols anhidrization and it is based on the NRTL [10] model, a model that can correctly describe the behaviour of the heterogenous azeotropic systems. The first stage consists of the check of the binary interaction parameters for the three binaries that can be built starting with three components (alcohol, water and entrainer), and the second stage is calculus of azeotropic points (binary and ternary) and to calculate and represent vapor-liquid-liquid equilibria in ternaru diagram.

All calculated data, based on rigorous model [8], show that the selected entrainers are from all categories presented by Stichlmair and Herguijuela [7]. So:

-components 2-methyl butane (NBP 27.84°C), *n*-pentane (NBP 36.07°C) , 2-methyl pentane (NBP 60.26°C) and *n*-hexane (NBP 68.73°C) are low boilers, having normal boiling points smaller than ethanol (NBP 78.29°C) - case A.1 from table 1;

-components benzene (NBP 80.09°C), cyclo-hexane (NBP 80.72°C), 3-methyl hexane (NBP 91.85°C) and n-heptane (NBP 98.43°C) are medium boilers, having intermediate normal boiling points - case A.2 from table 1;

-toluene (NBP 110.63°C) is high boiler, having normal boiling points greater than water - case A. 3 from table 1.

Ternary azeotropes formed by ethanol, water and every entrainer are minimum boiling azeotropes and have a lower boiling point than the original azeotrope (ethanol-water - NBP 78.15°C).

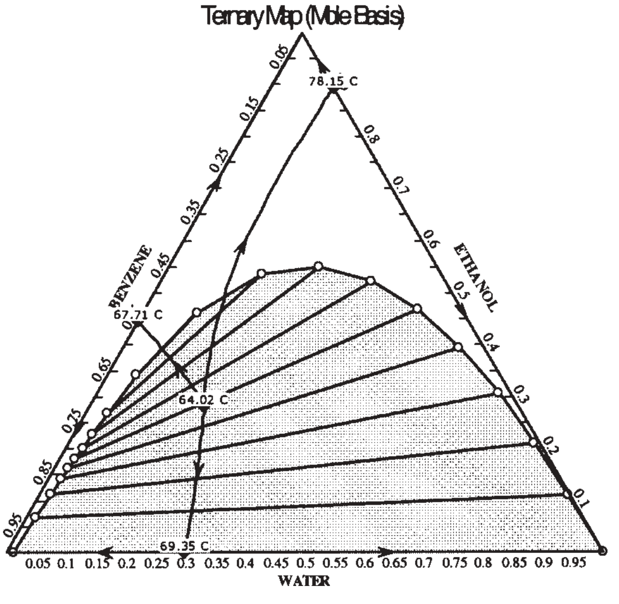

Fig. 1. Residue curve map (RCM) for system ethanol - water - benzene

For example, we present only one system, ethanol-water-benzene (table 2).

Also, we used NRTL model [8] to build ternary diagrams for the systems ethanol-water-entrainer, for all entrainers considered in this paper. All diagrams are build using Aspen software [9]. Considering space, we present diagram only for one system, ethanol-water-benzene (fig. 1).

All ternary azeotropes for the sytems presented in the paper are heterogenous, spliting into two phases: entrainer phase and water phase. This fact alows to use separation systems using two columns with common phase separator, but it is only a posibility, not a conviction. The simulations will demonstrate the capabilities of all these components for production of the anhydrous ethanol.

Computer Simulations

Our simulations have four goals:

- to demonstrate that all selected entrainer are adequate for ethanol drying;

-to demonstrate that the both technological variants (with two or three columns), using these entrainers, are adequate for ethanol drying and to find which are the best;

- to demonstrate (and this is the first and main originality of this study), that is more advantageous to leave a certain amount of hydrocarbons in anhydrous ethanol (ethanol product);

- to demonstrate (and this is the second originality of this study) to use petroleum cuts or gasoline pool like entrainer.

Concerning the third goal, the study will demonstrate that is easier to obtain anhydrous ethanol leaving certain amount of hydrocarbons in alcohol. This is because the separation ternary azeotrope – ethanol is not so tight. This amount of hydrocarbons in ethanol does not influence the quality of gasoline after blending with ethanol because all of these hydrocarbons are already presented in the gasoline pool. More, if hydrocarbons have high octane components, any content of such hydrocarbons is desirable. All entrainers considered in this study are presented in petroleum cuts or in gasoline pool. Also, all can be used “per se” or in composition of several petroleum cuts or gasoline component (the case of using of isomerizate C_5 fraction that contains as main component, i-pentane, 99.5% weight). Nowadays, this isomerizate contains, alongside *i*-pentane, *i*-hexane, also high octane component. This is a great advantage because all of these considered petroleum cuts are available in the refineries. Finally, any quantitiy of hydrocarbon left in alcohol reached the gasoline having no entrainer lost..

In this study there are considered two fundamental process flow diagrams for installation. One used a preconcentration column and is presented in figure 2 (classical scheme one), and another used only two columns, being presented in figure 3 [12, 13].

It is important to decide which the concentration of ethanol is after preconcentration column or after first column in the second scheme. In [12] is presented a study concerning this concentration, in fact this is an optimization calculus. We decided to impose a concentration of 70% weight ethanol. This is not so important because all the calculus results are presented comparatively.

The initial composition of raw ethanol is 10% weight (also not so important but close to industrial case) and in all variants ethanol production is 100 kg/h.

Concerning purity of the products we imposed a final content of water in anhydrous ethanol of 0.1% weight and a final content of ethanol in residual water of 0.1% weight. Hydrocarbons content is fixed at 0.1% weight in first instance and, for influence of hydrocarbon content in anhydrous ethanol, at 1, 2, 3, 4, or 5 % weight. All of these ensure the same comparison base in all simulations.

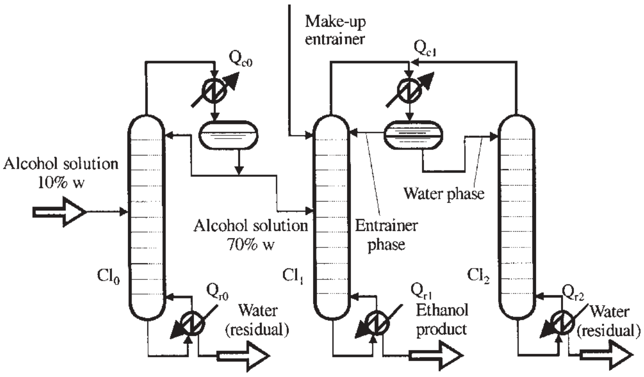

Fig. 2 Process flow diagram for installation (with concentrator) for ethanol dehydration

On these bases we did simulations for every case in this study. In all simulation [8] we use the same number of trays in the two or three columns systems for every entrainer and for each column. Also, we use in the column such pressure as the top separator temperatures are no more than 40°C in order to use for condensation only return water. So, for *i*-pentane and for *n*-pentane we used 3 bar and for all other, 1 bar.

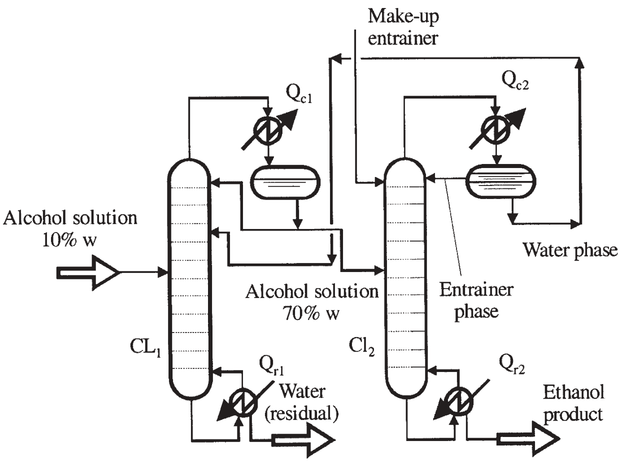

Fig. 3 Process flow diagram for installation with two columns for ethanol dehydration

The performance of every alternative can be appreciated with next parameters:

-duties of condensers for each columns;

-duties of reboilers for each columns;

-total duties of condensers for each installation;

-total duties of reboilers for each installation;

-total production (ethanol product);

-specific duties of condensers (duty/100 kg ethanol product);

-specific duties of boilers (duty/100 kg ethanol product);

-relatively duties (both condensers and reboilers), reported to minimum value for ethanol product.

It must be noted that ethanol product contains ethanol and, also, different quantities of hydrocarbons, according with specifications (1- 5% weight hydrocarbons).

The tables 3 -11 present all above data for each entrainer, respectively 2-methyl butane, *n*-pentane, 2-methyl pentane, *n*-hexane, cyclo-hexane, benzene, 3-methyl hexane, *n*-heptane, toluene, in the system with 3 columns.

The tables 12 - 20 present all above data for each entrainer, respectively 2-methyl butane, *n*-pentane, 2-methyl pentane, n-hexane, cyclo-hexane, benzene, 3-methyl hexane, *n*-heptane, toluene, in the system with 2 columns.

Table 3

FINAL RESULTS FOR 2-METHYL BUTANE IN THE SYSTEM WITH 3 COLUMNS

HC content, % weight	Condenser duty, 10^6 kJ/h			Reboiler duty, 10^6 kJ/h			
	1^{st} column	2^{nd} column	Total	1^{st} column	2^{nd} column	3^{rd} column	Total
0.1	0.397826	0.972796	1.37062	0.455225	0.938502	0.0521300	1.44586
1	0.397826	0.972711	1.37054	0.455225	0.937401	0.0521034	1.44473
2	0.397826	0.972612	1.37044	0.455225	0.936276	0.0520721	1.44357
3	0.397826	0.972515	1.37034	0.455225	0.935253	0.0520411	1.44252
4	0.397826	0.972414	1.37024	0.455225	0.934318	0.0520093	1.44155
5	0.397826	0.972312	1.37014	0.455225	0.933464	0.0519770	1.44067

HC content, % weight	Alcohol product, kg/h	Relative duties 10^3 kJ/100 kg alcohol product		Relative duties, Report to minimum value	
		Cond.	Reb.	Cond.	Reb.
0.1	99.8568	13.7259	14.4793	1.052	1.055
1	100.766	13.6012	14.3375	1.042	1.045
2	101.796	13.4626	14.1811	1.032	1.034
3	102.847	13.3241	14.0259	1.021	1.022
4	103.92	13.1855	13.8718	1.011	1.011
5	105.016	13.047	13.7186	1	1

Table 4

FINAL RESULTS FOR n-PENTANE IN THE SYSTEM WITH 3 COLUMNS

HC content, % weight	Condenser duty, 10^6 kJ/h			Reboiler duty, 10^6 kJ/h			
	1st column	2nd column	Total	1st column	2nd column	3rd column	Total
0.1	0.397826	0.706936	1.10476	0.455225	0.695531	0.0291879	1.17994
1	0.397826	0.706847	1.10467	0.455225	0.694947	0.0291701	1.17934
2	0.397826	0.706752	1.10458	0.455225	0.694323	0.0291512	1.17870
3	0.397826	0.706655	1.10448	0.455225	0.693721	0.0291318	1.17808
4	0.397826	0.706557	1.10438	0.455225	0.693142	0.0291125	1.17748
5	0.397826	0.706457	1.10428	0.455225	0.692581	0.0290925	1.17690

HC content, % weight	Alcohol product, kg/h	Relative duties 10^3 kJ/100 kg alcohol product		Relative duties, Report to minimum value	
		Cond.	Reb.	Cond.	Reb.
0.1	99.9161	11.0569	11.8093	1.0521	1.0544
1	100.826	10.9562	11.6968	1.0425	1.0451
2	101.857	10.8444	11.5721	1.0319	1.0337
3	102.909	10.7326	11.4478	1.0213	1.0224
4	103.983	10.6208	11.3238	1.0106	1.0112
5	105.079	10.5090	11.2001	1.0000	1.0000

Table 5

FINAL RESULTS FOR n-PENTANE IN THE SYSTEM WITH 3 COLUMNS

HC content, % weight	Condenser duty, 10^6 kJ/h			Reboiler duty, 10^6 kJ/h			
	1st column	2nd column	Total	1st column	2nd column	3rd column	Total
0.1	0.397826	0.706936	1.10476	0.455225	0.695531	0.0291879	1.17994
1	0.397826	0.706847	1.10467	0.455225	0.694947	0.0291701	1.17934
2	0.397826	0.706752	1.10458	0.455225	0.694323	0.0291512	1.1787
3	0.397826	0.706655	1.10448	0.455225	0.693721	0.0291318	1.17808
4	0.397826	0.706557	1.10438	0.455225	0.693142	0.0291125	1.17748
5	0.397826	0.706457	1.10428	0.455225	0.692581	0.0290925	1.1769

HC content, % weight	Alcohol product, kg/h	Relative duties 10^3 kJ/100 kg alcohol product		Relative duties, Report to minimum value	
		Cond.	Reb.	Cond.	Reb.
0.10	99.9234	11.0561	11.8084	1.0520	1.0543
1	100.832	10.9555	11.6961	1.0425	1.0451
2	101.867	10.8434	11.5710	1.0318	1.0337
3	102.876	10.7360	11.4515	1.0216	1.0224
4	103.965	10.6226	11.3257	1.0108	1.0112
5	105.078	10.5091	11.2003	1.0000	1.0000

As it can be seen, all simulations were done using entrainer from the list presented above. All of these components can be used “per se” or in mixtures. All of them are presented in different proportions in petroleum cuts or gasoline pool. However, the considered components are main components and the presences of another components are not so significant. More, all components not considered in the study (the reason is easy to understand) are from the same components family like all considered components: paraffins, iso-parrafin, aromatic, naphtenic. From thermodynamic point of view they are similar with studied components, and the result does not differ more. Practically, all components not considered can be assimilated with one from the list of studied components, based on similarity of chemical structure and number of carbon atoms in the molecule. The engineering is a balance between what we have and what we have not. In this case, the assumption is perfectly covered and the results are very close to reality.

The simulation of azeotropic distillation, generally, is hard because the systems are strong nonideal. This case does not differ. This is way it is important the algorithm for distillation simulation. Fortunately, PRO/II [8] has such algorithm, CHEMDIST, even if it is necessary to tune it carefully for convergence. The convergence is reached with great effort and is time consuming.

In order to appreciate the performance of each entrainer we will use condenser duties, reboiler duties, absolute value and reported to alcohol product. Among these parameters the most important is reboiler duties and this will be used. For the same reboiler duties we will consider condenser duties. Vapor loading influences both column

Table 6

FINAL RESULTS FOR n-HEXANE IN THE SYSTEM WITH 3 COLUMNS

HC content, % weight	Condenser duty, 10^6 kJ/h			Reboiler duty, 10^6 kJ/h			
	1st column	2nd column	Total	1st column	2nd column	3rd column	Total
0.1	0.397826	0.354888	0.75271	0.455225	0.707089	0.014502	1.176816
1	0.397826	0.353433	0.75126	0.455225	0.705849	0.014441	1.175515
2	0.397826	0.352937	0.75076	0.455225	0.705008	0.014418	1.174652
3	0.397826	0.352560	0.75039	0.455225	0.704247	0.014399	1.173871
4	0.397826	0.352222	0.75005	0.455225	0.703526	0.014382	1.173132
5	0.397826	0.351903	0.74973	0.455225	0.702833	0.014364	1.172422

HC content, % weight	Alcohol product, kg/h	Relative duties 10^3 kJ/100 kg alcohol product		Relative duties, Report to minimum value	
		Cond.	Reb.	Cond.	Reb.
0.1	99.862	7.5375	11.7844	1.0559	1.0556
1	100.782	7.4543	11.6639	1.0442	1.0451
2	101.765	7.3774	11.5428	1.0334	1.0337
3	102.879	7.2939	11.4102	1.0217	1.0224
4	103.923	7.2174	11.2885	1.0110	1.0112
5	105.023	7.1387	11.1635	1.0000	1.0000

Table 7

FINAL RESULTS FOR CYCLO-HEXANE IN THE SYSTEM WITH 3 COLUMNS

HC content, % weight	Condenser duty, 10^6 kJ/h			Reboiler duty, 10^6 kJ/h			
	1st column	2nd column	Total	1st column	2nd column	3rd column	Total
0.1	0.397826	0.343822	0.74165	0.455225	0.758329	0.014064	1.227618
1	0.397826	0.335945	0.73377	0.455225	0.752136	0.013741	1.221102
2	0.397826	0.333025	0.73085	0.455225	0.749162	0.013625	1.218011
3	0.397826	0.331982	0.72981	0.455225	0.747822	0.013580	1.216627
4	0.397826	0.331172	0.729	0.455225	0.746671	0.013545	1.215441
5	0.397826	0.330465	0.72829	0.455225	0.745609	0.013513	1.214347

HC content, % weight	Alcohol product, kg/h	Relative duties 10^3 kJ/100 kg alcohol product		Relative duties, Report to minimum value	
		Cond.	Reb.	Cond.	Reb.
0.1	99.854	7.4273	12.2941	1.0713	1.0635
1	100.794	7.2799	12.1148	1.0500	1.0451
2	101.765	7.1817	11.9689	1.0359	1.0337
3	102.868	7.0946	11.8271	1.0233	1.0224
4	103.955	7.0126	11.6920	1.0115	1.0112
5	105.047	6.9330	11.5600	1.0000	1.0000

diameter and condenser or reboiler duties. Reboiler duties reflect the greatest part of operation cost. Also, considering that: (1) the all simulation was done for the same number of theoretical trays, (2) the trays efficiency is almost the same, and we can say that the columns height is the same in all cases. Capital costs depends both an column height and column diameter. Finally we can conclude that reboiler duty gives information both for capital costs and operation costs.

In all cases we used theoretical trays because is difficult to appreciate tray efficiency in order to use practical trays. The study of tray efficiency is not the object of this study; the number theoretical trays can be used with enough trust.

The main conclusion of the simulation done for all considered components is that all are adequate for azeotropic distillation for anhydrous ethanol. The reasons for this are:

-all entrainers formed heterogeneous ternary azeotrope; this kind of nonideality allows using the two columns with common condenser and separator;

-the study reveals differences between operating performances, but these are flattening by proportion of each component in the mixture (petroleum cuts or gasoline pool) used like entrainer;

-the using of individual components if they are not obtained “per se” in the refinery is highly none recommended. Using of such components represents the objective of the supplying and storage effort;

Table 8

FINAL RESULTS FOR BENZENE IN THE SYSTEM WITH 3 COLUMNS

HC content, % weight	Condenser duty, 10^6 kJ/h			Reboiler duty, 10^6 kJ/h			
	1st column	2nd column	Total	1st column	2nd column	3rd column	Total
0.1	0.397826	0.800159	1.19799	0.455225	0.463875	0.355543	1.27464
1	0.397826	0.788666	1.18649	0.455225	0.459190	0.348671	1.26309
2	0.397826	0.786553	1.18438	0.455225	0.458282	0.347409	1.26092
3	0.397826	0.785228	1.18305	0.455225	0.457694	0.346618	1.25954
4	0.397826	0.784142	1.18197	0.455225	0.457207	0.345970	1.25840
5	0.397826	0.783162	1.18099	0.455225	0.456766	0.345386	1.25738

HC content, % weight	Alcohol product, kg/h	Relative duties 10^3 kJ/100 kg alcohol product		Relative duties, Report to minimum value	
		Cond.	Reb.	Cond.	Reb.
0.1	98.242	12.1943	12.9745	1.0671	1.0664
1	99.1554	11.9660	12.7385	1.0472	1.0451
2	100.173	11.8233	12.5874	1.0347	1.0337
3	101.211	11.6889	12.4447	1.0229	1.0224
4	102.27	11.5573	12.3047	1.0114	1.0112
5	103.351	11.4270	12.1661	1.0000	1.0000

Table 9

FINAL RESULTS FOR 3-METHYL HEXANE IN THE SYSTEM WITH 3 COLUMNS

HC content, % weight	Condenser duty, 10^6 kJ/h			Reboiler duty, 10^6 kJ/h			
	1st column	2nd column	Total	1st column	2nd column	3rd column	Total
0.1	0.397826	0.416613	0.81444	0.455225	0.969953	0.012868	1.438046
1	0.397826	0.414434	0.81226	0.455225	0.967042	0.012770	1.435037
2	0.397826	0.409495	0.80732	0.455225	0.965316	0.012738	1.433279
3	0.397826	0.404172	0.802	0.455225	0.963849	0.012714	1.431788
4	0.397826	0.402830	0.80066	0.455225	0.962521	0.012692	1.430438
5	0.397826	0.407323	0.80515	0.455225	0.961304	0.012670	1.429199

HC content, % weight	Alcohol product, kg/h	Relative duties 10^3 kJ/100 kg alcohol product		Relative duties, Report to minimum value	
		Cond.	Reb.	Cond.	Reb.
0.1	98.267	8.2880	14.6341	1.0641	1.0585
1	99.164	8.1911	14.4714	1.0517	1.0451
2	100.184	8.0584	14.3065	1.0347	1.0337
3	101.232	7.9224	14.1436	1.0172	1.0224
4	102.301	7.8265	13.9826	1.0049	1.0112
5	103.377	7.7885	13.8251	1.0000	1.0000

Table 10

FINAL RESULTS FOR n-HEXANE IN THE SYSTEM WITH 3 COLUMNS

HC content, % weight	Condenser duty, 10^6 kJ/h			Reboiler duty, 10^6 kJ/h			
	1st column	2nd column	Total	1st column	2nd column	3rd column	Total
0.1	0.397826	0.373952	0.77178	0.455225	0.718840	0.011465	1.18553
1	0.397826	0.363044	0.76087	0.455225	0.716922	0.011123	1.183269
2	0.397826	0.367563	0.76539	0.455225	0.715858	0.011313	1.182396
3	0.397826	0.362138	0.75996	0.455225	0.714932	0.010170	1.180327
4	0.397826	0.350462	**0.74829**	0.455225	0.714065	0.011410	1.1807

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5	0.397826	0.356815	0.75464	0.455225	0.713237	0.011395	1.179857

HC content, % weight	Alcohol product, kg/h	Relative duties 10^3 kJ/100 kg alcohol product		Relative duties, Report to minimum value	
		Cond.	Reb.	Cond.	Reb.
0.1	98.232	7.8567	12.0687	1.0763	1.0575
1	99.192	7.6707	11.9291	1.0508	1.0451
2	100.202	7.6385	11.8001	1.0464	1.0337
3	101.274	7.5040	11.6548	1.0280	1.0224
4	102.284	7.3158	11.5433	1.0022	1.0112
5	103.382	7.2995	11.4126	1.0000	1.0000

Table 11

FINAL RESULTS FOR TOLUEN IN THE SYSTEM WITH 3 COLUMNS

HC content, % weight	Condenser duty, 10^6 kJ/h			Reboiler duty, 10^6 kJ/h			
	1st column	2nd column	Total	1st column	2nd column	3rd column	Total
0.1	0.397826	0.716462	1.11429	0.455225	0.471584	0.336059	1.262868
1	0.397826	0.706093	1.10392	0.455225	0.466393	0.328448	1.250067
2	0.397826	0.703336	1.10116	0.455225	0.465335	0.328545	1.249104
3	0.397826	0.702858	1.10068	0.455225	0.464638	0.327589	1.247452
4	0.397826	0.702591	1.10042	0.455225	0.464056	0.327115	1.246396
5	0.397826	0.701400	1.09923	0.455225	0.463527	0.326666	1.245418

HC content, % weight	Alcohol product, kg/h	Relative duties 10^3 kJ/100 kg alcohol product		Relative duties, Report to minimum value	
		Cond.	Reb.	Cond.	Reb.
0.1	98.301	11.3355	12.8469	1.0664	1.0667
1	99.245	11.1232	12.5958	1.0464	1.0451
2	100.277	10.9812	12.4565	1.0330	1.0337
3	101.302	10.8653	12.3142	1.0221	1.0224
4	102.292	10.7576	12.1847	1.0120	1.0112
5	103.407	10.6301	12.0438	1.0000	1.0000

Table 12

FINAL RESULTS FOR 2-METHYL BUTANE IN THE SYSTEM WITH 2 COLUMNS

HC content, % weight	Condenser duty, 10^6 kJ/h			Reboiler duty, 10^6 kJ/h		
	1st column	2nd column	Total	1st column	2nd column	Total
0.1%	0.413411	0.959120	1.37253	0.483391	0.961087	1.44448
1	0.413406	0.959045	1.37245	0.483385	0.960028	1.44341
2	0.413400	0.958961	1.37236	0.483378	0.958955	1.44233
3	0.413394	0.958874	1.37227	0.483370	0.957981	1.44135
4	0.413388	0.958786	1.37217	0.483363	0.957098	1.44046
5	0.413382	0.958696	1.37208	0.483355	0.956297	1.43965

HC content, % weight	Alcohol product, kg/h	Relative duties 10^3 kJ/100 kg alcohol product		Relative duties, Report to minimum value	
		Cond.	Reb.	Cond.	Reb.
0.1	100.116	13.7094	14.4281	1.0520	1.0552
1	101.027	13.5850	14.2874	1.0424	1.0451
2	102.06	13.4466	14.1322	1.0318	1.0337
3	103.113	13.3084	13.9784	1.0212	1.0224
4	104.188	13.1701	13.8256	1.0106	1.0112
5	105.286	13.0319	13.6737	1.0000	1.0000

Table 13

FINAL RESULTS FOR n-PENTANE IN THE SYSTEM WITH 2 COLUMNS

HC content, % weight	Condenser duty, 10^6 kJ/h			Reboiler duty, 10^6 kJ/h		
	1st column	2nd column	Total	1st column	2nd column	Total
0.1	0.405916	0.643704	1.04962	0.472514	0.649134	1.12165
1	0.405916	0.643687	1.04960	0.472513	0.648686	1.12120
2	0.405915	0.643670	1.04959	0.472513	0.648215	1.12073
3	0.405915	0.643652	1.04957	0.472512	0.647769	1.12028
4	0.405915	0.643635	1.04955	0.472512	0.647348	1.11986
5	0.405914	0.643617	1.04953	0.472511	0.646951	1.11946

HC content, % weight	Alcohol product, kg/h	Relative duties 10^3 kJ/100 kg alcohol product		Relative duties, Report to minimum value	
		Cond.	Reb.	Cond.	Reb.
0.1	100.2473	10.4703	11.1888	1.0517	1.0537
1	101.1601	10.3756	11.0834	1.0422	1.0451
2	102.1937	10.2706	10.9667	1.0317	1.0337
3	103.2486	10.1655	10.8503	1.0211	1.0224
4	104.3254	10.0603	10.7343	1.0106	1.0112
5	105.425	9.9552	10.6185	1.0000	1.0000

Table 14

FINAL RESULTS FOR 2-METHYL PENTANE IN THE SYSTEM WITH 2 COLUMNS

HC content, % weight	Condenser duty, 10^6 kJ/h			Reboiler duty, 10^6 kJ/h		
	1st column	2nd column	Total	1st column	2nd column	Total
0.1	0.421072	0.481487	0.902559	0.491424	0.477503	0.968927
1	0.420679	0.479535	0.900213	0.490968	0.475274	0.966241
2	0.420549	0.478885	0.899434	0.490817	0.474299	0.965116
3	0.420452	0.478395	0.898847	0.490704	0.473511	0.964215
4	0.420367	0.477960	0.898327	0.490604	0.472804	0.963408
5	0.420286	0.477549	0.897835	0.490510	0.472147	0.962657

HC content, % weight	Alcohol product, kg/h	Relative duties 10^3 kJ/100 kg alcohol product		Relative duties, Report to minimum value	
		Cond.	Reb.	Cond.	Reb.
0.1	100.0619	9.0200	9.6833	1.0573	1.0586
1	100.9768	8.9150	9.5689	1.0450	1.0451
2	102.0096	8.8172	9.4610	1.0335	1.0337
3	103.0636	8.7213	9.3555	1.0222	1.0224
4	104.1393	8.6262	9.2511	1.0111	1.0112
5	105.2376	8.5315	9.1475	1.0000	1.0000

The most advantageous entrainer for the system with 3 columns is *n*-hexane (total reboiler duty $1.1768 \cdot 10^6$ kJ/h) and for the system with 2 columns is *n*-heptane (total reboiler duty $0.846 \cdot 10^6$ kJ/h). Unfortunately both entrainers are inadequate for two reasons: both have low octane number and both are difficult to obtain in pure state because they formed azeotropes with their izomers. The advantage of low reboiler duties (also low condenser duty) is nullified by above disadvantages.

For the same carbon atoms number in molecule the best entrainer are *n*-paraffins and, with comparable performances, cyclo-paraffins. But, as above, these components are not present “per se” and their obtaining is highly cost.

Iso-paraffins have almost the same performance, unconcerning the number of carbons atoms. Their performances are not so high but both *i*-pentane and-*i*-hexane have great advantage to be present in refineries as already existing products. It is not necessary to do any efforts to obtain them.

Both considered aromatics have good and almost the same performances. Differences, if there are, are insignificant and due of simulation calculus. Of course, it can be said that the aromatics are not desired in the gasoline, but considering the proportion of ethanol in gasoline and the low content of aromatics in ethanol product, this is not an impediment. For example, if we have 5% weight benzene in alcohol, this represents 3.76% volume, and for 4% alcohol volume in gasoline, the final content of benzene in gasoline is less than 0.15% volume (nowadays maximum admissible benzene content is 1%). For toluene situation is even more favorable (final 0.13% volume toluene, while admissible aromatic content is 30% volume). If in the refinery are presented aromatics

Table 15

FINAL RESULTS FOR n-HEXANE IN THE SYSTEM WITH 2 COLUMNS

HC. content, % weight	Condenser duty, 10^6 kJ/h			Reboiler duty, 10^6 kJ/h		
	1st column	2nd column	Total	1st column	2nd column	Total
0.1	0.446140	0.486950	0.933090	0.517662	0.481937	0.999599
1	0.444922	0.482478	0.927400	0.516358	0.477330	0.993688
2	0.444585	0.481234	0.925818	0.515997	0.475896	0.991893
3	0.444354	0.480377	0.924731	0.515749	0.474867	0.990616
4	0.444159	0.479655	0.923814	0.515540	0.473994	0.989534
5	0.443983	0.478995	0.922978	0.515350	0.473205	0.988555

HC content, % weight	Alcohol product, kg/h	Relative duties 10^3 kJ/100 kg alcohol product		Relative duties, Report to minimum value	
		Cond.	Reb.	Cond.	Reb.
0.1	99.8186	9.3479	10.0142	1.0636	1.0638
1	100.7493	9.2050	9.8630	1.0473	1.0451
2	101.7846	9.0959	9.7450	1.0349	1.0337
3	102.8392	8.9920	9.6327	1.0231	1.0224
4	103.9152	8.8901	9.5225	1.0115	1.0112
5	105.0134	8.7891	9.4136	1.0000	1.0000

Table 16

FINAL RESULTS FOR CYCLO-HEXANE IN THE SYSTEM WITH 2 COLUMNS

HC content, % weight	Condenser duty, 10^6 kJ/h			Reboiler duty, 10^6 kJ/h		
	1st column	2nd column	Total	1st column	2nd column	Total
0.1	0.484378	0.471766	0.956143	0.555175	0.467384	1.02256
1	0.479527	0.458605	0.938133	0.550219	0.454196	10.0441
2	0.477720	0.454083	0.931803	0.548313	0.449705	0.998018
3	0.477083	0.452339	0.929422	0.547661	0.447864	0.995525
4	0.476591	0.450989	0.927580	0.547157	0.446428	0.993585
5	0.476160	0.449815	0.925975	0.546715	0.445177	0.991891

HC content, % weight	Alcohol product, kg/h	Relative duties 10^3 kJ/100 kg alcohol product		Relative duties, Report to minimum value	
		Cond.	Reb.	Cond.	Reb.
0.1	99.8281	9.5779	10.2432	1.0835	1.0818
1	100.8012	9.3068	99.6427	1.0529	1.0451
2	101.513	9.1791	9.8314	1.0384	1.0337
3	102.5751	9.0609	9.7053	1.0250	1.0224
4	103.6558	8.9487	9.5854	1.0123	1.0112
5	104.7535	8.8396	9.4688	1.0000	1.0000

concentrates (that contain also another class of hydrocarbons), these are adequate for using them like entrainer.

The second goal of this paper is to evaluate the two considered process flow diagrams, first with three distillation columns (conventional solution) and the second with two distillation columns. Considering capital cost, at the first sight, the case with two column is more advantageous. Also, and this is very important, for the most selected entrainer, the case with two columns has lower reboiler duties. We can conclude that this is the best solution.

The third goal of this study is to demonstrate that the leaving in bottom product of azeotropic distillation column (alcohol product) of certain amount of entrainer, leads to lower heat consumptions. The increasing of the entrainer content decreases specific duties of reboiler (heat consumption reported to ethanol product flow rate). The difference between extreme cases (0.1 % weight and 5% entrainer in alcohol product) is important, from 5.43% for 2-methyl pentane to 12.71% for 3-methyl hexane. Almost the same ratio is for condenser duty too. This is a very important conclusion. So:

-leaving some entrainer in ethanol product decrease specific heat duty with important energy saving;

-the presence of entrainer do not affect the quality of ethanol that is used for adding in gasoline; contrary, the presence of certain quantities of some entrainers (like iso-paraffins and aromatics) bring a contribution to octane number of gasoline. Anyway, those entrainers are finally present in gasoline and does not matter if they are coming in gasoline with gasoline components or with ethanol;

Table 17

FINAL RESULTS FOR BENZENE IN THE SYSTEM WITH 2 COLUMNS

HC content, % weight	Condenser duty, 10^6 kJ/h			Reboiler duty, 10^6 kJ/h		
	1st column	2nd column	Total	1st column	2nd column	Total
0.1	0.463190	0.468619	0.931809	0.532486	0.465749	0.998235
1	0.453174	0.431439	0.884613	0.522202	0.428812	0.951014
2	0.451571	0.425485	0.877056	0.520545	0.422911	0.943456
3	0.450764	0.422490	0.873255	0.519711	0.419951	0.939662
4	0.450217	0.420455	0.870672	0.519144	0.417948	0.937092
5	0.449792	0.418872	0.868665	0.518703	0.416401	0.935104

HC content, % weight	Alcohol product, kg/h	Relative duties 10^3 kJ/100 kg alcohol product		Relative duties, Report to minimum value	
		Cond.	Reb.	Cond.	Reb.
0.1	99.3673	9.3774	10.0459	1.1325	1.1271
1	100.5835	8.7948	9.4550	1.0622	1.0451
2	101.6519	8.6280	9.2812	1.0420	1.0337
3	102.7212	8.5012	9.1477	1.0267	1.0224
4	103.8056	8.3875	9.0274	1.0130	1.0112
5	104.9101	8.2801	8.9134	1.0000	1.0000

Table 18

FINAL RESULTS FOR 3-METHYL HEXANE IN THE SYSTEM WITH 2 COLUMNS

HC content, % weight	Condenser duty, 10^6 kJ/h			Reboiler duty, 10^6 kJ/h		
	1st column	2nd column	Total	1st column	2nd column	Total
0.1	0.577823	0.611492	1.18931	0.642734	0.613124	1.25586
1	0.556122	0.562669	1.11879	0.621361	0.563938	1.18530
2	0.551531	0.552237	1.10377	0.616857	0.553353	1.17021
3	0.548918	0.546300	1.09522	0.614292	0.547320	1.16161
4	0.547007	0.541971	1.08898	0.612415	0.542922	1.15534
5	0.545484	0.538510	1.08399	0.610920	0.539412	1.15033

HC content, % weight	Alcohol product, kg/h	Relative duties 10^3 kJ/100 kg alcohol product		Relative duties, Report to minimum value	
		Cond.	Reb.	Cond.	Reb.
0.1	99.1572	11.9942	12.6653	1.1559	1.1502
1	100.001	11.1878	11.8529	1.0782	1.0451
2	101.135	10.9138	11.5708	1.0518	1.0337
3	102.241	10.7121	11.3615	1.0324	1.0224
4	103.344	10.5374	11.1796	1.0155	1.0112
5	104.467	10.3764	11.0114	1.0000	1.0000

Table 19

FINAL RESULTS FOR n-HEPTANE IN THE SYSTEM WITH 2 COLUMNS

HC content, % weight	Condenser duty, 10^6 kJ/h			Reboiler duty, 10^6 kJ/h		
	1st column	2nd column	Total	1st column	2nd column	Total
0.1	0.588531	0.306975	0.89551	0.541335	0.304622	0.845957
1	0.565906	0.281342	0.84725	0.530394	0.279185	0.809579
2	0.561069	0.275776	0.83684	0.528556	0.273688	0.802244
3	0.558290	0.272556	0.83085	0.527596	0.270529	0.798126
4	0.556242	0.270175	0.82642	0.526921	0.268202	0.795123
5	0.554594	0.268244	0.82284	0.526381	0.266321	0.792702

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HC content, % weight	Alcohol product, kg/h	Relative duties 10^3 kJ/100 kg alcohol product		Relative duties, Report to minimum value	
		Cond.	Reb.	Cond.	Reb.
0.1	99.2154	9.0259	8.5265	1.1461	1.1238
1	100.023	8.4706	8.0939	1.0756	1.0451
2	101.203	8.2689	7.9271	1.0500	1.0337
3	102.276	8.1236	7.8036	1.0315	1.0224
4	103.299	8.0003	7.6973	1.0159	1.0112
5	104.482	7.8754	7.5870	1.0000	1.0000

Table 20

FINAL RESULTS FOR TOLUENE IN THE SYSTEM WITH 2 COLUMNS

HC content, % weight	Condenser duty, 10^6 kJ/h			Reboiler duty, 10^6 kJ/h		
	1st column	2nd column	Total	1st column	2nd column	Total
0.1	0.414740	0.419601	0.83434	0.503306	0.473489	0.976795
1	0.405727	0.386267	0.79199	0.491914	0.435539	0.927453
2	0.403795	0.380469	0.78426	0.492279	0.429419	0.921699
3	0.403479	0.378171	0.78165	0.491179	0.426323	0.917502
4	0.403394	0.376728	0.78012	0.490851	0.424209	0.915060
5	0.402834	0.375142	0.77798	0.490589	0.422565	0.913154

HC content, % weight	Alcohol product, kg/h	Relative duties 10^3 kJ/100 kg alcohol product		Relative duties, Report to minimum value	
		Cond.	Reb.	Cond.	Reb.
0.1	99.312	8.4012	9.8356	1.1280	1.1251
1	100.112	7.9110	9.2642	1.0622	1.0451
2	101.198	7.7498	9.1079	1.0405	1.0337
3	102.283	7.6420	8.9702	1.0260	1.0224
4	103.302	7.5518	8.8581	1.0139	1.0112
5	104.454	7.4481	8.7422	1.0000	1.0000

-these entrainers are easy to find in refineries, especially iso-pentane and iso-hexane which are present in isomerizate (in some cases only iso-pentane, in the other cases both);

-this solution is easy to realize and does not bring important supplementary costs.

Finally, like entrainer could be used different petroleum cuts or gasoline pool that are presented in trade gasoline. For example, using the isomerizate (i-pentane and i-hexane) has performances proportional with the ratio of both components. The availability of such entrainer in refineries is a clear advantage.

Conclusion

The paper proposes o new class of entrainers, petroleum cuts and gasoline pool, and demonstrates that the considered entrainers are adequate for production of anhydrous ethanol. The study concludes that the best entrainer are isomerizate fractions (with iC$_5$ or with iC$_5$ and iC$_6$).

The study demonstrates the advantages of using of only two columns for production of anhydrous ethanol comparatively with classical one (with precontration column).

Finally, the study demonstrates the advantage of leaving of certain amounts of entrainer in ethanol product for decreasing of separation efforts (reduction of the reboiler duties with 12.71%).

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