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PhD THESIS

COMPARATIVE STUDIES CONCERNING THE REACTIVE DISTILLATION IN ESTERIFICATION AND ETHERIFICATION PROCESSES

(PhD Thesis Summary)

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In memory of my dear parents, Ioana and Florin.

INTRODUCTION

Lactic acid esters are biodegradable and can be used as high boiling solvents for varnishes, paints, nitrocellulose and ethylcellulose manufacturing, rubbers, oils, dyes, etc. They are also used as food additives, in biochemistry, pharmaceutical industry, detergents, cosmetics and so on [58-59]. Methyl, ethyl, isopropyl and n-butyl esters of lactic acid are usually obtained by conventional esterification with the corresponding alcohol.

Two of them, the methyl and isopropyl esters of lactic acid are the subject of the present paper. Knowing their physical properties is important, both for the engineering of the reaction system and for the choice of effluent separation methods.

Reactive distillation is an example of an innovative process. It can be defined as a thermal integration of the chemical reactor with the separation column in a single equipment, a column with a multifunctional role.

Reactive distillation offers some advantages over the conventional process, in which reaction and separation are separate processes.

Detailed information on the major industrial applications of reactive distillation was presented by Sharma and Mahajani [17] and by Luyben and Yu[7]. Industrial reactive distillation processes cover a wide range of reactions among the most important being: hydrogenation, hydrodesulfurization, esterification and etherification.

In this context, the main objective of the paper is to help improve the reactive distillation process in some industrial applications, by pursuing the following secondary objectives:

- deepening the theoretical knowledge of some processes in which reactive distillation can be applied, such as esterification and etherification;
- experimentation in the laboratory of esterification processes in a reactive distillation system, observing the influence of process factors and the mathematical modeling of these processes;
- experimentation of *in situ* etherification of the olefins from catalytic cracking gasoline with different alcohols, in a reactive distillation process;
- optimization of industrial scale processes including a reactive distillation sequence, using an appropriate simulation environment.

The doctoral thesis is structured in two parts, as follows:

A) BIBLIOGRAPHICAL RESEARCH

The literature study is included in the first chapter where the newest developments of the reactive distillation are presented.

The main advantages of reactive distillation are highlighted:

- ➢ high conversion;
- increased selectivity;
- Iow energy consumption;
- > avoiding the formation of azeotropes;
- simplifying the separation of components with close boiling points;
- reducing investment costs;
- > reducing the cost of recirculation of the excess reactant,

and the observed disadvantages:

- volatility constraints;
- operational constraints;
- catalyst life constraints;
- design and testing long period.

Also, the progress in reactive distillation is presented as well as different flowsheets for the industrial uses of reactive distillation, by exemplifying on the manufacture of ethyl acetate:

- Conventional esterification process;
- Discontinuous reactive distillation;
- Conventional reactive distillation;
- Reactive distillation pressure swing (RD-PS);
- Dividing wall column and reboiler-reactor;
- Reactive Dividing wall column (RDWC);
- Reactive distillation coupled with pervaporation

New findings on modeling and simulation of processes for the design of industrial chemical processes are synthesized and presented here.

B) SCIENTIFIC RESEARCH

In Chapter 2, original experimental studies are described, concerning the esterification of lactic acid with methanol and isopropanol, and the transesterification of methyl lactate with isopropanol, in distillation reactive system. The experimental results are commented, as well as the statistical processing and interpretation of these data

In Chapter 3, results of experimental studies are presented about the *in situ* etherification of olefins from catalytic cracking gasoline with methanol, ethanol, iso-propanol and n-buthanol, in a reactive distillation system; the influence of reactants molar ratio and the nature of the alcohol on the olefins conversion is discussed based on chromatographic analysis of raw material an products.

The Chapter 4 presents the simulations performed in ChemCad in order to find the optimum operating parameters in esterification of lactic acid with methanol and isopropanol, and also in transesterification of methyl lactate with isopropanol, in a reactive distillation system. Also, flowsheets of corresponding industrial processes were proposed and simulated here.

CHAPTER 2

EXPERIMENTAL STUDY OF ESTERIFICATION AND TRANSESTERIFICATION IN REACTIVE DISTILLATION SYSTEM

Original experimental study of obtaining the lactic acid esters in direct esterification or transesterification processes is described. The study consisted in:

- direct observations on the influence of process factors on the esterification results;
- mathematical models developed for quantifying the influence of process factors on product yields.

The study is to be expanded in Chapter 4 into a simulation environment (CHEMCAD), in order to optimize the process parameters.

2.1. LACTIC ACID ESTERIFICATION

The following aspects of the lactic acid esterification with various alcohols are presented:

- chemistry of the esterification reaction
- ➤ thermodynamics;
- ➤ mechanism;
- ➢ kinetics of the lactic acid esterification reaction with light alcohols,

as they appear in literature studies.

There are presented the factors that could influence the esterification of lactic acid with different alcohols:

- ➤ catalyst effect;
- ➤ temperature effect;
- \succ the effect of the initial molar ratio of the reactants.

2.2. STUDY OF LACTIC ACID ESTERIFICATION WITH METHANOL IN REACTIVE DISTILLATION SYSTEM

The esterification of lactic acid with methanol is catalyzed by sulfuric acid.

From literature data, the most important parameters were selected and studied at the esterification of lactic acid with methanol by reactive distillation:

- ➤ catalyst;
- ➤ temperature;
- molar ratio of reactants;
- liquid-vapor equilibrum.

2.2.1. Experimental Part

2.2.1.2. Apparatus and Procedure

The esterifications were carried out in a process of reactive distillation in batch, in a laboratory column made of glass, with an inner diameter of 20 mm, fitted with Rashig glass rings, $6 \ge 10 \ge 100$ mm, the height of the packing bed ranging from 400 mm to 100 mm. In the bottom, there is a glass flask with capacity of 500 ml, electrically heated, where the reactants are introduced (Figure 2.11). The column is thermally insulated. The catalyst is sulfuric acid and the reaction is homogeneously catalysed, so it is introduced into the bottom flask from the beginning, along with reactants.

The esterification process between lactic acid and methanol was carried out at different molar ratios: 1: 1, 2: 1 and 3: 1, alcohol : lactic acid. The temperature in bottom did not exceed 135° C during the reaction, to avoid thermal decomposition of the formed compound. The separation was carried out in the batch and two fractions were obtained successively: the first peak fraction is the recovered methanol, and the second fraction is composed of a mixture of methanol, water and traces of ester; at the bottom of the plant the lactic acid ester was obtained together with unreacted lactic acid. The temperature at the top of the column was between 62 - 66 ° C during the distillation of methanol and rose up to 96°C in the end. The reaction time was long enough (40-60 minutes) for the reaction to reach a high conversion [6, 91].



Legend: 1.glass column with Raschig rings packing; 2.condenser; 3.bottom glass flask; 4.electrical heater.



2.2.1.3. Analysis methods

1. **The lactic acid conversion** during a test, initial, was indirectly determined by measuring the concentration of the acid in the reaction mass through volumetric titration of samples with sodium hydroxide solution 1N and phenolphtaleine as an indicator in the samples collected every 15 minutes. The method was also used in the work [92]. In the reaction mass, besides the lactic acid, the sulfuric acid is also present (the catalyst), but the sodium hydroxide solution volume needed to neutralize it is constant during the reaction, so that the conversion of lactic acid could be calculated at time t of the reaction with the formula (2.12):

conversion,
$$\% = \frac{v_0 - v_t}{v_0} * 100$$
 (2.12)

where: v_0 – is the volume of 1 N NaOH solution used for titration at the initial moment of reaction (mL);

 v_t – the volume of 1 N NaOH solution used for titration at the moment *t* (mL).

The conversion of lactic acid was checked by methanol balance. The quantity of unreacted methanol was determined in the top with the help of the calibration curve for the methanol-water system. The difference between the amount of methanol introduced into the reaction and the amount of unreacted methanol is the reacted amount; through a simple stoichiometric calculation, the amount of reacted lactic acid can be found and from this, the conversion of lactic acid can be calculated.



Figure 2.12. Calibration curve for methanol-water binary mixure

2. The number of the theoretical plates (NTP) in the column was determined, for each height of the packing, corresponding to the methanol-water binary mixture. Determinations were performed both analytically, using Fenske's relationship (equation 2.13), and graphically, using the McCabe-Thiele graphical construction [93], the results being very close in both calculations (one-digit difference).

Fenske's relationship is as follows:

$$N_{min} = \frac{\log \frac{x_d}{1 - x_d} - \log \frac{x_b}{1 - x_b}}{\log \alpha_m}$$
(2.13)

where:

- > x_d and x_b the molar fraction of the volatile component (methanol) in the overhead fraction, respectively in the bottom fraction (mole fraction), determined on the basis of refractometric analysis (with aid of calibration curve 2.12);
- > α_m the relative volatility of the two components at the average temperature and pressure in the column.

 Table 2.2. The minimum number of theoretical plates at different heights of the packing bed in column

Sample	H _P [mm]	t _{overhead} [°C]	t _{bottom} [°C]	N _{min}
1	400	62	88	4.9
2	200	64	88	2.4
3	100	66	88	1.8

2.2.1.4. Results and discussions

a) Effect of molar ratio of reactants on the esterification reaction



Figure 2.13. The effect of the molar ratio of methanol: lactic acid on the conversion of lactic acid to the esterification of lactic acid with methanol (H_{packig}= 400 mm)

It is noted that with the increase in the initial molar ratio of methanol to lactic acid, the conversion of lactic acid increases. For esterification with methanol, the conversion of lactic acid increases from 57% to 80% when the alcohol: acid ratio increases from 1: 1 to 3: 1.

b) Influence of the number of theoretical plates on the yield of methyl lactate

There were runs at three different heights of the Raschig packing bed and to three molar ratios of methanol: lactic acid and 1: 1 respectively; 2: 1 and 3: 1. The proportion of catalyst (concentrated sulfuric acid) was 3% wt in the reaction mass for all determinations.

In the present paper, the yield of methyl lactate was calculated using equation (2.14) based on the lactic acid consumed in the reaction, by considering that the esterification reaction is singular, an acceptable hypothesis at low acid concentrations in the reaction mass

$$y = \frac{mole \ of \ lactic \ acid \ transformed \ in \ methyl \ lactate}{moles \ of \ lactic \ acid \ in \ the \ feed} * 100$$
(2.14)

T	Table 2.3. The methyl lactate yie	lds depending on the number of th	eoretical plates and the initial
n	nolar ratio of reactants [6, 91]		
		Malan natio	Mathed la state viold

No	N	Molar ratio	Methyl lactate yield
110.	¹ min	methanol: lactic acid	[%]
1	4.9	3:1	76.7
2	4.9	2:1	70.1
3	4.9	1:1	57.0
4	2.4	3:1	75.3
5	2.4	2:1	63.0
6	2.4	1:1	48.7
7	1.8	3:1	72.0
8	1.8	2:1	60.8
9	1.8	1:1	50.0

The results presented in Table 2.3 show that for the same number of theoretical plates, the yield of methyl lactate increases by increasing the molar ratio of methanol: lactic acid. From the data obtained it is observed that, he highest methyl lactate (ML) yield of 76.7% was obtained at an initial molar ratio of methyl alcohol: lactic acid of 3: 1, using a packed column equivalent to 4.9 theoretical plates.

2.2.1.5. Mathematical model for predicting the yield of methyl lactate

A mathematical model is proposed to predict the yield of methyl lactate ML, of the degree I polynomial.

The following model was found by regression (equation 2.16):

$$y = 34.22 + 2.36 x_1 + 11.23 x_2 \tag{2.16}$$

From the regression analysis, they resulted:

- > correlation coefficient r = 0.9876;
- \blacktriangleright determination coefficient r² = 0.9754;
- ➤ standard error 1.88 (%)

yield values being predicted with acceptable tolerance, the model is conclusive. The variance analysis (ANOVA) proved that all the model's coefficients are statistically sound.

2.3. STUDY OF LACTIC ACID ESTERIFICATION WITH ISOPROPANOL IN REACTIVE DISTILLATION SYSTEM

2.3.1. Experimental Part

2.3.1. 1. Experimental installation and Procedure

The experimental plant for the reactive distillation process in batch was presented in figure (2.11) and in [91]; it consists of a laboratory glass column with a 20 mm internal diameter, with Rashig glass rings 6x10x1 mm, the height of the packing bed ranging from 400 mm to 100

mm. The number of theoretical plates for the isopropanol-water binary mixture was determined experimentally, resulting in 2.9 theoretical plates (at 400 mm) and 1.9 theoretical plates, respectively (at 100 mm) and an height equivalent to one theoretical plates (HETP) 138 mm and 52 mm, respectively.

The separation was conducted in batch to give a peak fraction and a bottom fraction; the top fraction is a mixture of isopropanol and water and in the bottom results the isopropyl ester of lactic acid and unreacted lactic acid, as well as the catalyst.

The temperature at the top of the column reached 79-82°C until the end of a run, varying from one experience to another, and depending on isopropanol excess. The reaction time was long enough for the reaction to reach a higher conversion (40-60 minutes), as shown in [98].

2.3.1.2. Analysis methods

1. As in the experimental study for the production of methyl lactate, and in this case, to determine **the conversion of lactic acid**, during an experiment, the acid concentration in the reaction mass was analyzed by volumetric titration with 1N sodium hydroxide solution in the presence of phenolphthalein, from samples taken at 15 minute intervals, the conversion being verified using the balance of materials on isopropanol, considering that the only reaction in the system is the esterification.

2. The fraction collected at the top, containing isopropanol and water was determined isopropanol concentration by refractive index of the calibration curve n_D^{20} as a function of x (molar ratio of isopropanol).

3. The number of the theoretical plates (NTP) in the column was determined, at each height of the packing bed, for the isopropanol-water binary mixture.

Table 2.5. The minimum number of theoretical plates for different heights of the distillation column packing bed for the isopropanol-water binary mixture

Sample	H _P [mm]	t _{top} [°C]	t _{bottom} [°C]	N _{min}
1	400	80.5	87	2.9
2	200	80.5	86.5	2.1
3	100	80.5	86	1.9

2.3.1.3. Results and discussions

In order to determine the optimal conditions of the process, a factorial experiment 2^3 was performed (three process factors were varied at two levels).

The experimental results presented in Table 2.8. showed that all three factors taken into account (molar ratio of reactants, number of theoretical plates and catalyst concentration in the reaction mass) influence the conversion of lactic acid. The trend is to increase conversion by increasing the value of each factor. It has also been observed that in the case of coupling of the reaction with distillation, the conversion reached 63.6%, the value obtained being superior to those obtained in the conventional esterification process (max. 51% of the value according to [42] or max. 42% as reported in [92]).

Run	Experiment	Lactic acid
	code	conversion, %
1	0.	27.8
2	1.	50.2
3	2.	39.0
4	1.2.	62.3
5	3.	29.0
6	1.3.	54.1
7	2.3.	41.5
8	1.2.3.	63.6

 Table 2.8. Experimental results of esterification of lactic acid with isopropanol

2.3.1.4. A mathematical model for predicting the conversion of lactic acid into isopropyl lactate

A mathematical model is proposed to predict the conversion of lactic acid into isopropyl lactate IPL, a first order polynomial equation.

The equation resulted from numerical regression is (2.18):

$$y = -8.917 + 11.612 x_1 + 11.325 x_2 + 1.113 x_3$$
(2.18)

The most important variables of the process are: the molar ratio of reactants x_1 and the number of theoretical plates x_2 , this being observed by the high values of coefficients associated with these factors: $A_1 = 11.612$ and $A_2 = 11.325$. The positive value of the coefficients shows that increasing the value of each factor, the conversion of lactic acid will increase, which has been confirmed experimentally.

2.4. STUDY OF THE TRANSESTERIFICATION OF METHYL LACTATE WITH ISOPROPANOL IN A REACTIVE DISTILLATION SYSTEM

Transesterification is one of the classic organic syntheses with many uses in both laboratory and industrial applications.

Transesterification is a reaction in which one ester is converted into another by the exchange of alkoxy radicals. The reaction occurs with the liquid reactants and is limited by the thermodynamic equilibrium; the transformation can sometimes take place simply by mixing the reactants at the reaction temperature.

2.4.2. THE EXPERIMENTAL STUDY

2.4.2.1. Design of experiment

The isopropyl lactate was obtained in an experimental study by transesterification of methyl lactate with isopropyl alcohol in excess, in a reactive distillation column, in homogeneous acid catalysis with concentrated sulfuric acid. For the experimental matrix of the transesterification process by reactive distillation, a factorial experiment 2^3 has been designed, namely three factors at two levels of variation, and the levels of variation were proposed:

- the molar ratio of reactants (isopropyl alcohol: methyl lactate), minimum = 2:1 and maximum = 4: 1;
- the height of packing bed: minimum = 100 mm and maximum = 400 mm, equivalent to the number of theoretical plates 1.7 and 2.4, respectively;
- ▶ the reflux ratio in the reactive distillation column: minimum 2: 1 and maximum 7: 1.

2.4.2.2. Materials and method

The experimental study of methyl lactate transesterification with isopropyl alcohol by reactive distillation was carried out in the laboratory plant shown in figure 2.11 and in the paper [91].

Method

The transesterification process between isopropyl alcohol and methyl lactate was performed at various molar ratios. The temperature in the bottom did not exceed 130°C throughout the reaction to avoid thermal decomposition of the formed compounds. The separation was carried out in a batch giving a peak and a bottom fraction; the peak fraction is composed of the resulting methanol from reaction and the unreacted isopropyl alcohol; the isopropyl lactate ester together with the unreacted methyl lactate is obtained in the bottom fraction. The two esters do not form azerotropes. The temperature at the top of the column was initially 78-81°C (depending on the excess of alcohol used), and the temperature rose to 84°C as the distillation continued. The reaction time (50-60 minutes) was long enough for reaching high conversions.

In the peak fraction, the concentration of methanol was determined by refraction index, using a calibration curve for the methanol-isopropanol binary mixture, as plotted in figure 2.16. The isopropanol balance was performed and subsequeventely, the amount of reacted methyl lactate, through stoichiometric calculations.

Conversion is calculated with Eq. (2.19):



Figure 2.16. Calibration curve for the methanol-isopropanol binary mixture

In order to determine the optimal conditions of the reactive distillation system for the transesterification reaction in acid background to produce isopropyl lactate, the experimental conversion of methyl lactate to isopropyl lactate was determined in code no. 0. - 1.2.3. experiments; the results are presented in Table 2.14.

Run Experiment code		Conversion of methyl lactate, %
1	0.	57.0
2	1.	71.6
3	2.	69.3
4	1.2.	85.0
5	3.	63.8
6	1.3.	76.7
7	2.3.	74.3
8	1.2.3.	89.8

Table 2.14. Experimental results of methyl lactate transesterification with isopropyl alcohol

2.4.2.3. Mathematic model for predicting conversion of methyl lactate to isopropyl lactate

A linear model was proposed to predict the methyl lactate conversion in transesterification with isopropyl alcohol, in a reactive distillation system.

In regression analysis, the following model resulted:

$$y = 10.448 + 7.338x_1 + 17.607x_2 + 1.085x_3 \tag{2.21}$$

The regression coefficients of the model (equation 2.21) are:

- > The correlation coefficient r = 0.9981, this coefficient showing a good linear correlation between the dependent variable Y and the independent variables X;
- > the coefficient of determination $r^2 = 0.9963$.

By analyzing the absolute errors of the predicted conversion values, it is noted that they are acceptable (between -0,62% si 1,15%). ANOVA analysis proved that all the model's coefficients are statistically consistent (p<0.05).

In conclusion, the proposed mathematical model is of good quality.

CHAPTER 3

STUDY OF THE ETHERIFICATION *IN SITU* OF THE OLEFINES FROM FLUID CATALYTIC CRACKING GASOLINE IN REACTIVE DISTILLATION SYSTEM

Ethers such as tert-amyl methyl ether (TAME), tert-amyl ethyl ether (TAEE) and ethyltert-butyl ether (ETBE) are components used in the composition of petrol as additives for increasing the performance of spark ignition engines (to increase the octane number) and decreasing the impact on the environment [123]. In the newest technologies for ethers manufacturing, the reactor and the ether separation column are combined into a reactive distillation column, so thermally coupling the reaction process with the distillation process, in order to reduce energy consumption, equipment and machinery costs.

3.2. PREVIOUS RESEARCH ON ETHER SYNTHESIS BY ADDITION OF ALCOHOLS TO OLEFINE

Experimental studies of etherification reactions of iso-olefins C4-C5 with methanol have led to the development of modern manufacturing processes for MTBE and TAME [137,138] as well as ETBE and TAEE [15, 130, 139], or isopropyl tert-butyl ether [135].

Preliminary studies of *in situ* etherification of olefins from catalytic cracking gasoline in the reactive distillation system, were carried out at Ovidius University in Constanta, between 2014-2016 [150-152], searching the effect of the etherification with different alcohols on octane number of gasoline.

An experimental distillation plant similar to that described in Chapter 2 was used, with a packing and a layer of acidic ion exchange resins.



Figure 3.2. Motor Octane Number (MON) of in-situ ether gasoline with various alcohols at a molar ratio of 1.5:1 alcohol / olefin [150]

Following these preliminary experiments it was considered necessary to continue the etherification study with isopropanol (which gave preliminary encouraging results) and in particular, to study the process more deeply to find the explanation for these transformations.

3.3. THE EXPERIMENTAL STUDY ON THE ETHERIFICATION *IN SITU* OF THE OLEFINES FROM FLUID CATALYTIC CRACKING GASOLINE WITH ISOPROPANOL

3.3.1. Equipment and Procedure

The experimental plant consists of a laboratory distillation column with an inner diameter of 8 cm and a height of 1 m, equipped with a 70 cm Rashig glass packing 6x10x1 mm the catalyst being introduced into a textile bag placed in the column between the bottom and its

top, so located in the column that the temperature in the reaction zone be in the range 60-70°C, since this is the optimal temperature for the etherification reactions. The bottom of the column is a flask of 2L capacity, electrically heated to achieve a distillation rate of approx. 0.5 mL/sec. and a smooth operation that ensures a good separation of the components between the top and bottom of the column. (Figure 3.4.).

The runs were conducted at the desired molar ratio of alcohol / olefins. The temperature in the bottom, at the end of the distillation was between 100 and 140 $^{\circ}$ C, depending on:

- \succ the alcohol used;
- \succ the molar ratio of reactants;
- ➤ the amount of distillate that has been collected.

The temperature at the top of the fractionation column at the start of the distillation is between 22-25°C, depending on the cooling water temperature at the condenser, but it did not exceed the temperature of 35°C, seeking to recover most of the gasoline in the bottom, in order to provide the necessary quantity for the octane number analysis.



Figure 3.4. Experimental installation for *in situ* etherification of olefins from catalytic cracked gasoline

The content of the flask was also analyzed chromatographically to determine the composition. If chromatographic analysis is performed for the gasoline- raw material and for bottom product it is possible to calculate the components balance in order to determine the conversion of olefins into ethers.

Table 3.4. PONA analysis of catalytic cracking gasoline - raw material (standard method SR EN ISO 22854)

Characteristic	U.M.	Value
Parafin+ i-Parafin	%	26.04
Olefins	%	14.40
Naphthenic	%	11.04
Aromatic	%	48.52

For etherification, alcohol was used with as little water as possible: isopropanol from S.C. SILAL TRADING S.R.L. with a maximum water content of 0,1% by mass.

3.3.3. Analysis methods

To determine the octane number, the the standard engine CFR ASTM -Waukesha F1 / F2, USA, was used. Each sample was analyzed 3 times, and the result of the analysis is the mean of these three determinations according to the standard method (ASTM D-2700).

A gas chromatograph with a special analyzer (AC Reformulyzer® M3 Analyzer) was used to analyze feedstock and reaction products; this analyzer performs concurrently determination of composition by hydrocarbon classes (PONA) and determination of the concentrations of oxygenated compounds - standard method SR EN ISO 22854.

3.3.4. Results and discussions

The molar ratio of reactants in etherification with methanol and ethanol has also been studied [150-152], in this paper, in situ etherification experiments were carried out with isopropanol at various molar ratios of isopropyl alcohol / olefins: 1/1, 1.5 / 1 and 2/1, in order to determine the optimal molar ratio.

The results presented in Figure 3.5 show that the optimal isopropyl alcohol/olefin alcohol ratio is 1.5/1. At this molar ratio, the maximum octane number (ON) of gasoline after etherification is obtained (two ON units), compared with an increase of only 1.1 units of octane number for a 2/1 molar ratio, respectively an increase of only 0.1 units of octane number at a molar ratio of 1/1 [153].



Figure 3.5. Influence of the isopropanol / olefin molar ratio on octane number gasoline after olefin etherification with isopropanol

Mass balances were made on C5-C9 cyclo-olefins and on C5-C9 olefins, according to the quantities of products obtained and chromatograms for all 4 alcohols used for etherification. Then the conversion of the olefins of the formula:

$$conversion, \% = \frac{\text{the amount of oletins in the raw material-the amount of oletins in the product}{\text{the amount of oletins in the raw material}} \cdot 100 \quad (3.1)$$

the results being presented in Tables 3.6.-3.9.

Further, it is exemplified by experimental data from etherification with isopropanol and the main conclusions resulting from the processing of these data. The conclusions of the data processing for etherification with other alcohols are presented in "General Conclusions".

Table 3.8. The mass balance on olefins and their conversion during *in situ* etherification with isopropanol

The amount of raw material, g		502.71			
The amount of isopropanol, g		60.52			
The amount of eth	nerified product, g	343.25			
The amount of dist	illed + losses, g	219.98			
	% mass in the	The	% mass in the	The	- ·
Component	raw material	amount	etherified	amount of	Conversion,
Component	(Chromatogram)	of olefins	product	olefins in	%
	(Chromatogram)	in r.m, g	(Chromatogram)	product, g	
Cyclo C5	0.13	0.65	0.00	0.00	100
Cyclo C6	0.66	3.32	0.07	0.24	92.8
Cyclo C7	0.95	4.78	0.60	2.06	56.9
Cyclo C8	0.51	2.56	0.61	2.09	18.3
Cyclo C9	0.22	1.11	0.30	1.03	6.9
Olefins C4 (n+i)	3.61	8.75	0.02	0.07	100
Olefins C5	3.34	18.15	0.07	0.24	99.2
Olefins C6	1.44	16.79	0.17	0.58	98.7
Olefins C7	0.76	7.24	0.53	1.82	74.9
Olefins C8	0.39	3.82	0.83	2.85	25.4
Olefins C9	3.61	1.96	0.57	1.96	0

Isopropanol etherification (Table 3.8) gives very good results for C5 -C6 olefins (n + i) and cycloolefins C5-C6 (conversion over 90%) and C7 (conversion 74,9%); however, the conversion of C8-C9 olefins is poor (below 25%) being null at C9 olefins. There are the major conversions to etherification with isopropanol, compared to other alcohols, thus explaining the largest increase in the octane number (2 units) of all etherification products.

CHAPTER 4

CHEMCAD SIMULATION OF THE ESTERIFICATION AND TRANSESTERIFICATION PROCESSES IN A REACTIVE DISTILLATION SYSTEM

The objectives of simulating the reactive distillation sequence were: confirmation / refutation of the need to use the reactive distillation process and determination of the optimal operating parameter values, namely:

- the optimal molar ratio of the reactants;
- > the number of theoretical equilibrium in the reactive distillation column;
- > optimum reflux ratio for the reactive distillation column.

The flow sheets of technological processes have been drawn up according to the physical properties of the systems and the desired results (yields, purity). During the simulations, the process flowsheet have undergone changes to achieve these goals.

4.1. SIMULATION OF METHYL LACTATE MANUFACTURING PROCESS BY ESTERIFICATION OF LACTIC ACID WITH METHANOL IN REACTIVE DISTILLATION SYSTEM

Simulations have taken into account the thermodynamic constraints.

4.1.1. Simulation of the reactive distillation sequence

1. The reaction zone is simulated using the "continuous kinetic reactor" of the CHEMCAD reactor, since the kinetics of the esterification reaction of lactic acid with methanol are known [155], respectively the pre-exponential factor and the activation energy from the Arrhenius equation, to:

- molar ratio of alcohol: lactic acid: 1: 1 10: 1;
- \blacktriangleright working temperature 96- 77°C, depending on molar ratio of reactants;
- > pressure 1.2 bar

2. The distillation area of RD was simulated at:

- \blacktriangleright the pressure 1.2 bar, set at reactor output;
- variable number of trays, between 4-14 real trays, with the feed on the bottom tray, taking into account that the reaction zone is in the bottom of the column;

 \blacktriangleright the reflux ratio was varied between 0.5: 1 and 7: 1.

The simulations were performed as follows:

a) To *determine the optimal molar ratio* of alcohol: lactic acid reagents, the conversion of lactic acid to methyl lactate was targeted, varying the molar ratio of methanol: lactic acid reactants from 1: 1 to 10: 1.

The conversion of lactic acid to methyl lactate increases from 57.13% to 88.87% with increasing molar ratio of methanol: lactic acid from 1: 1 to 10: 1, but over 4:1, the increase is slow.

Table 4	1.1. Conversion	of lactic acid	l to methyl	l lactate at o	different mol	lar ratios of	the reactants

Molar ratio Alcohol: Lactic acid	Conversion of Lactic Acid to Methyl Lactate [%]	Reboiler duty [kcal/h]		
1:1	57.13	244263		
2:1	74.65	429200		
3:1	81.15	614405		
4:1	84.88	794697		
5:1	86.08	956679		
10:1	88.87	1793800		
E 11 · d	· 1 /· ·	CUTTNICA		

Following the simulations in CHEMCAD and processing of data, an optimal molar ratio of methanol: lactic acid of 4: 1 was set, at which the conversion of lactic acid to methyl lactate is approx. 84.8%.

b) Simulations to determine the optimal number of theoretical plates

These simulations were performed at the optimal ratio of the reactants previously determined. The number of plates of the reactive distillation column varied between 4 and 14 plates, tracking the degree of methanol recovery and minimizing reboiler duty.

Thus, it has been determined that for the reactive distillation column, **the optimum number of plates is 8 at the molar ratio of methanol: lactic acid of 4: 1.** At this value, the recovery degree of methanol at the top of the column is about 98.3% with a purity of 98.2% wt.



Figure 4.3. The recovery degree of methanol at the top of the column (2), according to the number of theoretical plates in the column

c) Simulations to determine the optimal reflux ratio of the reactive distillation column

Once the number of the theoretical plates of the distillation columns has been determined, simulations were performed in order to determine the optimal reflux ratio of the column following the alcohol recovery degree at the top of the column and the minimization of reboiler duty at RD column; the reflux ratio varied from 0.5 / 1 to 7/1.

Table 4.3.	The recovery	degree of	methanol	in the	peak	fraction	of RD	column	vs.	the	reflux
ratio of RD	column										

Reflux Ratio	Reboiler duty [kcal/h]	Methanol recovery [%]
0.5	604370	97.88
1	794697	98.30
2	1171600	98.84
3	1547200	99.12
4	1927500	99.30
5	2301300	99.41
6	2681400	99.50
7	3053900	99.55

Simulations have shown that a degree of alcohol recovery of 99.12% at a reflux ratio of 3: 1 is obtained. At higher reflux ratio, increasing the recovery of methanol is insignificant, instead, the reboiler duty doubles to a 7: 1 reflux ratio. For this reason, the 3: 1 reflux ratio is considered optimal.

4.1.2. Simulation of methyl lactate manufacturing process flowsheet

Reactive distillation is the core of the technological process but, in order to obtain the pure product, it works only together with a separation scheme.



Figure 4.5. Flowsheet of the methyl lactate manufacture process

As shown at point 4.1.1, the reactive distillation sequence was simulated as a reactordistillation column succession, with the feed of the column on the last bottom tray, the column having only a rectifying zone.

The reactor is fed with reactants in the molar ratio established as optimal.

At the top of the column (2), a light fraction is formed from the unreacted alcohol and the water formed in the esterification reaction, and the bottom fraction contains the ester formed together with the unreacted lactic acid. The bottom product of the column (2) passes into a vacuum fractionation column due to temperature constraints (to avoid the decomposition of the ester), in order to recover the ester (5).

The flowsheet is designed with recirculation of lactic acid and of the catalyst from the bottom of the column (5), to the reaction zone of the reactive distillation column. The top fraction of the column (2) is subject to rectification in the column (8) for methanol separation from water and recirculation of the alcohol.

With this scheme, 96% of the ester contained in the effluent is recovered at a purity of 94.5% wt.

4.2. SIMULATION OF ISOPROPYL LACTATE MANUFACTURING PROCESS BY DIRECT ESTERIFICATION OF LACTIC ACID WITH ISOPROPANOL IN REACTIVE DISTILLATION SYSTEM

In the residual map traced in CHEMCAD using the UNIFAC method for the isopropanol-water-isopropyl lactate ternary system, it is observed that the studied system forms, at atmospheric pressure, three binary azeotropes:

- isopropanol-water at 80.32°C with concentration of 68.5% mol isopropanol, 31.5% mol water;
- ➢ isopropanol-isopropyl lactate at 167.93℃ with 19.2% mol isopropanol, 80.8% mol isopropyl lactate;
- ▶ water-isopropyl lactate at 167.93°C with 22.2% mol water, 77.8 % mol isopropyl lactate.

This complex azeotropy will induce difficulties in separating the components from the effluent and will be reflected on the proposed manufacturing scheme.

4.2.1. Simulation of the reactive distillation sequence

1. The reaction zone is simulated using the "continuous kinetic reactor" in CHEMCAD, since the kinetics of the esterification reaction of lactic acid with isopropanol are known [92], respectively the pre-exponential factor and the activation energy from the Arrhenius equation, to:

- molar ratio of isopropanol: lactic acid: 1: 1 10: 1;
- ▶ working temperature 90- 80°C, depending on molar ratio of reactants;
- > pressure 1.2 bar.

2. The distillation area of RD was simulated at:

- \blacktriangleright the pressure at reactor output 1.2 bar;
- variable number of trays, between 4-12 real trays, with the feed on the bottom tray, taking into account that the reaction zone is in the bottom of the column;
- \succ the reflux ratio was varied between 0.5: 1 and 5: 1.

The simulations were performed as follows:

a) To *determine the optimal molar ratio* of the reactants, the molar ratio of isopropanol: lactic acid ranged from 1:1 to 10:1 and watch how the conversion of lactic acid varies.

As can be seen from data obtained, the conversion of lactic acid to isopropyl lactate increases from 49.8% to 73.2% when increasing molar ratio of isopropanol: lactic acid from 1:1 to 10:1. Following the simulations in CHEMCAD and data processing, **an optimal molar ratio of isopropanol: lactic acid of 3: 1, molar was set;** at this molar ratio, the conversion of lactic acid is about 73%, and mentained over 3:1 (see Table 4.4.)

Molar ratio Isopropyl Alcohol: Lactic acid	Conversion of Lactic Acid to Isopropyl Lactate [%]	Reboiler duty [kcal/h]		
1:1	49.8	229854		
2:1	63.4	446702		
3:1	73.03	651040		
4:1	73.22	843935		
5:1	73.22	1042300		
10:1	73.22	1153800		

Table 4.4. Conversion of lactic acid to isopropyl lactate vs.molar ratio of reactants

b) The simulations for determining the optimal number of trays were performed at the optimal ratio of the reactants determined at the point a). The number of plates of the reactive distillation column was varied from 4 to 12 real plates, tracking the isopropyl alcohol recovery and minimizing the reboiler duty.

The optimum number of plates was set at 8 for a molar ratio of isopropanol: lactic acid of 3: 1. The reboiler duty (and, correspondingly, of the condensor) is minimal at this number of trays. At this value, the recovery rate of isopropanol is about 90.53%, with a purity (isopropanol) of 98.2% wt; with increasing number of trays, the alcohol recovery at the top of the column does not change significantly.

Number of plates	Reboiler duty [kcal/h]	Isopropanol recovery [%]		
4	653154	90.13		
6	651264	90.28		
8	651040	90.53		
10	651537	90.65		
12	651941	90.79		

Table 4.5. The degree of recovery of isopropanol in the peak fraction of the column (2) according to the number of plates of the RD column

c) Once the number of theoretical plates of the distillation columns has been established, it was passed to simulations *to determine the optimal reflux ratio* of the reactive distillation column, aiming at obtaining a recovery degree of alcohol at the top of the column as high as possible, to a small reboiler duty.

Table 4.6. The degree of recovery of isopropanol in the peak fraction of RD column as a function of the reflux ratio

Reflux Ratio	Reboiler duty [kcal/h]	Isopropanol recovery [%]
0.5	498328	90.10
1	651040	90.53
2	958340	91.25
3	1264700	91.73
4	1571600	92.01
5	1878800	92.21

Simulations have shown that a 91.73% alcohol recovery rate is obtained at a 3: 1 reflux ratio. At higher reflux ratio, the increase in isopropanol recovery slows down, since the reboiler duty increases linearly with increasing the reflux ratio. For this reason, the optimal reflux ratio was set at 3: 1.

4.2.2. Simulation the flowsheet of isopropyl lactate manufacturing process by direct lactic acid esterification

The proposed scheme for simulating the process of esterification of lactic acid with isopropanol is more complex.

At the top of the column (2), a light fraction is obtained as the azeotropic isopropyl alcohol - water mixture, and the bottom fraction contains a mixture consisting of the lactic acid ester formed, unreacted lactic acid, traces of alcohol and water. The RD column distillate (azeotrope isopropyl alcohol-water) can be separated by pervaporation (membrane 8), and the isopropyl alcohol obtained is recycled in the reactor feed.



Figure 4.10. Process flowsheet of the isopropyl lactate manfacture by direct esterification

The bottom product of the column (2) contains lactic acid and isopropyl lactate; the mixture is cooled and water and acid may be separated by a selective membrane (11), after that the alcohol separates to the top of a rectification column (12) operating at atmospheric pressure; following the simulation, this column has to be equipped with 20 plates, and the feed goes on the 10th plate. The isopropyl alcohol recovered at the top of the column (12) is recirculated in the feed of the reactor, and the bottom product of the column (12) passes into a vacuum purification column of the ester to avoid ester decomposition, and the optimal absolute pressure resulting from the simulation is 0.013 bar.

The degree of recovery of the ester, made in this scheme designed with recirculation of lactic acid, catalyst and isopropanol, is 98.9%.

4.3. SIMULATION OF ISOPROPYL LACTATE MANUFACTURING PROCESS BY METHYL LACTATE TRANSESTERIFICATION WITH ISOPROPANOL IN A REACTIVE DISTILLATION SYSTEM

The residual curve traced in CHEMCAD for the isopropanol-methyl lactate-isopropyl lactate ternary system (Figure 4.11) shows that the studied system does not form azeotrope.

4.3.1. Simulation of the reactive distillation sequence

As in previous cases, simulations were first made to optimize the reactive distillation process to determine optimal parameters.

The simulations were performed as follows:

- 1. The reaction zone (1) was simulated using the "stoichiometric reactor" from CHEMCAD reactors palette, since the kinetics of the methyl lactate transesterification reaction with isopropanol is not known. Conversions were calculated using equation 2.21, (the model developed in the frame of the experiment), and the following parameters varied:
- > molar ratio of alcohol: methyl lactate ranging from 1: 1 to 5: 1;
- \blacktriangleright reaction temperature of 80-90°C;

- \blacktriangleright pressure 1.2 bar.
- 2. The RD distillation zone was simulated with the following data:
- pressure 1.2 bar;
- ➤ variable number of plates, between 4-16 real plates;
- \blacktriangleright the ratio of reflux varied between 0.5: 1 and 6: 1.

a) The reactive distillation process was initially simulated, varying the number of theoretical plates from 4 to 16 plates, at a fixed reactants molar ratio of 4: 1

Thus, the correlation between the number of plates in the column and the reboiler duty, respectively the condenser duty, was invastigated, and also was investigated the effect on isopropyl lactate concentration (IPL) in the distillate as an expression of IPL recovery degree in the bottom product.

Over 6 theoretical plates all these parameters decrease very little and for this reason the *optimum number of real plates is considered 6*.



Figure 4.12. Influence of number of stages in the RD column on the reboiler (*a*) and condenser duties (*b*), and on the IPL concentration in distillate (*c*)

b) Simulations were then carried out to determine the optimal reflux ratio by varying the RR (reflux ratio) from 0.5: 1 to 6: 1, searching its effect on methanol and isopropyl alcohol recovery degrees in the distillate (Fig.4.13).





4.3.2 Simulation of isopropyl lactate manufacturing process flowsheet by methyl lactate transesterification in reactive distillation system

The proposed scheme for simulating the methyl lactate transesterification process with isopropanol is relatively simple and there are no difficult separations.





Based on the experimental data, a scheme was developed to produce isopropyl lactate by transesterification in a reactive distillation system.

The reactor is fed with reactants in various molar ratios, and the reaction mass feeds the column (3) under the last bottom plate, the column having only the rectification zone.

At the top of the column (3), it is obtained a mixture of unreacted isopropyl alcohol and methanol formed as a result of the transesterification reaction, and the bottom fraction contains the formed ester together with the unreacted methyl lactate.

The top fraction of the column (3) is introduced into the column (4) to separate the methanol (as a byproduct of the process) and the isopropanol, which is subsequently recirculated.

The bottom product of the column (3) is introduced into a vacuum fractionation column (5) due to temperature constraints, for the recovery of esters. The scheme is designed with a methyl lactate recycle.

The process was simulated for a production of 1.3 t / h isopropyl lactate.

After establishing the optimal parameters in the reactive distillation rectification zone (6 theoretical plates and reflux ratio= 2), simulations of the methyl lactate transesterification process with isopropanol were performed at the IPA / ML molar ratios: 1.06:1; 2:1; 3:1 and 4:1.

The main objective of the simulation is to minimize the energy specific consumption (kcal / t IPL) to obtain an IPL purity of min. 95% and a high recovery degree of the products from the reaction mass.

Molar ratio ML:IPA	Heating duty per ton IPL, <i>kcal/t</i>	Cooling duty per ton IPL, <i>kcal/t</i>	IPL purity, % wt.	IPL recovery degree, %wt.	Methanol byproduct purity, % wt.	
1.06:1	$1.26^{-}10^{6}$	$1.26^{-}10^{6}$	96.0	99.998	97.8	
2:1	$1.34^{\circ}10^{6}$	$1.34^{-}10^{6}$	96.0	99.994	92.5	
3:1	$1.45 \ 10^6$	$1.45 \cdot 10^{6}$	96.0	99.997	96.9	
4:1	1.3610^6	$1.36 \cdot 10^{6}$	96.0	99.998	97.0	

Table 4.7. Results of process simulation for manufacturing 1.3 t/h isopropyl lactate

From Table 4.7 it is noted that the purity and degree of IPL recovery, expressed in % wt., has approximately the same values in all cases (close to 100%), while the purity of methanol ranges between 92.5% and 97.8% wt.

For the proposed scheme of the isopropyl lactate manufacture by transesterification of methyl lactate with isopropanol in a reactive distillation system, producing 1.3 t / h IPL of 96% wt. purity, the lowest energy consumption was found at:

- molar ratio IPA:ML of 1.06: 1;
- in a reactive distillation column equipped with 6 theoretical plates (equivalent to 2.4 real plates);
- ➤ at a reflux ratio of 2.

The reactive distillation process can be successfully applied to the process of transesterification of methyl lactate with isopropanol to produce isopropyl lactate in a reactive distillation system.

GENERAL CONCLUSIONS

Within the research project of the doctoral stage, systems of esterification reactions and etherification reactions have been approached in the reactive distillation configuration, with products of commercial value.

In this context, the **main objective** of the paper was to contribute to the development of knowledge in the field of reactive distillation and to recommend the reactive distillation process for some industrial applications.

This objective was pursued through the following **secondary objectives**:

- deepening the knowledge of esterification processes (by explaining phenomena, interactions, the influence of some factors on processes efficiency), in particular for the esterification of lactic acid with various alcohols to produce methyl lactate and isopropyl lactate respectively, as well as the transesterification of methyl lactate with isopropyl alcohol to produce isopropyl lactate;
- Iaboratory testing of esterification reactions of lactic acid with various alcohols as well as the transesterification reaction of methyl lactate with isopropanol in reactive distillation systems;
- application of reactive distillation to *in situ* etherification of olefins contained in the catalytic cracking gasoline, in order to increase its octane number;
- optimization of industrial esterification and transesterification processes, through a simulation program (ChemCAD).

A. CONCLUSIONS OF BIBLIOGRAPHICAL RESEARCH

Based on the literature study, it was concluded:

- efforts were made to improve technological processes with a focus on finding hybrid processes that include reactive distillation and another process (e.g. pervaporation, pressure swing)
- minimizing the energy consumption of reactive distillation is currently an objective in improving the process.
- the emergence of new syntheses where reactive distillation can be applied, especially if it is included in a hybrid process, usually coupled with pervaporation;
- the need to develop more accurate models for the design of reactive distillation columns is another direction to which researchers' efforts are directed;
- the need to simulate technological processes that include reactive distillation sequences or strict simulation of the reactive distillation process is another concern of chemical engineers.

B. CONCLUSIONS OF SCIENTIFIC RESEARCH

I. The experimental study of esterification and transesterification by a reactive distillation system, for quantifying the influence of process factors on process results (yields, conversions) to obtain lactic acid esters.

The experiments were performed in the laboratory on a reactive batch distillation column, 20 mm in diameter, packed with Rashig glass rings with dimensions of 6x10x1 mm, the height of the packing bed ranging from 400 mm to 100 mm. The 500 ml flask of the bottom plant is a glass was electrically heated, progressively achieved with the help of a rheostat. The reagents were fed in the bottom, at the beginning of each experiment. The reaction takes place in the bottom flask and the column only has a rectifying area.

Following the laboratory experiments the following results were obtained:

1. In *the experimental study on the esterification of lactic acid with methanol* by reactive distillation.

The yield of methyl lactate was calculated using equation (2.14), based on the lactic acid consumed in the reaction, considering that the esterification reaction is singular, an acceptable hypothesis at low acid concentrations in the reaction mass:

 $y = \frac{\text{mole of lactic acid transformed in methyl lactate}}{\text{mole of lactic acid in the feed}} * 100$ (2.14)

The results obtained show that the methyl lactate yield increases when increasing the molar ratio of methanol: lactic acid; the highest yield of methyl lactate (ML) of 76.7%, was obtained at:

- > an initial molar ratio of methyl alcohol: lactic acid of 3: 1,
- ➤ using a packing column equivalent to 4.9 theoretical plates.

A mathematical model of first degree polynomial type was proposed for the esterification of the lactic acid with methanol by reactive distillation. Model coefficients were determined by regression. The values of the predicted yield with this model are close to the experimental values, and the model is valid.

2. In the *experimental study of isopropyl lactate* (an important intermediate in drug synthesis), *by direct esterification of lactic acid with isopropanol*, in a reactive distillation system, the lactic acid conversion is calculated with Eq.2.12:

conversion,
$$\% = \frac{v_0 - v_t}{v_o} * 100$$
 (2.12)

where: v_0 – is the volume of 1 N NaOH solution used for titration at the initial moment of reaction (mL);

 v_t – the volume of 1 N NaOH solution used for titration at the moment *t* (mL).

Following experimental results, it was observed that all three factors influence the conversion, in the sense of increasing conversion with the increase of the values of each factor. Thus, a maximum conversion of 63.6% was obtained at the chosen maximum levels of each factor influencing the process:

- > molar ratio of reactants of 3: 1 isopropanol: lactic acid,
- ➤ 2.9 theoretical plates;
- ➢ 5% mass of catalyst concentration.

It is proposed a mathematical model for the esterification of lactic acid with isopropanol in a reactive distillation system, a first degree polynom, for prediction of lactic acid conversion; this is valid in the range chosen in this experiment for the three factors. It is statistically verified and it was proved that there is a good verification of the experimental data with those predicted by the model and all the statistical coefficients are significant, so the model is viable with a correlation coefficient r = 0.9989.

3. *Experimental study of transesterification of methyl lactate with isopropanol* in a reactive distillation system.

Knowing the methanol concentration in the distillate and distillate quantity, the amount of methanol resulting from the reaction is calculated, then the amount of reacted methyl lactate was stoichiometrically clculate, and in the end the conversion was calculated using the relationship (2.19):

$$conversion, \% = \frac{the amount of methyl lactate reacted}{the amount of initial methyl lactate} x \ 100$$
(2.19)

Process performance was measured by conversion of methyl lactate which had good values for all experiments performed, ranging from 57.2-89.7%.

The highest conversion of methyl lactate (ML) of 89.82% is obtained in the following conditions:

- > an initial molar ratio of isopropanol: methyl lactate of 4: 1;
- > a packing height in the column equivalent to 2.4 theoretical plates;
- \triangleright at a 7: 1 reflux ratio.

A mathematical model was proposed for the conversion of methyl lactate to isopropyl lactate by transesterification of methyl lactate with isopropanol of linear type, statistically validated.

The yields and conversions in the reactive distillation system are higher than those obtained in the conventional reaction systems, as available in literature for the esterification of lactic acid with methanol [42, 92]. Therefore, it can be considered that, choosing reactive distillation to carry out these processes is a good solution.

The experimental data obtained in these studies and the resulting mathematical models can serve to design industrial processes.

II. Experimental study of in situ etherification of olefins contained in the catalytic cracking gasoline

The experimental study was carried out in the laboratory, on a plant similar to that used for esterification, but the distillation column had a higher capacity, with the following dimensions:

- ➢ inner diameter : 8 cm;
- ➢ height: 1 m;
- ➢ 70 cm packing bed of Rashig glass rings, 6x10x1 mm.

The catalyst is acid ion exchange resin of sulphated ion type with the trade name Purolite. The conclusions of the study are as follows:

- ✓ through *in situ* etherification of olefins and isoolefins from catalytic cracking gasoline with different alcohols, the Motor Octane Number MON increases by up to two units (from 84 to 86);
- ✓ the increase in the octane number is explained by the formation of oxygenated compounds in the gasoline undergoing etherification, according to the chromatographic analyzes, corroborated with the mass balance on the components;
- ✓ *In situ* etherification of catalytic cracked gasoline with isopropyl alcohol is optimal at the molar ratio of 1.5/1 alcohol/olefins;
- ✓ based on the experimental results in the reactive distillation process to obtain oxygenated compounds, in situ etherification of olefins contained in catalytic cracking gasoline may be an economic option for classical etherification of the isoamylenes fraction, followed by the addition of gasoline with ethers [154]; this experiment shows that even heavier olefins are etherified with a positive effect on the octane number;
- ✓ the chromatographic study of the etherification products allowed a more detailed analysis and made possible the calculation of the conversion of the olefins on components. Here are some interesting conclusions:
 - ➢ isopropyl alcohol causes the highest conversion of olefins;
 - negligible conversions of C8-C9 cycloolefins are found in the reaction of *in situ* etherification of catalytic cracking gasoline with methanol;
 - ➢ lower conversions are obtained with n-butanol.

- the correlation between olefins conversion and the increase of octane number of gasoline has been demonstrated.
- ✓ Distillates containing alcohol and light hydrocarbons can be utilized by separating and recirculating the alcohol excess to the reaction zone, on one hand, or the use of light hydrocarbon fractions as a component in the formulation of gasoline, or for other commercial purposes (e.g. solvent), on the other hand.

III. Simulation in CHEMCAD of esterification and transesterification processes

CHEMCAD simulations of lactic acid esterification processes in acid homogeneous catalysis (3% concentrated sulfuric acid catalyst based on reaction mass) were performed:

- for the production of methyl lactate by direct esterification of lactic acid with methanol in a reactive distillation system,
- ➢ for the production of isopropyl lactate by direct esterification of lactic acid with isopropanol in a reactive distillation system,
- for the production of isopropyl lactate by transesterification of methyl lactate with isopropanol in a reactive distillation system.

The simulations performed in ChemCad have used data from own original experiments, along with literature data.

Simulations have been performed to determine the optimum operating parameters for reactive distillation, namely:

- the optimal molar ratio of reactants, alcohol / lactic acid in the case of esterification processes, respectively alcohol / methyl lactate, in the case of the transesterification process, in a reactive distillation system;
- the number of theoretical equilibrium in the reactive distillation column;
- the optimum reflux ratio in the reactive distillation column,

for selected variation intervals of the parameters.

Analyzing the data obtained through simulation, the following conclusions were drawn:

the optimal molar ratio of reactants is:

- ✓ 4: 1, methanol: lactic acid to obtain methyl lactate by esterification of lactic acid with methanol;
- ✓ 3: 1, isopropanol: lactic acid, to give isopropyl lactate by direct esterification of lactic acid with isopropanol;
- ✓ 1.06: 1 isopropanol: methyl lactate, to produce isopropyl lactate by transesterification of methyl lactate with isopropanol (established after simulations on the whole plant);
- > the optimal number of real plates in the reactive distillation column is:
 - ✓ 8 real plates for esterification of lactic acid with methanol (at optimal ratio of 4: 1, methanol: lactic acid);
 - ✓ 8 real plates in case of direct esterification of lactic acid with isopropanol (at an optimal molar ratio of 3: 1 isopropanol: lactic acid);
 - ✓ 6 real plates for isopropyl lactate by transesterification of methyl lactate with isopropanol at optimal molar ratio of 1.06:1 isopropanol:methyl lactate;
- > *the optimal reflux ratio* of the reactive distillation column is:
 - ✓ 3: 1 for the process of producing methyl lactate by esterification of lactic acid with methanol;

- ✓ 3: 1 for the process of producing isopropyl lactate by esterification of lactic acid with isopropanol;
- \checkmark 2: 1 in the process of transesterification of methyl lactate with isopropanol.

In order to obtain high purity products, technological schemes were proposed for the esterification and transesterification processes studied based on the conclusions of the previous simulation stage combined with own experimental results.

A processing capacity of 10 kmol / h of lactic acid was established for direct esterification and 1.3 t / h of isopropyl lactate production by transesterification.

The targets were:

- obtaining a great purity of the esters and
- ➢ higher recovery rates of esters from reactor effluent,

in conditions of lower energy consumption.

Technological schemes are designed to recover unreacted compounds and recirculate them to the reactor, which has a positive impact on the recovery rate and, consequently, on product yields, but also impacting on the plant's energy consumption.

The simulations performed in this paper confirm that the reactive distillation process can be applied with good results to the esterification and transesterification reactions.

CONTRIBUTIONS TO THE DEVELOPMENT OF KNOWLEDGE IN THE FIELD AND EXPECTATIONS

The topic "COMPARATIVE STUDIES CONCERNING THE REACTIVE DISTILLATION IN ESTERIFICATION AND ETHERIFICATION PROCESSES" is a generous one because, due to its importance, the reactive distillation process is in full swing.

As a result of the literature and experimental studies carried out in this paper, as well as the conclusions withdrawn from them, some contributions were made to the knowledge in the field, as follows:

- 1. The literature study and simulations in CHEMCAD have shown that the reactive distillation process, applied isolated, is still a large energy consumer despite the advantages of thermal integration and intensification of the chemical process, *the current trend being to include reactive distillation in a hybrid process and optimize the resulting process schemes;* some improvements have been included in the present work by proposing technological schemes by coupling reactive distillation with pervaporation or the use of pressure swing reactive distillation.
- 2. The experiments of the esterification and transesterification for the production of lactic acid esters were carried out in a reactive distillation system, experiments rarely approached in the literature, the vast majority of experimental esterification studies being made to obtain acetic acid esters, while those for lactic acid esters were either experimentally made in batch reactors or studied theoretically in different simulation environments.
- 3. Experimental studies of esterification and transesterification *have allowed the quantification of the influence of process factors* through robust mathematical models statistically verified; these models allow predicting the yield of the main product according to these factors. *The magnitude of the mathematical model coefficients has enabled to identify the factors controlling the process.* Thus, it has been found that the most important process variables are *the molar ratio of the reactants and the number of theoretical plates* in the column, while the catalyst concentration is a minor factor and can be set within some of the usual limits.

- 4. The study of *in situ* etherification of olefins contained in the catalytic cracking gasoline with different alcohols in a reactive distillation system proved, for the first time, that *the etherification with isopropanol results are as good as the etherification with the lower alcohols, increasing the octane number of gasoline with two units* after etherification. Access to an advanced GC chromatographic analysis method with a special analyzer (on the AC Reformulyzer ® M3 Analyzer) allowed *the conversion of olefins and cycloolefins to be calculated as well as explaining their influence on the octane numbers* of the products.
- 5. Technological schemes have been proposed for the production of methyl and isopropyl esters of lactic acid. *For the ChemCad simulation* of the reactive distillation sequence in the scheme, *own experimental data and kinetic data in the literature were used*, and the simulations explored the process beyond the boundaries of the experimental studies, resulting in important practical conclusions, with optimization of the energy consumption scheme.

The research topic opens opportunities for future experimental works, such as:

- ✓ esterification of 2-phenyl ethanol with propionic acid in a reactive distillation system to produce phenyl propionate, an important intermediate in the cosmetic industry;
- ✓ the production of higher molecular weight acetates and levulinates by transesterification in a reactive distillation system coupled with pervaporation;
- \checkmark experimentation of *in situ* etherification of olefins in the catalytic cracking gasoline, in a continuous process.

The simulations of the studied processes will be performed to improve the technological schemes and to optimize the process performances.

DISSEMINATION OF THE RESULTS OF SCIENTIFIC RESEARCH

During the doctoral stage, the results of the scientific researches were valorized by publishing in journals and communicating scientific papers as follows:

A. Articoles in ISI rated journals:

1.ȚAGA (SĂPUNARU), O.V, KONCSAG, C.I., MARES, A.M., JINESCU, G., Isopropyl lactate obtaining by esterification in a reactive distillation system, Rev. Chim. (Bucharest), 69, no. 12, 2018, p. 3423, **IF** (**pe 2017**)=**1,412, SRI=0,164.**

1. ȚAGA (SĂPUNARU), O. V., KONCSAG, C. I., SIVRIU, A. M., JINESCU, G., Isopropyl lactate obtaining by transesterification in reactive distillation system, Rev. Chim. (Bucharest), 70, no. 1, 2019, in press, **IF** (**pe 2017**)=**1,412, SRI=0,164**

2. ȚAGA (SĂPUNARU), O.V, KONCSAG, C.I., JINESCU, C., MARES, A.M., Simulation and optimization of isopropyl lactate manufacturing process, Rev. Chim. (Bucharest), 2019, in press, **IF** (**pe 2017**)=**1**,412, **SRI=0**,164.

IF (TOTAL)= 1,412+1,412+1,412= 4,23; SRI (TOTAL) = 0,492

B. Articoles in journals indexed in BDI:

1. ȚAGA (SĂPUNARU), O. V., KONCSAG, C. I., JINESCU, G – The study of lactic acid esterification with methanol through reactive distillation, UPB Scientific Bulletin, Series B: Chemistry and Material Sciences, **79**(3), 2017, p.37-48.

C. Works with the abstract published in volumes of national and international conferences

- Țaga (Săpunaru), O. V., Koncsag, C. I., Mares, A. M., Sivriu, A. M., Jinescu, G., Optimization of the lactic acid esterification in reactive distillation process, 4th International Conference on Chemical Engineering, 30 octombrie – 2 noiembrie 2018, Iași, Romania, *Book of abstracts*, S1-32.
- Ţaga (Săpunaru), O., Koncsag, C. I., Mares, A. M., Jinescu, G., Process design for etherification of FCC gasoline's olefine in situ, International Symposium of Chemical Engineering and Materials, SICHEM, 6-7 septembrie 2018, Bucuresti, *Book of abstracts*, p. 80.
- 3. Țaga (Săpunaru) O., Koncsag, C.I, Jinescu, G., Performing esterification reactions through reactive distillation, Conferinta Internationala "Chimia", 24-26 mai 2018, Constanta, *Book of abstracts*, Vol. 3, p.78.
- 4. Țaga, (Săpunaru) O., Brânzei, M., Pascu, S., Jinescu, G., & Koncsag, C. I. Simulation of reactive distillation process for enhancing the octane number of gasolines, SICHEM–Bucuresti, 8-9 septembrie 2016, *Book of abstracts*, 92.
- Ţaga, (Săpunaru) O., Pascu, S., Brînzei, M., Koncsag, C. I., & Jinescu, G. Augmenter l'octane de l'essence par etherification in situ, LE NEUVIÈME COLLOQUE FRANCO – ROUMAIN DE CHIMIE APPLIQUÉE, CoFroCA, 29 iunie – 2 iulie 2016, Clermont Ferand, Franta, *Book of abstracts*, p. 191.
- 6. Branzei, M., Țaga (Săpunaru) O., Koncsag, C.I, Influence of azeothopy on the etherification in situ of FCC gasoline, Conferinta Internationala "Chimia", 26-28 mai 2016, Constanța, Book of abstracts, PD4, p.67.

SELECTIVE BIBLIOGRAPHY

- 6. Țaga, (Săpunaru) O.V., Intensificarea proceselor de esterificare prin distilare reactivă, Disertație, Universitatea Ovidius din Constanța, 2018;
- 7. Luyben, W. L., & Yu, C.-C., Reactive distillation design and control, NJ, UnitedStates: Wiley: UnitedStates: Wiley, 2008;
- 15. L.A. Smith, US 4215011, 1980;
- 17. Sharma, M. M., Mahajani, S. M., Industrial applications of reactive distillation, in: K. Sundmacher, A. Kienle (Eds), Reactive Distillation, Wiley-VCH, Weinheim, 2003, pp. 3-29;
- 36. Luyben W.L., Principles and case studies of simultaneous design, First Edition, John Wiley &Sons, 2011;
- 42. Taylor, R, Krishna, R., Modelling reactive distillation, Chem Eng Sci, 55, 2000, p. 5183– 5229;
- 58. Clary, J.J., Feron, V.J., van Velhuijsen, J.A., Safety assessment of lactate esters, Regul. Toxicol. Pharmacol., 27, 1998, p. 88–97;
- 59. Stoye, D., Solvents, in: Ullman's encyclopedia of industrial chemistry, vol. A 24, 5th revised ed., VCH Verlagsgesellschaft, 1993, p. 448–454, 481, 494;
- Ţaga (Săpunaru), O. V., Koncsag, C., Jinescu, G., The study of a lactic acid esterification with methanol through reactive distillation, UPB Scientific bulletin, series B: Chemistry and Material Sciences, 79 (3), 2017, p.37-48;
- 92. Toor, A. P., Sharma M., Sakshi Th., Wanchoo, R.K., Ion-exchange Resin Catalyzed Esterification of Lactic Acid with Isopropanol: a Kinetic Study Bulletin of Chemical Reaction Engineering & Catalysis, 6 (1), 2011, p. 39-45;

- 123. Su, W., & Chang, J., Modelling and simulation of tubular reactor in the tert-amyl methylether synthesis process. Ind Eng Chem Res, 39, 2000, p. 4140–4147;
- 130. Lei, Zh., Zhang, H., Liu, J.-J., Yang, B.-L., Synthesis of *tert*-amyl ethyl ether for gasoline additive, Energy Procedia, 75, 2015, p. 3265 3270;
- 135. Pera-Titus, M., Bausach, M., Tejero, J., Iborra, M., Fite, C., Cunill, F., Izquierdo, J. F., Liquid-phase synthesis of isopropyl tert-butyl ether by addition of 2-propanol to isobutene on the over sulfonated ion-exchange resin Amberlyst-35, Applied Catalysis A: General, 323, 2007, p. 38–50;
- 137. Thiel, C., Sundmacher, K., Hoffmann, U., Residue curve maps for heterogeneously catalysed reactive distillation of fuel ethers MTBE and TAME, Chem. Eng. Sci., 52, 1999, p. 993–1005;
- 138. Subawalla, H., Fair, J.R., Design guidelines for solid-catalyzed reactive distillation systems, Ind. Eng. Chem. Res., 38, 1999, p. 3606–3709;
- 139. Soto, R., Fité, C., Ramírez, E., Tejero, J., Cunill, F., Effect of water addition on the simultaneous liquid-phase etherification of isobutene and isoamylenes with ethanol over amberlyst 35, Catalysis Today, 256, 2015, p. 336–346;
- 150. Pascu, S., Eterificarea *in situ* a benzinelor de caracare catalitica, Disertație, Universitatea Ovidius din Constanța, 2015;
- 151.Brînzei, M., Pascu, S., Using alcohols as etherification agents for boosting the octane number of gasolines. XIII International Conference Students for Students UBB Cluj Napoca: Book of Abstract, 2015, p. 112-113;
- 152.M.Brînzei, Application of reactive distillation in oil refineries, Dissertation, Ovidius University of Constanța, 2016;
- 155. Thotla, S., Mahajani, S., Reactive distillation with side draw, Chemical Engineering and Processing, 48, 2009, p. 927–937.